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THE EFFECT OF ULTRASOUND ON THE HYDROLYSIS OF CARBOHYDRATES

New Jersey Institute of Technology

D.ENG.SC. 1983

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THE EFFECT OF ULTRASOUND ON THE HYDROLYSIS OF CARBOHYDRATES

BY ADEL A. KHAMIS

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A Dissertation submitted to the Faculty of the Graduate School of the New Jersey Institute of Technology in partial fulfillment of the requirements for the degree of Doctor of Engineering Science 1983

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APPROVAL SHEET

Title of Thesis: The effect of ultrasound on the hydrolysis of carbohydrates

Name of Candidate: Adel A. Khamis Doctor of Engineering Science, 1983

Thesis and Abstract Approved:

Dr. David Kristol Date Professor of Chemistry

Dr. Richard Parker Professor of Chemistry

Dr. Angelo Perna

Date

Date

~ ++++ mm Dr. Kenneth Sohn

115

Date

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Date

Dr. Carol Venanzi

ABSTRACT

Acid hydrolysis of dextran and cellulose were studied with and without irradiation with ultrasonic waves of different frequencies (17 - 150 KHz), and powers $(0.4 - 200 \text{ w/cm}^2)$. In the case of both materials, the hydrolysis reaction was found to be first order with respect to the activity of hydrogen ions in the reaction medium. Weight average molecular weight was evaluated at different durations of the reaction course. The reaction rate of dextran was found to be proportional to the weight average molecular weight average to the power 4/3, and raised to the power 4 for cellulose.

The value of the activation energy was shown to be the same, either with or without ultrasound irradiation for both materials. It was found to be equal to 30,000 cal/mole for dextran, and 28,600 cal/mole for cellulose in a heterogeneous system.

A mathematical model for the rate constant under the effect of ultrasonic waves, temperature, and hydrogen ions activity, was proposed. This model then was used to predict the optimum enhancement, which was proved to be in agreement with experimental data.

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INTRODUCTION

Although ultrasound has been known for more than 55 years(1,2,3,4) its application to chemical reactions and its biological effect has not been investigated thoroughly. Much work has been done during the past three decades in the area of its application to chemical reactive systems, and medical treatment. Increased yields are obtained in some systems, no effects occur in others, and some generate a whole new series of reaction products(4). A large amount of data has been accumulated; however, it has only been in the past fifteen years that a reasonable explanation has been proposed. Researchers in the field have generally agreed that acoustical cavitation is necessary before any chemical reaction effect due to the application of ultrasonic waves can be observed(4).

It was reported that ultrasonically induced cavitation in certain liquids has the effect of promoting certain chemical reactions within them. This may be due to electrolytic action brought about by the appearance of equal and opposite free electric charges at opposite ends of the bubbles(4). Other possible causes of chemical effects are the instantaneous and enormous increases in pressure, up to thousands of atmospheres, and temperature up to hundreds of degrees, in the vicinities of the cavities upon their collapse(5). Chemical changesare believed also to be brought about as a result of the energy from resonant bubbles.

When cavitation occurs in water H^+ and OH^- ions separate, Lindstrom and Lamm(6) explained that by one or more of the following reactions:

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$$H + OH = H_2O$$

$$H + H = H_2$$

$$H_2 + OH = H_2O + H$$

$$OH + OH = H_2O_2$$

$$H + H_2O_2 = H_2O + OH$$

Certain substances may be oxidized or reduced if they were dissolved in cavitated water. Oxidation may occur because of the release of hydrogen peroxide (H_2O_2) , which would provide oxygen to such a reaction, and reduction as a result of the release of hydrogen ions. For example, dissolving potassium iodide (KCl) crystals in cavitated water produces free iodine.

It was also observed that irradiating a high polymeric substance by ultrasound could break the molecules down to form smaller ones. This action was observed with starch, gelatin, polystyrene, nitrocellulose and rubber. This has proved that cavitation is a valuable tool for accelerating chemical changes.

The past decade has seen the introduction on the commercial market of an increased number of high power ultrasonic transducers for liquid processing which combined both a lower cost per radiated acoustic power and increased reliability under heavy duty conditions. This is particularly true for glazed cobalt barium titanate transducers which operate in the higher region of the ultrasonic spectrum (500 to 1000 kHz). With the availability of powerful, rugged and reliable transducers, physicians, chemists and chemical engineers have indeed paid more attention to the potential contribution of ultrasound to medicine and standard chemical operation such as extraction, dissolution, and dispersion beside chemical reactions.

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In the recent years ultrasound has become widely used tool in Biology and Medicine without the mechanism by which it affects biological materials being fully understood. The effects of high energy ultrasonics on living matter include the disruption of cells by cavitation, the damage of body tissue by agitation, and the heating of bone and muscle. Airborne ultrasonics of sufficiently high power, having frequencies, up to 30 kHz, have been shown to cause unpleasent and sometimes harmful effects on both human beings and animals. For example, persons operating high-power ultrasonic equipment for long periods are subjected to fatigue and sometime nausea. On the other hand, high energy ultransound have proved successful in scaring away birds(4).

Much research has been done on the destruction of malignant tissue by ultrasound, which only this year,1983, it was proven that it is very effective in conjuction with the laser beam. However the heating effect of the ultrasound, appears to them the most promising in medicine at present, and there are wide applications of this in the United states and Germany to the treatment of such muscular ailments as lumbago. Because of the necessity of focussing the waves into selected cones, frequencies as high as one or two megacyles are often used. Some work has also been done on the application of ultrasonic heating to the temporary blocking of nerves with a view to analgesia. The margin of safety, however, between the reversible and irreversible blocking is too narrow for the method to be brought into practice at present.

However, ultrasonics have been used successfuly to kill bacteria suspended in liquids, one application being the sterilization of milk. Another biological effect of ultrasonics which has been applied in the food industry is the tenderizing of meat by the action of breaking down its fibers(5).

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Since ultrasound has been proven to be a very useful tool, tremendous applications are expected in the future. Therefore, it is very impotrant to understand its chemical, biological, and physical effects; this work is a contribution towards this purpose. Dextran and cellulose has been subjected to ultrasonic irradiation under different conditions of temperature, frequency, and power, and control subjected to the same conditions except the ultrasound. From this study a mathematical model has been proposed, then used to predict the ultrasound effect under different conditions. This model, for the first time explains the relation between the ultrasonic power and the reaction promotion in the range of the experimental data obtained.

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ULTRASONIC WAVES

Ultrasonic waves are those waves of a frequency above that of the upper frequency limit of the human ear; in other words, any sonic wave of frequency above 16 kHz is an ultrasonic wave. The upper frequency range is largely dependent on the generator. Practically, it is possible to achieve frequencies up to 500 MHz. The wavelength is temperature, and medium dependent, since the speed of sound is not the same in liquids and solids for example.

Sound transmission is essentially dependent on particle vibration, each particle of the medium displaced sequentially as the wave travels through the medium. Any material possessing elasticity provides a restoring force that tends to return each element of the material to its starting point. The inertia present will cause the particle to oscillate about a mean position and each particle will execute an orbit as the wave progresses. Because the wave takes a finite time to pass through the medium there is, in general, a difference in phase betweeen the orbital movements of particles at any two points.

WAVE TYPES

The method of applying the propagating source to the medium will decide the pattern of the orbital path taken by successive elements. If this path is parallel to the line of propagation the wave is known as a longitudinal or L wave, If the orbits are normal to the direction of propagation the wave is then known as a transverse, shear or S wave. It is also possible for a wave to be propagated over a surface without influencing the bulk of the medium below the surface. This is known as a surface or Rayleigh wave. Only longitudenal waves can be propagated in liquids.

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Orbital movements can influence the external conditions experienced in the medium. They are known as waves of dilatation if a volume change occurs, while if no change of volume takes place they are classed as waves of distortion. A wave of dilatation is also described as irrotational because there is no elemental rotation. Both longitudinal and shear waves can be either dilatational or distorational. A given medium cannot always support all types of wave motion. Longitudinal waves in a normal material have been found experimentally to be almost entirely dilatational, while shear waves are primarily distortional.

Modulation impressed on a wave does not influence its general characteristice; the propagated wave can be continuous, modulated or pulsed.

1. LONGITUDINAL WAVES

Longitudinal waves are commonly employed in ultrasonic applications since they are easily generated and detected. They can be propagated in solids, liquids and gases and travel at high velocity, so that their wavelength is short, in most media. The wavelength in common materials is usually small in comparison with the cross sectional area of the vibrating element, or transducer, producing the waves. Hence, ultrasonic 'beams' may be propagated through a volume of the medium without disturbing the material outside the beam confines, Figures 1 and 2.

L waves may be generated by the vibration of any surface on the body. The velocity of this wave type can be calculated for a given solid material, using the equation

$$c = \left(\frac{E_r}{p} - \frac{1 - u}{(1 + u)(1 - 2u)}\right)^{\frac{1}{2}}$$

where E_r is Young's modulus, c is the velocity, u is Poisson's ratio and p is the density of the material. It will be seen that the velocity is determined by the density and elastic constants of the medium.

Experiments have indicated that the velocity may vary with the intensity of the applied vibration, velocities as high as three times normal having been reported(17). It is known that under high intesities the elastic properties undergo a change in value due to the extreme stresses experienced and this could conceivably alter the velocity.





Figure (1). Total vibration of a body due to longitudinal waves



In liquids and gases it is usually assumed that the vibrations take place too rapidly for that to exchange. The velocity in either a liquid or a gas is then

$$c = (\frac{k}{pB_{is}})^{\frac{l_2}{2}} = (-\frac{1}{pB_{ad}})^{\frac{l_2}{2}}$$

where k is the ratio of specific heats, B_{is} the compressibility at constant temperature and B_{ad} is the adiabatic compressibility(18).

2. SHEAR WAVES

Shear waves may exist in a limited volume or throughout the entire body. Usually they are in the form of a beam of small cross sectional area in comparison with the overall area of the body and normally do not extend to the surface parallel to the direction of travel.



Figure(3). Particle movement due to shear waves



Figure(4). Total vibration of a body due to shear waves

Figure 3 represents the particle motion caused by shear waves, generated by applying a shearing force to one face of a solid. The whole body may also vibrate in a shear manner, Figure 4. Since there is no elasticity to shear in a liquid or gas, it is not possible to propagate shear waves within them.

The shear wave velocity is about 48 per cent of that of a longitudinal wave in the same material and the lower value gives a much shorter wavelength. The velocity can be given as

 $c = (G/p)^{\frac{1}{2}}$

where G is the modulus of rigidity and p the density. When materials are being investigated by study of acoustic propagation times the use of shear waves enables less sensitive timing circuits to be used, due to the lower velocity. The shorter wavelength will cause shear waves to be easily scattered by small inclusions in the material and polarization effects may be noticed since the direction of particle vibration is dependent on the orientation of the transducer. A material possessing numerous inclusions or a coarse grain structure may therefore exhibit different properties when the transducer is rotated.

3. SURFACE OR (RAYLEIGH) WAVES

If an area of a solid surface is shaken in a manner similar to the generation of shear waves, a wave can be propagated over the surface without penetration into the main volume, Figure 5. The

Figure(5). Representation of surface waves



wavelength is always extremely short and the plate on which the wave travels must be at least several wavelengths thick. Surface waves consist of both longitudinal and shear types of particle motion and their velocity is about nine tenths of the shear wave velocity. It is approximately equal to

$$c = 0.9 (G/p)^{\frac{1}{2}}$$

the constant 0.9 varying with the properties of the medium.

In a bar having a large diameter: wavelength ratio the propagation is constrained within the bulk of the material, but as the diameter approaches the wavelength a reflection from the surface will produce a phasing effect and thus an apparent alteration in the velocity. Fundamentally, it can be stated that the long bar velocity is the value for a zero diameter: wavelength ratio, while the bulk velocity is for an infinite diameter: wavelength ratio.

The usual relation between frequency, velocity and wavelength can be applied to ultrasonic waves, namely

 $\lambda = c/f$

where λ is the wavelength, c the velocity and f the frequency.

CAVITATION

Cavitation is a phenomenon which is observed in boiling water and also in sea water, in the vicinity of a rotating ship's propeller. It occurs in those regions of a liquid which are subjected to rapidly alternating pressures of high amplitude. One would thus expect that cavitation would take place in a liquid irradiated with high energy ultrasonics.

Consider a small region in a liquid through which sound waves are travelling. During the negative half of the pressure cycle the liquid is subjected to a tensile stress and during the positive halfcycle it experiences a compression. Any bubbles which are present in the liquid will thus expand and contract alternately. Where the pressure amplitude is sufficiently high and the initial radius of the bubble is less than a critical value, R_0 as given by the expression:

$$w^{2}R_{o}^{2} = 3 \gamma (P_{o} + 2T_{s}/R_{o})/p$$

the bubble collapses suddenly during the compression. In this equation, w represents the angular frequency, Po the hydrostatic pressure in the liquid,? the ratio of the principal specific heats of the gas contained in the bubble, and T_s the surface tension at the surface of the bubble. This sudden collapse is known as cavitation and it can

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result in the release of a comparatively large amount of energy almost instantaneously. The magnitude of the energy released in this way depends on the value of the ratio Rm/Ro. where Rm represents the radius of the bubble when it has expanded to its maximum size. This ratio depends on the value of the acoustic pressure amplitude and hence, the acoustic intensity.

Although the presence of bubbles facilitates its onset, cavitation can also occur in gas-free liquids when the acoustic pressure amplitude exceeds the hydrostatic pressure in the liquid. For part of the negative half of the pressure cycle the liquid is in a state of tension. Where this occurs, the forces of cohesion between neighboring molecules are opposed and voids are formed at weak points in the structure of the liquid. These voids grow in size and then collapse in the same way as gas-filled bubbles. Cavities produced in this way contain only the



Figure (6), Variation of threshold intensity with frequency for water at room temperature(11).

vapor of the liquid. Cavitation in a gas-free liquid may be induced by introducing defects in its lattice structure such as by adding impurities or by bombarding the liquid with neutrons. The onset of cavitation is often indicated by a hissing sound called 'cavitation noise'. The minimum intensity or amplitude required to produce cavitation is called the 'threshold of cavitation'. This quantity and also the amount of energy released may be determined from the loss of weight due to the erosion of a solid sample placed in the liquid.

Figure(6) shows the threshold intensity varies with frequency for both aerated and gas-free water. As one might expect, the threshold intensity is considerably greater for gas-free water than for aerated water. It is seen that this quantity remains constant for frequencies up to about 10 kHz; there is then a steady increase as the frequency is raised to about 50 kHz and finally a rapid increase as the frequency is raised still further.

As a general rule, there is an increase in threshold intensity with rising pressure and a decrease with rising temperature. There are, however, a number of exceptions to this rule(11). The threshold intensity decreases as the time of exposure to sound is increased. This is because of a time delay between the acoustic excitation and the onset of cavitation. Thus, for pulsed waves, the threshold intensity is reduced in value as the pulse length is increased, until an upper limit is reached, after which it remains independent of pulse length. This upper limit is dependent upon frequency and would be of the order of 20 m sec for a frequency of 20 kHz.

The quantity of energy released by cavitation is dependent upon the kinetics of the growth and collapse of the bubbles. This should increase with the surface tension at the bubble interface and decrease with the vapor pressure of the liquid. Water, because of its comparatively high surface tension is a very effective medium for cavitation. It can be made still more effective by the addition of about 10 per cent alcohol, which results in a considerable increase in vapor pressure but a decrease in surface tension. However, the added effect due to the rise in vapor pressure more than compensates for any losses due to the fall in surface tension.

Cavitation may be accompanied by a weak emission of light; this phenomenon is known as "sonoluminescence", for which continuous spectra have been observed. There is some doubt as to the origin of this phenomenon, and the various theories put forward have been discussed by Jarman(12). He suggested that the most likely explanation is that micro-shocks are produced in the cavities during their final collapse. As a result of these shocks the vapor becomes incandescent and there is a temperature rise of several thousand degrees. He also proposed that chemical reaction caused by cavitation might be responsible for some part of the observed sonoluminescence.

For optimum conditions a low frequency is chosen but there is a lower frequency limit at about 20 kHz by considerations of the health and comfort of the operators, who would experience unpleasant and harmful effects at frequencies below this. The method of coupling the sound energy to the region of cavitation requires careful considerations, because of the necessity of avoiding cavitation in the intervening medium, where the bubbles would scatter the sound waves, thus giving rise to attenuation. This can be done with the use of a focussing system which ensures that the threshold intensity level is exceeded only in the region where cavitation is required. Alternatively the threshold level of the coupling fluid can be suitably increased by maintaining it at an increased pressure.

ULTRASOUND EFFECT ON ORGANIC COMPOUNDS

The influence of ultrasonic irradiation on the kinetics and mechanism of a very large number of chemical reactions has been studied. Organic compounds grasped more attention from investigators than all the other compounds. However, no theory proposed succeeded to explain the effect of ultrasound on chemical reactions, or predict any chemical change satisfactorily. Empirical formulas or mathematical models were proposed to explain or predict chemical changes under the influence of ultrasound only in the range of the experimental data found.

1. CARBOHYDRATES, POLYHYDRIC ALCOHOLS, AND ALIPHATIC ACIDS

Szent-Gyorgyi was the first who observed the influence of ultrasonic waves on carbohydrates, when he discovered a number of dextrins in an irradiated aqueous solution of starch(19).

Reduced substances were detected by Gohr and Wedeking(20) in irradiated solution of 1% glycogen with ultrasound. Khenokh(21) investigated the action of ultrasound on aqueous solutions of mono- and disaccharides. Formaldehyde appeared after 13 hours exposure of these solutions to ultrasound of intensity of 7 w/cm². He also detected chromatographically the detachment of fructose from prolonged irradiated solutions of inuline and sucrose. He inferred that ultrasound action on aqueous solutions of carbohydates led to the formation hydroxymethylfurfural:



Hexose

Hydroxymethylfurfural

It was found that an alkaline solution of glucose, arabinose, and maltose can rapidly undergo deep and diverse degradation on being heated to 90° , changing from colorless to red. The decomposed products have an absorption maximum in the ultraviolet at wavelength 2650 A. Ultrasound degradation showed the same absorption maximum without any change in color even after long exposures(22).

Heating alkaline solutions of sucrose and raffinose up to 2 hours to 90° C does not change their colors and remain transparent in the ultraviolet region. Yet those solutions reveal an absortion band in the ultraviolet if they subjected to the action of ultrasound(22).

It was proposed that heat does not induce chemical transformation to sucrose and raffinose because the aldehyde group of these molecules is in the bound state. Ultrasonic waves break the oxygen bridges between the monosaccharides contained in these compounds, giving rise to compounds with free aldehyde groups. This aldehyde group is an enol form, which would assist further chemical changes under the action of ultrasound. The amount of reducing substances released, increased with the increasing of the duration of irradiation(22).

The release of aldehyde groups by ultrasound is indicated by the appearance of reducing substances in irradiated solutions of sucrose and raffinose. The amount of reducing substances increase with the increase in the duration of irradiation.

Reducing substances are formed both in acid and alkaline solutions of sucrose and raffinose under the action of ultrasound. If an irradiated acid solution of sucrose is made strongly

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alkaline (to pH 13) by the addition of alkali, subsequent heating of this solution on a water bath leads to a further change in the carbohydrate and the formation of substances with an absorption maximum in the ultraviolet at 2650 A. Sucrose which has not been irradiated does not exhibit such absorption even after prolonged heating in an alkaline medium.

When a sucrose in acidic or alkaline aqueous solution is subjected to ultrasonic treatment, its degradation rate will increase(23). In the presence of oxygen or air in the solution the rate of hydrolysis is higher than that in the presence of Hydrogen, nitrogen, or carbon dioxide(23). In the presence of oxygen, carbon dioxide and formic acid formed, but in the presence of Hydrogen only, slight degradation occured without acid formation(24). The higher the frequency, the faster the hydrolysis rate, for example, irradiation with 1 mHz ultrasound of power 5 and 10 w/cm² showed faster rate than 500 kHz at 50 and 70° C. (24). The hydrolysis rate is also inversely proportional with the sucrose concentration. 0.1 M sucrose solution hydrolysis is faster than 2 M solution under the same conditions(23).

The structure stability under the action of ultrasonic vibrations was studied by Velikodnyi and Chernogorenko(25). They found that, when the sucrose is dissolved into water two structures occured, the sucrose structure which is more stable up to 30% concentration and its stability increases by increasing the concentration in this limit, and the sucrose hydrate structure which is more stable in solutions with sucrose concentration over 30%. Although increasing the frequency of the ultrasonic vibrations increases the hydrolysis rate of sucrose, but also increasing the power, promotes the hydrolysis rate(26). When an aqueous solution of sucrose was treated with an ultrasonic vibrations of the frequency 1 kHz and the power of 0.23 w/cm² no splitting was observed. When the power was raised to 200 w/cm² the splitting occured. This result was also observed either in aqueous or diluted nitric acid solutions.(26).

The hydrolysis of sucrose under the action of ultrasonic waves in solvents other than water was also studied (27). When 5% sucrose solution in a glass vessel is immersed into a supersonic fountain (produced by a frequency of 1.2 mHz, applied to a piezoelectric quartz plate with a concavity having a focal distance of 10 cm), the sucrose decomposed. Increasing the duration of exposure showed an increase in the rate. Thus in 8 minutes the decompisition reaches 0.12%, in 60 minutes 0.36%. This takes place in acid or alkali solutions, as well as in acetate, phosphate, and other buffers. This phenomenon is greatly enhanced if CC1, is added to the solution (0.01 ml $CCl_{L}/15-20$ ml, sucrose solution) in 8 minutes, the decomposition reaches 0.3-0.4% and in 60 minutes 1.48%. Thus the presence of CC1, shows a 3-4 fold increase in decomposition. Addition of acetic anhydride to an aqueous solution of sucrose and CC1, retards the decomposition of sucrose(27).

Most work on the irradiation of molecules in solution has been done with ultrasound which causes collapse cavitation, which takes place in times of about 10 μ s in a 100 kHz sound field, causes intense shock waves. The temperature at the collapse center could reach 2000^oK. It is thought that collapse cavitation

is the main agent of degradation. However depolymerization was observed under noncavitating ultrasound vibrations (Schmid and Rommel(77)). A study of sucrose hydrolysis treated with noncavitating ultrasound vibration was carried out to prove that the enhacement occured is not necessarily due to collapse cavitation. A high frequency of 1.0 mHz, was choose (28) and intensities of 3 and $8w/cm^2$, which is below the threshold intensity to form collapse cavitation with this frequency (500 w/cm^2) . The apparatus used consisted of a lead-zirconate-titanate alloy transducer. The sucrose solutions were put on top of the crystal face and held by a ring. Above the sucrose solution castor oil was floated to absorb the energy of the ultrasound and prevent it from reflecting back at the water-air interface so that no interference occurs. A rubber diaphragm of 0.002 in thickness separated the water from the sucrose solution with no air bubbles in between.

A sucrose solution in 0.1 N NaOH was irradiated with pulsed ultrasound (to eliminate any possibility of forming collapse cavitation) of intensities of 3 and 8 w/cm² for 20, 25, 30, 40, and 60 minutes then every solution was tested for reducing sugars using Benedic's reagent and also placed into spectro-photometer for wavelength between 0.2 and 0.35 um. The temperature was allowed to rise, where a similar solution as control was heated with an adjustable electrical power supply to give the same rate of temperature rise as that achieved with ultrasound. The samples irradiated with intensity 3 w/cm² showed temperature rising to 50°C after 60 minutes irradiation, to 60°C after 120 minutes irradiation and to 65° C for that irradiated with intensity of 8 w/cm². No hydrolysis occured in that irradiated with intensity of 3 w/cm². Even heating the control sample to 100° C no sign of hydrolysis was abserved. The sample irradiated with intensity of 8 w/cm² showed same hydrolysis. Therefore the combination of heat and irradiation initiated hydrolysis in solution of 0.1 N NaOH which normally does not occur(28).

The same experiment was done at pH of 3.5 and 5.5 and intensity of 8 w/cm² but no hydrolysis occured. Sucrose was then irradiated in 0.1 N HCl solution for periods up to 20 minutes, under which conditions, the rate of hydrolysis is approximately three times that produced by heat alone.

These results show that heat and ultrasound vibrations are necessary in conjunction to initiate hydrolysis of sucrose. The collapse cavitation is not necessary to start a reaction. Intensity is an important factor, and it must be large enough to start a reaction. Changes due to irradiation are ion-dependent (28).

Exposing alkaline aqueous solutions of polyhydric alcohols to ultrasound also showed chemical degradation forming substances that have an absorption band in the ultraviolet with a maximum at 2650 A.

When an alkali is added to an irradiated acid solution of mannitol (to pH 13) heating causes further transformation of this polyhydric alcohol and substances with an absorption band in the ultraviolet are formed. Similar action occured when glycerol was subjected to ultrasonic waves.

Therefore, it is believed that polydydric alcohols dissolved in water undergo oxidation in ultrasonic field forming aldehydes, which are enolized in alkaline medium. On further thermal or ultrasonic treatment, the aldehyde in enol form undergoes changes which can easily be detected by spectrophotometry in an alkaline medium in the ultraviolet when hydrochloric acid is added to the solution to bring its pH value to 2. The absorption maximum is shifted toward shorter wavelengths and appears at wavelength 2450 A. It is known that, absorption maximum in this region of the ultraviolet is usually given by organic substances characterized by the possession of a conjugated double bond(29). Such organic substances include Land D-ascorbic acid. This acid gives an absorption band in the ultraviolet with a maximum at a position detemined by the pH of the medium; at 2650 A in an alkaline medium, and at 2450 A in an acid medium.

Ascorbic acid undergoes considerable degradation under the action of ultrasonic waves. This can be detected by spectrophotometry. With increase in the duration of ultrasonic action the height of the absorption maximum of this compound steadily diminishes irrespective of whether the irradiation and spectrophotometric determination are conducted in an acid or alkaline medium(22).

Kasahara and Kawashima(31) observed the degradation of ascorbic acid in an ultrasound field. El' gort et al found polarographically the formed aldehyde also undergoes chemical transformation in An ultrasonic field(32).

It was also found that treating aliphatic acids with ultrasound in aqueous solutions gives rise to reducing substances, which would undergo more complex transformations(33). Irradiation in an alkaline medium transforms some of them to compounds

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which also exhibit absorption in the ultraviolet with a maximum in the wavelength range characteristic of substances of the cyclic series or for molecules with conjugated double bonds. Succinic, citric, and malic acid undergo such transformations.

Some aliphatic acids show very high stability in ultrasonic field even after very long exposure(2 hrs). Such acids are oxalic, malonic, tartaric, Glutaric, adipic, formic, and acetic. This means that chemical changes depend strictly on the structure of the irradiated aliphatic acids. Even slight differences in the structure of these molecules can affect the stability of the irradiated subestance in an aqueous medium containing air.

2. AROMATIC AND HETEROCYCLIC COMPOUNDS

It is known that benzene resists the action of strong oxidants, yet in an ultasonic field, an aqueous solution of benzene disintegrates (37). Benzoic acid, phenol, indole, guanine, thymine, and barbituric acid were exposed to ultrasound (38,39). The absorption band of those compounds in the ultraviolet disappeared.

Treating toluene in aqueous solution with ultrasound of $5w/cm^2$ intensity for 15 hours, caused the appearance of formaldehyde, and phenol(40). It was found that phenol is more resistant in an ultrasonic field than benzene or toluene. In saturated aqueous solutions of benzene and its derivatives exposed to ultrasound for a short time, French investigators(34) found the same decomposition products which Stein and Weiss(35) found as a result of the action of x rays on aromatic compounds. Standing of the irradiated benzenesaturated aqueous solution for 12-24 hours led to the precipitation of a deposit, in which the authors detected phenol, and resorcinol. In other runs they also detected diazotized paranitroaniline, and substances of an aldehyde nature(34). From these results Robert, Prudhomme, and Grabar concluded that the action of ultrasound also leads to fixation of atmospheric nitrogen by aromatic compounds.

This is confirmed by other experimental results cited by Robert(36). This author studied the effect of ultrasound on an aqueous solution of phthalic acid in the presence of air. After a 60-min irradiation, the solution was evaporated, and a brown amorphous deposit containing traces of nitrogen was found. In addition, he found that in the case of a short irradiation(30 min) of an aqueous solution of benzene in the presence of air, the maximum of the absorption band in the ultraviolet was shifted from 2640 to 2680 A. This, in Robert's opininon, indicates that ultrasonic treatment of aromatic substances leads to the introduction of atmospheric nitrogen into the benzene ring, i.e., to the formation of nitrobenzene. Irradiation of aromatic amines in an air-saturated aqueous medium produces derivatives of diazo compounds(36).

Aromatic and heterocyclic rings are thoroughly degraded by ultrasound even at room temperature(41). When an aqueous solution of silver nitrate and bromobenzene, iodobenzene, -bromothiophene, -iodothiophene, or -bromofuran was irradiated with ultrasound, a precipitant containing acetylenides and diacetylenides formed (41, 42). This means that degradation of aromatic or heterocyclic compounds in an ultrasonic field includes the formation of a triple bond between the carbon atoms(C=C).

 \rightarrow Br + Ag⁺ = AgC=C-CH=CH-CH=CHBr + H⁺

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An aqueous solution of 1,2-benzpyrene, which is a strong carcinogen, was irradiated ultrasonically, a stable fluorescent colloidal solution formed and carcinogenic properties disappeared(43).

El'piner and Stekol'nikov subjected a number of alkoids (atropine, cocaine, and quinine) to ultrasonic field of 800 Hz, and intensity of 10 w/cm² in the presence of air (oxygen), the color changed to yellow. The intensity of the color increased with increasing the duration of irradiation. They found that the solution remained colorless in the presence of hydrogen or inert gases (helium, argon).

After 30 minutes irradiation, in the presence of oxygen atropine gave a negative Vitali-Morin reaction, which indicates cleavage of the tropic acid residue in the atropine molecule. The Vatali-Morin reaction was positive if the aqueous solutions of atropine were irradiated in the presence of H_2 , He, or Ar.

Cocaine-the methyl ester of benzoylergonine resists the action of ultrasound(43). Cocaine differs little in structure from atropine



Atropine



Cocaine





NO chemical change was found of the cyclic residues in the molecule of cocaine irradiated with ultrasound in aqueous medium containing O_2 , H_2 , He, or Ar.

Quinine lost its pharmacological activity if it was irradiated in the presence of air (oxygen).

3. PURINE AND PYRIMIDINE BASES

Ultrasound waves also lead to changes in six-membered ring derivatives containing one or two nitrogen atoms. Pyrimidine, and the complex heterocyclic compound purine are the most important of such compounds. Purine and pyrimidine bases







Purine

(uracil, adenine, guanine, hypoxantine, xanthine etc.) are essential nutrients to animal organisms, and stimulate selectively the growth of a number of bacteria(44).

Aqueous solutions of uracil, adenine, and guanine were subjected to ultrasound of frequency 500kHz, and intensity of $5w/cm^2$ (45).

The absorption band of uracil solution (alkaline medium) is shifted toward longer wavelengths (lower frequencies), and the absorption maximum is accordingly shifted in the same direction. In addition, the absorption curve of guanine dissolved in an acid medium shows two absorption maxima in the ultraviolet region.

The changes in the different substances differed only in quantitative aspect. This means that these compounds differ from one another in their sensitivity to ultrasound. Uracil was found to be more sensitive to this physical agent; adenine and guanine were less sensitive.

The reduction in the absorption maximum is most probably due to breakage of the pyrimidine or purine ring in the investigated molecules. Such a breakage would result in the loss of the ability of these molecules to absorb ultraviolet light. It is more difficult to explain the shift in the absorption maximum toward longer wavelengths and the observed reduction in light absorption of these solutions with prolongation of ultrasonic action. These changes can also be attributed to the fact that ultraviolet irradiation causes intramolecular regroupings, which lead to the formation of less stable rings, relatively easily destroyed by further irradiation with ulraviolet(45). Another possibility, is the ionization and subsequent cleavage of water molecules in the cavitation bubbles and the formation of free valence-unsaturated radicals (OH, HO₂, H,),
which have a strong oxidization or reducing action.

Oxidation processes in an ultrasonic field are possibly further enhanced by the ionization or dissociation in the cavitation bubbles of the molecular oxygen dissolved in the irradiated aqueous solution. This explains why prior removal of molecular oxygen from the irradiated (by saturation with gaseous hydrogen)inhibits oxidation of the investigated substances. For instance, in a hydrogen atmosphere, only 3.5% of the adenine present in the solution is degraded even after 120 min of ultrasonic irradiation. In an atmosphere of air the amount of adenine is reduced by 45-48% after such an exposure(46).

The kinetics of chemical oxidation apparently depend not only on the presence of 0_2 or free OH and H0₂ radicals, but also on the chemical affinity of the investigated compounds for the particular oxidizing substance, Runs using spectrophotometry showed that irradiation in the presence of 0_2 (but not air) led to the complete disappearance of adenine after 60 min of irradiation (the oxygen was obtained by decomposition of KMn0₄). A solution of 0.2 mg of adenine in 10 ml of 0.14 N NaCl was irradiated. A smaller amount of adenine was destroyed by irradiation in the presence of argon, and none was destroyed in the presence of helium(46).

EFFECT OF ULTRASOUND ON MONOMERS AND POLYMERS

Polymerization can be assisted by ultrasonic treatment, this has been studied in a number of reactions. Polymerization of acetic acid to aldol can be effected by ultrasonic waves of varying frequencies(47). Increasing frequency and longer duration of application of the ultrasonic field yield more polymers, but the best results were obtained by changing the frequency during the progress of the reaction. Emulsion polymerization reactions used in the production of synthetic rubber have been speeded up by ultrasonic irradiation(48). Two test frequencies were used, 15 kHz generated by a mickel bar transducer, and 500 kHz, produced by a quartz crystal. At a solution temperature of 50° C the principal effect was elimination of the induction period with only a slight increase in the rate of reaction. At a temperature of 40° C the effect was more pronounced.

An explanation of the polymerizing effect of ultrasound has been given (49). At steady state conditions a constant fraction of the primarily and secondarily produced free radicals is available to induce the polymerization of the existing monomer. This, however, is not the only cause of the polymerization effect; in addition there is a kind of autokinetic effect that can be attributed to the depolymerizing action that occurs concurrently. Thread molecules of colloidal size will have their C-C bonds broken by the frictional forces and the end groups at the fracture may be unsaturated and of a radical nature, similar to the active end group in a growing polymer molecule. The fragments obtained in the splitting of a polymer molecule are thus capable of continued polymerization.

Depolymerization by ultrasonics is also well known for many polymers in solution, among which are starch, agar, gelatin, gum arabic, polystyrene, polyvinyl acetate, polyacrylates, nitrocellulose, proteins and rubber. As the molecular weight increases, the depolymerizing action can be produced at a faster rate. It is usually not possible to carry the depolymerization all the way down to the monomer.

The action of ultrasonic waves on solutions of high polymers may produce two different effects. First, H. Freundlich and D. W. Gillings(50) found that weak irradiation of fresh solutions of gelatin in water causes a considerable reduction in the magnitude of the non-Newtonian viscosity.

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On standing for several days the solution regains almost as high a viscosity as it had before irradiation. This effect is believed to be due to the temporary breaking of the loose gel network of van der Waals bonds between adjacent polymer molecules and does not take place to any appreciable extent in the absence of cavitation. The intermolecular van der Waals forces are generally of the order of 1-10 kcal/mole.

The second way in which ultrasonic waves may affect high polymers is to cause depolymerization. That is, the actual breaking of chemical bonds in the chain, to give molecules of a smaller size than the original and therefore a permanent decrease in viscosity. These chemical bonds are between 50-100 kcal/mole.

As an example of the first case, irradiation of a 5-10 per cent solution of gelatin in water, or rubber in toluene, shows a decrease in the apparent viscosity with ultrasonic inputs of $10-20 \text{ W/cm}^2$. When irradiation ceases the solution returns to a value near the original viscosity. This action can be interpreted as follows. High polymer solutions do not possess viscosity as defined by the fundamental laws of Newton, Poiseuille, or Stokes, as the long and irregularly entangled chainlike molecules form a flexible framework in which the solution is entrapped. The system therefore offers a considerable resistance to shearing forces, and while the forces are too weak to tear the network to pieces it appears to have a high viscosity or even the characteristics of a gel.

According to Freundlich and Gillings(50), cavitation action inside the framework disrupts the continuous network by severing the bonds between the different chain molecules. These bonds are comparatively weak and only a minor cavitation action is necessary. It was shown that the action was purely a function of cavitation by a negative result obtained

when the liquid was fully degassed and irradiated under pressure. After irradiation ceases the macromolecules slowly reproduce the original random network by their irregular brownian movement.

The irreversible viscosity decreases occurring after ultrasonic irradiation of high polymers have been demonstrated by G. Schmid(51), using a frequency of 300 kHz and a power of 10 W/cm². It was noted that solutions of nitrocellulose, polyvinyl acetate and polystyrene irradiated for a few hours at 70° C show considerable viscosity decreases, and the original viscosity cannot be restored, even by evaporating the solution and redissolving the dry polymer in the solvent.

The importance of cavitation in the depolymerization process can be seen in the degradation of hydroxyethyl cellulose in water. Weissler(52) has demonstrated that the process is not dependent on the solvent, by irradiating a 0.8 per cent aqueous solution of hydroxyethyl cellulose for three hours at 200 W input with a frequency of 400 kHz. After irradiation the solution was diluted to 0.4 per cent and gave a very slight viscosity change, from 112.2 to 111.3 seconds, in degassed dolutions. In ordinary solutions, a decrease to 73.6 seconds was noted. With the viscometer used in these experiments distilled water had a viscosity of 61.1 seconds. When the power level was varied, an even more direct relation between degradation and cavitation was demonstrated; it was observed that a threshold level for cavitatation could be detected as the power input was raised, the level being higher in viscous solutions. By subjecting successive portions of hydroxyethyl cellulose solutions to five-minute irradiations at increasing power levels, it was found that no depolymerization occurred at the low levels where cavitation was absent. At the approximate point where cavitation began, degradation also commenced, and became greater as the

power was increased. The action occurred irrespective of the nature of the dissolved gas, and nitrogen, oxygen, or helium could be used.

To explain the depolymerizing effect of ultrasound, Schmid(51) considered two ideal cases:

- 1. the long-chain molecule is rigidly held in the solution;
- the long-chain molecule moves freely in the solution. An analysis
 of the behavior of polystyrene in an ultrasonic field is given as
 an example.

The polystyrene molecule is pictured as a long thread free of friction forces, and with separate "balls"-benzene rings, with a radius of 3 A, attached to it at equal distances from one another.

In the case of the rigidly fixed state of the macromloecules an ultrasonic field will give rise to friction forces between the fast-moving solvent molecules and the macromolecules. The friction forces developed in this case can be calculated from Stokes' formula,

where n is the viscosity of the solvent; r is the radius of the benzene ring; v_s is the maximum velocity with which the solvent molecules move as a result of the great acceleration impatred to them in the ultrasonic field; P_n is the number of units comprising the macromolecule.

According to (71) $v_s=50$ cm/sec, r=3 A, n=0.0062 (in CGS units). P_n=3000. Then f_o is equal to 5.37×10^{-4} dyn. Such a value of f_o is sufficient to effect the breakage of the C-C bond(87).

The forces acting on a macromolecule in an ultrasonic field will be many orders less if it is assumed that the molecules can move in the irradiated solution along with the solvent molecules. The force acting on macromolecules can be determined from the following formula:

$$f_o = P_n \frac{m}{N} w \cdot v_s$$

where m is the molecular weight of the monomer, N is avogadro's number, $w=2\pi/T$, T=2.1x10⁻⁶ sec (period of ultrasonic wave);the acceleration amplitude in the vibratory motion is wv_{c} .

In the above-indicated experimental conditions, the product $(m/N)wv_s$ will be equal to 2.77×10^{-14} dyn. In other words, in dilute solutions, e.g., in the absence of interaction between the dissolved molecules, the depolymerizing effect will be infinitesimally small, which is not observed in fact.

Mark(72) gives a rather different treatment of the depolymerizing effect in an ultrasonic field on the basis of the following considerations. According to modern ideas, long-chain molecules in dilute solutions(in appropriate solvents) are not stretched out in a straight line nor curled up in a ball. They are most probably of another configuration-moderately sinuous, slightly twisted. In the solution the individual units of the sinuous molecule will perform independent mechanical vibrations and rotations, distinguished by a relatively high speed (micro-Brownian intramolecular motion). The small units of the molecular chain change their position in 10^{-3} sec. The chaotic motion of the molecule as a whole (macro-Brownian motion) is much slower. The average velocity of the macromolecule reaches 0.5-1.0 µ/sec.

In an ultrasonic field, according to Mark's hypothesis, the motion of the whole macromolecule will lag well behind the motion of the solvent molecules. According to Mark's calculations, the friction forces arising between the macromolecules and the solvent molecules are so great that they greatly exceed the strengths of the chemical bonds C-C,C=C,C=0. The latter, according to spectroscopic data, are equal to 4.5×10^{-4} , 5.77×10^{-4} , and 9.77×10^{-4} dyn, respectively. Mark estimated the friction force between the macromolecules and the solvent molecules (at a velocity of 40 cm. sec⁻¹) as $(2-3) \times 10^{-4}$ dyn per bond. This means that when the ultrasonic generator is switched on, the macromolecules containing these

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groups will immediately break up into small molecules. However, Schmid's experimental data(51), show that even after a long irradiation only a small proportion of the groups contatined in the longchain molecule undergo breakage-approximately 5 per 1000. Hence, Mark concluded that the majority of individual units of the macromolecule, which rotate freely around the valence line, follow the rapid vibratory movements of the solvent in an ultrasonic field without offering any resistance to these movements. Sufficient friction to break the atomic bonds is developed only rarely and at scattered points.

It should be noted that rotation of the individual units of high-polymer compounds is not free, but is greatly restricted by the interaction between the units of the molecule(73).

It must be added that, according to the ideas developed in(74-76), the stress arising in microregions of the specimen (solid or liquid) at relatively slight deformations is not distributed uniformly and may be concentrated at separate points, thus leading to breakage of separate covalent bonds of the macromolecule. This can presumably occur either in regions of compression or regions of rarefaction in the path of propagation of the ultrasonic wave, since the length of the ultrasonic wave is many times greater than that of the highpolymer molecule.

The views of Schmid and Mark have aroused lively discussion. The only undisturbed point is Schmid's equation representing the kinetics of decomposition of macromolecules in an ultrasonic field. This equation was obtained from an analysis of the following experimental facts.

In a study of the effect of ultrasonic waves on solutions of individual fractions of polystyrene in toluene (molecular weight of first fraction 85,000; second fraction 350,000; third fraction 195,000). Schmid and Rommel(77) found that in the first few minutes of irradiation depolymerization was fairly fast, but subsequently slowed down and ceased altogether when the molecular weight of the polymer approached 300,000. The rate of depolymerization was greater, the higher the initial molecular weight or, rather, the greater the initial length of the investigated polymer. Similar data were given by Mostafa(75).

Schmid and Rommel(77) found the same relationship in an investigation of the effect of ultrasonic waves on dilute solutions of polyvinyl acetate, the methyl ester of polyacrylic acid, nitrocellulose, and rubber.

The existence of a limit degree of polymerization (i.e., a minimum number of monomers in the formed depolymarized polymer) was also established by other investingators(78) in a study of the effect of ultrasound on aqueous solutions of polyvinyl alcohol (initial molecular weight 77,000). The degree of polymerization of the investigated monomers, according to the results of measurement of diffusion and viscosity coefficients, reached the limit values after 90 to 120 min of irradiation (frequency 450 kc, intensity 20 W/cm²). Schmid(51) gave a mathematical expression of the described effect in the foolowing form:

$$\frac{dx}{dt} = k(p_t - p_e)$$

where dx is the number of chemical bonds broken in unit volume in a given time of irradiation dt, p_t is the degree of polymrization of the long-chain molecule at a given instant t, p_e is the limit degree of polymerization of the macromolecule, which undergoes no further destruction by ultrasonic action. This means that the rate of depolymerization does not depend on the structure of the polymer. It depends on the difference in the initial and limit degree of polymerization and on the concentration of the irradiated polymer.

At very high degrees of polymerization schmid found a reduction in the rate of depolymerization of irradiated polymers. The reduction

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was particularly pronounced in a solution with a high concentration of macromolecules and a high viscosity. No depolymerizing effect was found in gels.

Schmid's equation holds for dilute solutions, up to a concentation of about 0.02 mole/liter. For higher concentrations the following equation(79) is more satisfactory:

$$\frac{dx}{dt} = k \log \frac{P}{P_{o}}$$

Ultrasonic depolymerization may be due to the appearance of pulsating cavitation bubbles in the irradiated liquid(79). Velocity gradients appear in the liquid close to these bubbles and may cause breaks in macromolecules.

In irradiated solutions with a high concentration of polymer the rate of decay of the bubble vibrations becomes very great, and this, in Henglein's opinion, leads to a reduction (in particular conditions) of the depolymerizing effect of ultrasound(79).

According to Weissler(80,8), depolymerization of macromolecules is due to cavitation effects. He observed depolymerization in the presence of cavitation in polystyrene in toluene and hydroxyethyl cellulose in water (frequency 175 Hz). According to his data, the molecular weight of the irradiated polymer was reduced to 0.1 of its initial value.

irrespective of the gas, air, or helium, saturating the irradiated solution.

Prudhomme and Grabar(82), who also investigated the effect of ultrasonic waves on polystyrene in toluene and carboxymethyl cellulose in water (frequency 960 kc, ultrasonic intensity $6.8W/cm^2$) came to similar conclusions. They observed depolymerization of the long-chain molecules when the irradiated liquid was saturated with gases promoting cavitation. In a degassed liquid or in a liquid saturated with carbon dioxide, no depolymerization occurred.

The results of similar investigations are given in(83). Small cavitation bubbles and the so-called cavitation noise are produced fairly easily in irradiated benzene containing nitrogen, hydrogen, argon, or methane. Cavitation is very weak in benzene saturated with ammonia or carbon dioxide. It does not occur at all in the presence of SO_2 even at high ultrasonic intensities (10 W/cm²). There is a definite correlation in it. The greater the solubility of the gas, the greater the amount which penetrates into the cavitation bubbles, and the smaller the intensity of the shock waves created by the collapse of the bubbles.

More attempts have been done to explain the effect of ultrasonic waves on depolymrization of macromolecules (55,56,58,). The mathematical models proposed were more complicated, and yet, applicable only in a few cases. Woodcock and Connolly(28) showed that even non-cavitating ultrasonic waves has an effect on molecule degradation. This can not be explained by any of the previous proposed mechanism of the effect of ultrasound on molecule degradation, since all require the presence of cavitation before any chemical change to occur.

THE EFFECT OF ULTRASOUND ON LIVING ORGANISMS

The action of intense sound waves of both sonic and ultrasonic frequency on living organisms is of a complex and not easily understood nature. It is obvious that living cells must be influenced in varying ways by the combination of high acceleration values and rapid pressure changes produced in an ultrasonic beam. Similarly, secondary effects such as cavitation and the generation of heat within the cell will also contribute to changes of state.

When human beings are exposed to intense ultrasonic waves generated in air several characteristic effects are produced that vary somewhat depending on the subject. Using a high power siren it has been found that unusual fatigue is produced, often accompanied by a loss of equilibrium and nausea. Other effects include a hammering sensation in the head near the ears and a disagreeable tickling in the mouth and nose. After prolonged exposure, a headache may persist for some time, with some loss of hearing in the upper audible frequencies. These results are generally obtained at frequencies in the lower ultrasonic range, from 16-30 kHz. Difficulties in the generation of high power ultrasonic waves at higher frequencies have prevented experimental observations being made, but it is thought that any effects would be less noticeable. It is believed that the results of irradiation are due to stimulation of the aural nerves by bone conduction and it has been found that most nerve stimulations cease at frequencies above about 30 kc/s. Apart from the symptoms described it will be appreciated that little energy can actually enter the body when a gas is used as a coupling medium, for the impedance ratio between a solid and a gas is far too high. Many animals have a threshold of hearing considerably higher than a human and in them an ultrasonic frequency is presumably sensed in the same way as normal sound. Dogs and other animals will respond to fre-

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quencies as high as 25 kHz without signs of discomfort, although higher frequencies are apparently disturbing and painful.

Attempts have been made to utilize high frequency sound as a means of scaring birds(4). Great damage is done to the stonework of buildings by the droppings of birds that roost on the structure. Landing fields for aircraft must be kept free from birds as propellers and cockpit enclosures can be smashed by impact with flying birds at the high aircraft landing speeds now common with modern airoplanes. Similarly the landing areas on water are required to be kept clear of roosting seabirds since they tend to rise into the path of a seaplane when alighting or taking off. Various experiments have been carried out using high power sirens as a means of providing ultrasonic energy, usually incorporating focusing horns to enable the sound to be beamed over the area required to be cleared. Initially, the birds are disturbed and will fly off, but eventually they become accustomed to the sound and do not appear to be unduly worried.

At closer distances to the sound source the effects of irradiation are very pronounced, and experimental studies have been carried out on the lethal effect of ultrasonic waves(88). A high power siren, of the type developed by Allen and Rudnick was used and this was fitted with a plywood horn to produce a unidirectional source. A wind screen was fitted above it to deflect the d.c. flow and a reflector was placed about six inches above, and parallel to, the face of the horn to reduce the sonic wind. The siren frequency was 20 kHz with a chamber pressure of 2 atmospheres. The gas flow velocity was 10^5 cm/sec, the acoustic level produced by these values being 160-165 dB.

A study of the lethal effects showed that a temperature rise in the subject under treatment was the primary cause of death. White mice placed in the sound field died after exposure for one minute. Thermocouple measurements indicated very definitely that the heating produced was sufficient to be lethal without considering any other symptoms that may have been caused by the intense sound waves. The fur temperature was 93° C at some points and the internal temperature rose to 60° C after 200 seconds. A mouse with its fur removed lived for about $2\frac{1}{2}$ minutes longer and showed a slower internal temperature rise. From these results it was concluded that sound absorption resulting in that raises the temperature sufficiently to kill, as there is obviously a higher absorption in fur. The reflecting surface offered by bare skin would tend to decrease the absorption and require longer exposure times for the same temperature rise. It is possible that other effects such as cellular or fibrous rupture and cavitation within liquid filled cavities may contribute to the causes of death. An autopsy showed no internal damage, but several small bubbles were apparent in the colon.

Experiments were also carried out on insects with similar results. The roach, Periplaneta americana, a relatively large insect about 2 inches long was quickly killed by the heating effect. The temperature rise was duplicated by placing the insect in hot water at the measured temperature produced in the sound field, and the appearance of the body after death was similar. The jirebrat, Thermobia domestica, an insect that thrives in relatively high temperatures was killed in 120 seconds. Exposure resulted in the loss of many body scales and some of the legs, while the abdomen was considerably twisted. Newly emerged male and female yellow fever mosquitoes, Aedes aegypti, were killed in 10 seconds. Both wings were completely shattered, the body was badly battered with all scales gone and the abdomen was full of bubbles. A mosquito irradiated for 5 seconds was alive but badly battered, and died later. Newly emerged but fully expanded blow flies, phormia regina, died in 10 seconds exposure, the wings being shattered and the

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abdomen caved in. Meal worms, Tenebria molitor, died in 15 seconds without apparent internal damage. Halisidota caterpillars required 40 seconds exposure as a lethal dose. These insects are clothed in a dense coat of hairs and after exposure the hairs were twisted and bent. The monarch butterfly caterpillar, Danais plexippus, required the much longer time of 215 seconds, but the hairs on this insect are very short.

Although experiments on humans were not directly studied owing to the unknown nature of the results, cerain effects were noted during the work on animals and insects. The well known heating effect produced between the fingers when they nearly but not quite touch was troublesome during the seting up of the equipment. This effect is generally considered to be caused by friction set up by the rapid oscillatory movement of air between the surfaces. It was found to be difficult to place or retrieve objects in the sound field without being burnt and a rapid firm grasp of the object was required to avoid burns.

In contrast to the sharp quick burning in cavities between the fingers, a direct heating of broader areas has been observed. If the hand directly over the siren with the fingers outstretched and apart, and the palm down, a warming of the palm was experienced. A loss of equilibrium or slight dizziness is noticed even if ear plugs or deflectors are used, showing that the relatively low intensity reaching the auditory nerve is sufficient to produce ill effects. After prolonged exposure with protective ear pads fitted, it was noted that fatigureand lassitude were produced. The cause of this is unknown.

The heating effect of airborne ultrasonic waves can be strikingly demonstrated in the ignition of combustible materials at the focal point of an intense sound field. If a glass funnel is inverted over the piston source of a St Clair type electromagnetic transducer, and a wad of cotton wool is losely pushed into the neck, a short exposure is sufficient to ignite the fibres.

Ultrasonic waves have been applied in medicine in the three fields therapy, diagnosis and for biological measurements. The field of therapy has been widely exploited and many fantastic claims have been made for the use of ultrasonics as a curative means. Many hundreds of papers have been published on the subject and it is difficult to assess from them with any accuracy the true worth of the method. During the years 1945-55 the practice of ultrasonotherapy was enthusiastically adopted by physicians in several European countries and if all the literature published by manufacturers of ultrasonic medical equipments is read it will be concluded that ultrasonics is the universal panacea for all ills, from asthma to virulent cancer. Many physicians have been using the equipment without making properly controlled investigations into the mode of action of ultrasonics in therapy and it is unfortunate that there is always a tendency to be reticent over negative results. To give some idea of the extent of the practice it has been quoted that by 31 May 1951 some 5350 ultrasonic devices were being employed by physicians in Western Germany alone. This indicates that there is one ultrasonic generator in medical use for every six physicians practising in that country(89). Manufacturers of generators have issued pamphlets with their equipment in which lists of diseases are included that are said to respond favorably to treatment, the range of intensities to be used for each disease, the duration of exposure, and the number of treatments said to be required for relieving symptoms. It is obvious that this information was based on procedure which in many cases ignored proper controls, or reported entirely subjective evaluations of response to therapy.

The earliest suggestion for general application of ultrasonics in medicine would appear to be that of H. Freundlich, K. Sollner and F. Rogowski(90), who in 1932 recommended the possible use of ultrasonic waves for heating body tissues. Their observations were based on ex-

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periments carried out on the heating effects produced in dead bone. Excellent work has been performed by many serious investigators such as E. N. Harvey(91), L. A. Chambers et al.(92) W. T. Richards(93), R. W. Boyle et al(94), but in recent years these investigators seem to have lost their early enthusiasm and tend to be discouraging over the future possibilities. This discouragement arises mainly from the fact that reliable measurements of the effects produced by ultrasonics are difficult to make even in the simplest of homogeneous media. An accurate measurement of the intensity of an ultrasonic field is particularly difficult under ideal conditions. Obviously, measurements inside living tissues would be almost impossible. The reproducibility of results is unsatisfactory because considerable variability occurs in ultrasonic field patterns.

In order to obtain some basic facts on ultrasonic therapy a team of workers was organized at the Mayo Foundation, Minnesota, and in view of the widely diverse statements that have been made on the subject, their observations are of considerable interest(95). After studies of the effects of ultrasonic waves on malignant neoplasms, both transmissible and spontaneous, in the rat, mouse, chicken, and dog, it was found that no selective destruction of malignant tissue occurred. In the past, therapeutists have entertained the opinion that the mechanical effects of ultrasonic waves were the main reason for the therapeutic value of ulttasonics, likening it to a form of internal massage. It has been shown that the heating effect first described by Freundlich and his associates is the main source of action. No other available therapeutic agent for heating bodily tissues can raise the temperature of bone to high levels at so rapid a rate. It is assumed that the extreme pain experienced under intense irradiation is caused by the heating of tissue covering the bone.

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If the femur of dog is exposed to an average intensity of 2 W/cm^2 the temperature is raised 40° C in two minutes. Regions of necrotic bone can be produced and fractures may occur at these sites. Histo-logical exmination of femora following ultrasonic treatment demonstrates the formation of new bone at both ends of the section of necrotic bone. When the growing ends of long bones of young dogs and rabbits are exposed to fairly moderate intensities the growth of new bone is inhibited (96).

It is possible that these effects can be used with advantage, provided the margin of safety beween the desired effect and serious permanent injury is sufficiently large. The formation of new bone may be useful in the healing of fractures, while the inhibition of bone growth may prove of value in inhibiting the growth of bone tumors.

From a consideration of the respective acoustic impedances of bone and surrounding tissue it will be seen why a selective heating of bone occurs. There is an abrupt interface at the soft tissue and bone junction, the acoustic impedances being about 1.5×10^5 g/cm²/sec for tissue and 4.2×10^5 g/cm²/sec for bone. Apart from the heat dissipation caused by reflection and scattering at the interface there is reason to believe that transformation occurs in the wave type, from the propagated compressional waves to shear waves. The latter are rapidly attenuated with the production of heat. Finally, bone is a very good absorber of ultrasonic waves and this also contributes to the temperature rise.

Nerves are also selectively heated by ultrasonic waves(97). When critical temperatures are reached, the nerve loses its ability to conduct a nerve impulse, and this effect suggests a possible use for therapeutic blocking of nerves. General conclusions cannot, however, be drawn until detailed studies are made on mammalian nerves, and it is also possible that diseased nerves may respond differently from normal nerves. A narrow margin to safety was found between reversible and irreversible blocking of nerves and this margin is too narrow for practical use unless reliable methods for preventing permanent blocking can be developed and applied.

J. F. Lehmann(98) has studied the biological and therapeutic effects of ultrasonics with consideration of other possible modes of action than the fundamental heating effect. The tails of white mice were used for the investigation as the temperature of this tissue is quickly adapted to that of the surrounding water bath. Intensities varied from 1.5-3.1 W/cm^2 and reactions varied considerably with the water bath temperature. Initial reactions were observed at a temperature of 30-31°C while severe reactions were displayed at a temperature of 38-39°C. With a decreased ultrasonic intensity the threshold of temperature of the ultrasonic reactions was higher. Comparison of the temperature measured in the tissues during irradiation with the temperature threshold of the reactions produced by heating alone disclosed that the increase in temperature in the tissues was sufficient to explain the biological results. When the tissues was cooled to between 3-4°C during applications of energy, no reaction were observed, even when exposure was of twofold intensity and of eightfold duration.

Changes in the metabolism of the tissues were also dependent on the temperature reached during irradiation. If the tissue was cooled during application no difference was found between the consumption of oxygen of the exposed tissues and that of the controls(99). At higher temperatures the consumption of oxygen was depressed, no difference being noted between the metabolism of the tissues after irradiation and after heating them to a corresponding temperature.

An attempt was also made to distinguish between the reactions caused by the mechanical forces occurring in the ultrasonic treatment and those created by their thermal component. The biological results of continuous exposure were compared with results obtained after application of pulsed ultrasonic energy. The pulse sequence of sixty per second was fast enough for a steady average of the temperature to be reached in the tissues and the duration was such that the total energy applied to the tissue in both cases was the same. The mechanical forces acting on the tissues were therefore the same but it was found that the increase in temperature was less when the duration of the pulses was shorter and the pulse rate less. The amount of hyperaemia decreased according to the decrease in temperature in the tissues, suggesting the major contribution of the heating effect.

Finally, an investigation was made of the functional relationship between the amplitude of movement of the particles of the medium and the biological reactions. It was shown mathematically that the amount of hyperaemia could be calculated from the amplitude of the particle movement and it was found thet the calculated curve was in good agreement with the experimentally observed occurence of hyperaemia if it was assumed that the ultrasonic energy was first converted into heat by absorption and the heat itself created the reactions.

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DEXTRAN

Dextran is a collective name of a large group of structurally related polysaccharides, usually of high molecular weight(10⁵ to 10⁷), which are elaborated by various micro-organisms, especially by strains of Leuconostoc, when grown on sucrose. The term dextran was used oringinally to denote polysaccharides having a positive optical rotation in contradistinction to the levans (fructans) of negative optical rotation, which are formed by other micro-organisms under similar consitions of growth. Dextrans are used as blood plasma extenders. They also have wide industrial applications, such as, pharmaceuticals, water-loss inhibitor in oil-well drilling muds, agriculture, cosmotics, photography, synthetic resins, and veterinary medicine.

The various dextrans all contain linear chains of 1-6' linked a-Dglucopyranose residues as the dominant structural feature, but differ in the degree of branching and in the nature of the linkages, 1-3' and 1-4', and less frequently 1-2', at the branching points. The main 1-6' linkage is indicated by the isolation of 2,3,4-tri-0-methyl-D-glucose as the major cleavage product from methylated dextrans, and the first evidence for the presence of other types of linkage came from the characterisation, from different methylated dextrans, of 2,3-and 2,4-di-O-methyl-D-glucoses. Direct confirmation of the presence of these other types of linkages has been obtained by the isolation from various dextrans of maltose, nigerose, and kojobiose, 2-0-x-D-glucopyranosyl-D-glucose as fragmentation products(106,107). It is noteworthy that partial hydrolysis of dextrans with aqueous mineral acid leads to the ready isolation of isomaltose and its polymer homologues, but that other types of linkage are preferentially hydrolysed so that oligosaccharides arising from branching points are not easily obtained. In contrast, acetolysis leads to more rapid cleavage of

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the 1-6' linkages and provides a convenient method for the isolation of oligosaccharides with other linkages. An example of the value of this procedure is provided in studies of a dextran from one strain (NRRL 1355-S) of Leuconostoc mesenteroides containing an unusually high proporttion (35%) of bonds of the 1,3'-type, with 57% of the 1,6'and 8% of the 1,2'-or 1,4'-types. Graded acetolysis resulted in the isolation of nigerose in 20% yield, together with the trisaccharide with mixed linkages (2% yield) and isomaltose in only 2% yield(107).

Additional evidence for the structures of two branched dextrans (NRRL B-1416 and NRRL B-1415) containing 1-3' and 1-4' linkages respectively at the branch points has been obtained by catalytic oxidation followed by partial hydrolysis(108). Only the non-reducing D-glucose end groups in dextrans contain primary hydroxyl groups which may be oxidized by oxygen in the presence of a platinum catalyst to give D-glucuronic acid residues. Partial acid hydrolysis of the oxidized dextrans gave respectively the aldobiouronic acids, 3-0-and 4-0(-D-glucopyranosyluronic acid)-D-glucose. Since linkages other than 1-6' are found only at branch points, it follows that the side-chains in both dextrans consist of single D-glucose residues and may be represented in partial structures (A,B).



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A further dextran from Leuconostoc mesenteroides (NRRL B-512) has been shown to contain 4% of 1-3' linkages, but catalytic oxidation experiments led to the isolation of the aldobiouronic acid, 6- O-(Q'-Dglucopyranosyluronic acid)-D-glucose, showing that in this polysaccharide the side-chains contain two or more residues(109).

MECHANISM

Most dextrans are synthesized from sucrose. The structure of sucrose is one molecule of beta D-fructoside joined with one molecule of alpha Dglucoside as follows,



(+)-Sucrose

For dextran to form, fructose has to be detached from the sucrose molecules leaving the glucose molecules to be joined.



The activated molecule will start the propogation step by a single-chain mechanism(102), where another molecule of sucrose would join the activated molecule releasing a molecule of fructose.



Two enzymes at least participate, according to one theory(102), dextransucrase is responsible for synthesis of the linear sequences of alpha 1, 6-linked D-glucose units. The second enzyme, less clearly defined, is responsible for branching at positions C-2, C3, and C-4. Termination step occurs by the separation of the enzyme from the polymer. Another theory states that a single enzyme controls all branchings, where it occurs at its position in the reaction complex.

Three species of Leuconostoc; family Coccaceae, are distinguighed according to their ability to ferment xylose and L-arabinose as well as sucrose (L. mesentroides) (110 and 111), or sucrose but not the pentoses (L. dextranicus), or neither pentoses nor sucrose (L. citrovorus). The dextrans are obtained by growing the bacteria on solutions containing sucrose and nutrients. Afterwards, the culture medium is evaporated, and the dextran is precipitated by the addition of alcohol. The synthesis of the polysaccharide from sucrose through the agency of enzymes present in bacteria-free filtrates of Louconostoc cultures has been reported(112).

Three dextrans, obtained in this manner, distinguished by Hibbert(110) and associates by the suffixes I,II and III. Two (I,II) are produced by strains of L. mesenteroides and one (III) by L. eextranicus. Methylated dextran-I is hydrolysed to tetramethylglucose, 2,3,4,-trimethylglucose and 3,4-dimethylglucose in the relative proportions of 1:3:1. Hydrolysis of methylated dextran-III gives 90% yields of 2,3,4-trimethylglucose and 10% of dimethylglucose. Although Fairhead, Hunter and Hibbert (113) could find no tetramethylglucose, a small amount (0.23%) later was obtained(115). The basic structure of the dextran-III molecule is a chain of 1,6' linked \ll -glucopyranose residues. The formation of dimethyl-glucoses indicates branching to be present providing the methylation is complete, but since the position of the methyl groups has not been determined, the location

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of the branches is not known. Osmotic pressure measurements show that the molecule must contain at least 200 glucose units.

A dextran synthesized by a strain of L.mesenteroides has been studied by Hassid and Barker. It seems to be similar to the dextran-II of Hibbert and associates and to be composed of a-glucopyranose residues with 1,6' polymeric linkages. Viscosity measurements indicate a molecular weight of 11,700 while the ultracentrifuge (sedimentation equilibrium method) gives a value of 2600+50.

The dextrans form precipitates not only with L. antisera but also with types 2,12 and 20 pneumococal antisera(112).

A very similar dextran is synthesized by Betabacterium vermiforme from sucrose, but it has a much smaller repeating unit since 4 to 5% of tetramethylglucose is produced along with 90% of 2,3,4-trimethylglucose (114). As the degree of polymerization is about 500 (osmotic pressure method), the molecule must contain 20 repeating units each of which consists of 25 \propto -glucopyranose residues.

Photographs of one of the L. mesenteroides dextrans by use of the electron microscope show a branched, thread-like structure(116). The chains have a thickness of about 50 A° . Since the length of a glucose chain is about 5 A° , the threads could be composed of central linear chains with side chains of about 5 glucose residues.

STRUCTURE OF DEXTRAN

As an example, the results(115) obtained from the structural studies on the dextran synthesized by the action of Leuconostoc mesenteroides on sucrose will be cited in detail. The methylation of the dextran is carried out first with sodium hydroxide and dimethyl sulfate in an atmosphere of nitrogen and completed in liquid ammonia solution using sodium and methyl iodide. The methoxyl content of the final product agrees with the theoretical value of 45.6 per cent. By treatment of the methylated dextran with hydrogen chloride in methyl alcohol at 140° C., the linkages between the glucose units are broken, and a mixture of methylated methyl glucosides are obtained. These compounds are separated into fractions by fractional distillation in a modified Podbielniak column. The results are tabulated in following Table,

Fractionation of Methylated Methyl Glucosides Obtained by Methanolysis of Methylatad Dextran

Fraction No.	Weight of Fraction	^{%0СН} 3	"Tetra" Content	"Tri" Content	"Di" Content
1 2 3 4 5 6	g. 1.204 0.207 0.605 2.811 0.397 1.013	61.0 57.8 52.8 52.4 46.5 42.0	g. 1.204 0.113 	g. 0.094 0.605 2.811 0.172	g. 0.225 1.013
Total Ratio("tri" content assumed as 3.00)			1.317 1.07	3.682 3.00	1.238 1.01

The theoretical methoxyl contents of methyl di-, tri- and tetra-methylglucosides are, respectively, 41.9, 52.6 and 62.0 per cent. Fractions 1,2, 4 and 6 are then essentially pure, but the much smaller fractions 2 and 5

are mixtures for which the composition is calculated from the methoxyl analysis. The nature of the fractions is shown by conversion to crystalline derivatives of known properties. The approximate molar ratios of the three products is found to be: methyl 2,3-dimethylglucoside, 1; methyl 2,3, 6-trimethylglucoside, 3; and methyl 2,3,4,6-tetramethylglucoside, 1. Although these results do not lead to an unequivocal structure, they fix the general pattern. As the basic repeating unit is composed of five glucose residues, the side chains cannot be longer than four glucose units. If the side chains have four units, the main chain consists of glucose residues each of which carries a side chain (Formula I) and which are responsible for the dimethylglucose produced. The side chains cannot be shorter than the one glucose unit which yields the tetramethylglucose found in the analytical procedure; in this limiting case, the units with three unsubstituted hydroxyls must lie in the main chain between those carrying the side chains (Formula II). It is not possible at present to distinguish between these possibilities or any intermediate type of structure, e.g., two units in the side chains and one between the glucose residues in the main chain to which the side chains are attached.





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PROPERTIES

Pure dextrans are white, tasteless solids which possess high positive specific optical rotation. They are soluble in water, viscosity varies considerably according to the causative strain. 1,6 linkage dextrans show the highest solubitity in water, formamide, dimethylformamide, ethylenediamine and dilute alkali. Best solvents for dextrans are 6 M urea, 50% glucose, and 2 M glycine. They precipitate from aqueous solution by ethanol 45-50% concentration leaving those molecules of degree of polymerization lower than 5. Most dextrans show Newtonian viscosity, where viscosity is independent of shear stress. B-512(F) dextran shows specific optical rotation $\left[ex \right]_{D}^{25}$ values of +199°, +203°, and+215° in water, 1 M KOH, and formamide, respectively. For dextrans having less than 75% 1,6 linkages, rotation is a function of the number of 1,3, 1,2 and 1,4 linkages(117).

1,6 linkages dextran shows high stability to degradation under either acidic or alkaline conditions. The activation energy for acid hydrolysis is between 30 and 35 kcal/mole(118). Most derivatizations of dextran occur at hydroxyl groups sites, and those at C-2 are the first to react (119).

HYDROLYSIS

Dextran can be depolymerized by acids, alkalies, enzymes, or heat. Acid hydrolysis is the most favored because the reaction can be simply carried out in conventional equipment, controllable, and does not require the isolation of dextran in dry form. The depolymerization of dextran is a first order reaction with respect to dextran concentration (120-122) and the rate contants are proportional to number average molecular weight raised to the power 2/3 (122, 123). In 1,6 linear chain dextran the

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nature of the chemical bonds between monomers are the same, which would lead to thinking that the breakage probability is the same for all bonds, which does not agree with experimental data. Basedow et al (122) showed that bonds located at the terminals of the polymer chain are more easily attacked than the central bonds(122). Samples of 10 ml, were taken, then poured immediately into cold methanol at-30[°]C where dextran would precipitate. The precipitant was dried, then its molecualar weight was deterimed. When the dextran concentration increased higher than 2% a deviation from first order occured(123). A comparison between hydrochloric, and sulfuric acids showed that, at the same pH value, hydrochloric is more active at room temperature(121). In general hydrochloric acid is prefered because it is less corrosive.

THE EFFECT OF ULTRASOUND ON DEXTRAN

Basedow and Ebert(125) showed that the ultrasonic waves enhance the depolymerization rate of dextran. They found that the rate constants are proportional to the enthalpy of vaporization of the solvent(125). The experimental results confirm the general assumption, that the cavities, which are caused by ultrasound, are responsible for the degradation reaction (125). Basedow and Ebert believe that the inhomogeneous flow fields at first stretch the polymer coil, whereas the shock wave, which immediately follows, breaks the molecule. Basedow and Ebert(123) reported that, the rate constants of ultrasound degradation of dextran are proportional to the number average molecular weight raised to the power 4/3, for molecular weights higher than a limiting value, otherwise raised to the power 5/6.

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CELLULOSE

Cellulose is the chief constituent of plant cell walls. It usually occurs in plants not in the pure form, but with what are called embedded substances. Absorbent cotton, cotton textiles and linen, as well as high grades of filter paper consist for the most part of cellulose, somewhat altered in processing. The purest natural cellulose is the fibre of the cotton plant; it contains over 90% of cellulose and 6-8% of water. Cellulose accounts for about 50% of the wood of coniferous trees, but in deciduous trees its content is much lower.

Cellulose does not dissolve either in water, or in ether, or in alcohol; in ordinary conditions it is quite stable to the action of dilute acids, alkalis, and weak oxidizing agents.

Cellulose dissolves in Schweitzer's reagent (a dilute solution of cupric hydroxide in concentrated ammonia), in a hydrochloric solution of zinc chloride, and in concentrated sulphuric acid.

Enormous quantities of cellulose in more or less pure form are prepared in the manufacture of paper. Up to the mid-nineteenth century paper was made almost exclusively from linen and cotton rags, which are nearly pure cellulose. With the expansion of book-and newspaper-publishing the production of paper from rags proved quite inadequate to meet the demand, and techniques were therefore evolved for obtaining cellulose from timber. At present the plainer sorts of paper are made from firtimber. Paper of this kind, when stored, especially in the light, becomes brittle. The better sorts of paper are made from paper pulp, which is a mixture of wood pulp with more or less clean cellulose.

Several methods are used for the industrial manufacture of cellulose, the most widespread being the sulphite method. Under this method wood

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chips (mainly fir) are boiled at an increased pressure in huge 300 cu m and larger autoclaves with a solution of calcium bisulphite $Ca(HSO_3)_2$. The wood decomposes and partly passes into the solution; the cellulose in it survives in the form of a fibrous mass.

After the boiling the contents of the autoclave are pressed into a huge blow pit, a concrete reservoir with a floor of perforated plates. There the cellulose is separated from the solution and washed with water. The cellulose is then pressed, dried, and sent to the paper mills for further processing.

The solution separated in the blow pit is known as sulphite liquor and contains a considerable amount of saccharoid substances, which can be used for the manufacture of alcohol by fermentation. Such "hydrolytic" alcohol, used for industrial purposes, is made from raw materials that cannot be used for food production.

Apart from paper manufacture, considerable amounts of cellulose are utilized in the production of artificial fibre, plastics, lacquers, and gun-powders.

HISTORICAL

In 1838 Payen suggested that cellulose is built solely from glucose units and is isomeric with starch. Nageli(1858) used the word "micelles" to name the crystalline particles which build the cellulose fiber and he descriped it as anisotropic, submicroscopic crystals. The first industrial application of alkali-cellulose interaction was introduced by Mercer(1844). The rayon industry started when Schweizer in 1857, succeeded in dissolving cellulose in cuprammonium solutions(127). Cellulose nitrate, the first of the cellulose derivatives to be synthesized,was prepared by Braconnot in 1833. This derivative was used latter as a vehicle for coating cars in the automobile industry. Gunpowder, which is highly nitrated cellulose was synthesised by Bottger and Schonbein in 1847. Cellulose acetate was then introduced to the industry in 1879 after Franchimont showed that sulfuric acid and zinc chloride are very affective catalysts in the preparation. Hydrolysis and oxidation were studied by Girard(1881) and Witz (1883) respectively. Nishikawa and Ono (1913) applied van Laue's technique of x-ray diffraction to cellulose, which led to Meyer and Mark(1928) to propose a monoclinic unit cell for the crystalline material of cellulose. Freudenberg and his co-workers (1930s) proved that cellulose is a betalinked polycondensate of glucose units. In 1934 Kerr and Bailey explored with light microscopy the structural order in the plant cell. The invention of the modern instrumental analysis technique such as, small-angle scattering, infrared spectroscopy, paper chromatography, ultracentrifugation, and electron microscopy have contributed to better understanding of the chemistry and physics of cellulose.

STRUCTURE OF CELLULOSE

Fuming hydrochloric acid (40% HC) hydrolyzes cellulose to D-glucose in a yield of 95 to 96% (128).

As the empirical formula is $C_6H_{10}O_5$, cellulose might be either an anhydrohexose or a chain polymer formed by the elimination of a mole of water from successive pairs of glucose units. The chain would have to be sufficiently long so that the analytical results could agree with either $C_6H_{10}O_5$ or $(C_6H_{12}O_6)_n - (n-1)H_2O$. The extremely low reducing power of cellulose and the production of reducing sugar as a result of acid hydrolysis agree with both of these possible types of structure. Inasmuch as molecular weight determinations support the latter formula and completely eliminate the anhydroglucose structure, cellulose must consist of glucose residues with connections formed by the elimination of the elements of water.

The presence of three unsubstituted hydroxyl groups for each glucose residue is demonstrated by the formation of triacetates, trinitrates and trimethyl ethers of the formula $(C_6H_70_5(CO-CH_3)_n, (C_6H_70_5(NO_2)_3)_n, (C_6H_70_5(CH_3)_3)_n$. The formation of a monotrityl derivative of cellulose (129), is due to the presence of a primary hydroxyl group in each glucose residue. The formation of monotosyl derivatives and the replacement of the the tosyloxy groups by iodine through reaction with sodium iodide in acetone or acetonylacetone solution proves the existence of unsubstituted primary alcoholic groups(129).

Of particular importance for showing the nature of the polymeric linkage are the acetolysis experiments. Cellulose under acetylating conditions in the presence of an acid catalyst is degraded with the formation of high yields of cellobiose octaacetate(130). After correction for the amount of cellobiose octaacetate acetolyzed under the same conditions, the maximal yield of the disaccharide is estimated by Freudenberg as 50 to 60%. This yield compares with a value of 30% calculated on the assumption that the cleavage of the linkages is entirely a random process. On the assumption that the ease of hydrolysis increases with decrease of the degree of polymerization of the hydrolytic products and that all linkages in each degraded particle are hydrolyzed with the same ease, a theoretical yield of 67% is calculated. In a study of the yields of cellobiose octaacetate produced, Spencer(130) reported a maximum of 42.3% but, in disagreement with Freudenberg, found that the octaacetate was not appreciably degraded under the acetolysis conditions.

Since cellobiose octaacetate is not synthesized from glucose under the conditions of acetolysis, and since no other disaccharides are pro-

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duced, the cellobiose type of linkage must be the major type present in the original polysaccharide. As described elsewhere the disaccharidic bond of cellobiose lies between carbon 1 of one glucose residue and carbon 4 of the other and has a beta configuration. A chain structure with B-glucosidic linkages agrees with the studies of the optical power during hydrolysis of cellulose by strong acids and of the kinetics of the process. These studies show that cellulose has the properties predicted by the extrapolation to infinite chain length of those of the short-chain cellohexaose, cellobiose, etc., of known structure(131).

The 1,4' type of connection between the glucose components is given final substantiation by the practically quantitative yield of 2,3,6-trimethylglucose obtained from the hydrolytic products of fully methylated cellulose. The following structure illustrates a cellulose chain with the cellobiose structure as the repeating unit.



The special properties of cellulose result from the association of bundles of microfibrils of individual molecules held together in a highly ordered structure. Estimates of the width of these microfibrils, based on electron microscopy, vary for different samples of cellulose and generally fall within the range 50-100 Å. The highly ordered crystalline structure of cellulose permits the application of X-ray crystallography and of infrared spectroscopy using polarised radiation. The results of these studies have provided much information on the shape of individual cellulose molecules but the nature of intermolecular association has yet to be unambiguously established. The situation is complicated by the fact that cellulose is obtained in several different crystalline modifications, the most important of which are cellulose 1, the native cellulose found in cotton and wood, and cellulose II which is formed when native cellulose is swollen in alkali (mercerisation) and when the polysaccharide is precipitated from solution, e.g. in cuprammonium hydroxide, or is regenerated from derivatives, e.g. from the controlled saponification of cellulose triacetate. Cellulose II appears to be the thermodynamically more stable form and the factors which control the biosynthesis of native cellulose are largely unknown.

The first crystal stucture for cellulose based on X-ray diffraction data was proposed by Meyer and Misch in 1937(132). The unit cell dimensions (a=8.35, b=10.3, c=7.9 Å; B=84°) together with the twofold screw axis along the chain are indicated below in the structure A in which the fiber repeat distance of 10.3 Å corresponds to that of a cellobiose unit. This "straight" chain conformation, however, suffers from the disadvantages of repulsions between the $C_{(1)}$ and $C_{(4)}$ ' hydrogens and of overlap of the van der Waals radii of the $O_{(2)}$ and $C_{(6)}$ ' atoms. A more satisfactory chain conformation involving "bent" cellobiose units with alternate glucose residues in the same plane overcomes these difficulties while

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maintaining the fiber repeat distance and the twofold screw axis(133). Structure B indicates the arrangements of primary hydroxyl groups in the cellobiose units and of intramolecular and intermolecular hydrogen bonds in the cellulose I unit cell. The hydrogen bonding indicated is consistent with the data from polarised infrared studies(134). The proposed unit cells for cellulose involve an anti-parallel arrangement of adjacent chains in order to accommodate intermolecular hydrogen bonding, but direct evidence on this point is lacking. There is, however, argument by analogy from studies on the crystal structure of chitin, in which polysaccharide 2-acetamido-2-deoxy- β -D-glucopyranose residues replace those of β -D-glucopyarnose and in which the same fibre distance of 10.3 Å distance is observed.(135).






(B)

SOLUBILITY

An aqueous solution of hydrazine or ethylenediamine causes cellulose to swell. At high amine concentrations, some penetration of the lattice takes place. Tetraethylammonium hydroxide, benzyltrimethylammonium hydroxide and some other quaternary bases dissolve cellulose, but each of these organic bases exerts its maximum solubilizing effect at a definite concentration (about 2 N) which decreases with the molecular weight of the base(136).

The solubility of cellulose in ammoniacal solutions of copper oxide (Schweizer's reagent) is well known, and extensive use has been made of this property in the manufacture of synthetic fibers (cuprammonium rayon) and in the determination of molecular weights by the methods previously described. The cuprammonium reagent produces very little degradation of the cellulose, and in the absence of oxygen and light, the regenerated cellulose obtained by the addition of acids or alkalies to the solution is only slightly degraded(137).

Copper oxide dissolves in the ammonia solution due to the formation of cuprammonium hydroxide, $Cu(NH_3)_4(OH)_2$. Dissolution of cellulose in the solution takes place with the liberation of ammonia from the complex ion, and presumably the cellulose takes the place of the ammonia in the complex ion. Similar compounds are formed by cuprammonium solution and simple polyalcohols, and Fehling's solution probably has an analogous composition.

The ease of oxidation of cuprammonium solutions of cellulose prevents their use for some purposes. In such instances, aqueous solutions of cupric hydroxide-ethylenediamine provide excellent solvent media because of the stability of the cellulose in this solvent(138).

The action of sodium hydroxide has particular importance because it is involved in the preparation of mercerized cotton, viscose and certain cellulose ethers. At concentrations of the sodium hydroxide less than 8 to 9%, the reaction apparently takes place at the surface of the micelles since the X-ray diagram is not affected. The combined alkali at this stage averages one mole for each two glucose residues. The X-ray diagrams of cellulose treated at higher concentrations of sodium hydroxide exhibit a new diagram superimposed upon that for the original cellulose, and, at alkali concentrations in the range 13 to 19%. only the new diagram is obtained. At this stage, the combined alkali averages one mole per glucose residue . Still another diagram is obtained when the concentration of sodium hydroxide is raised to 21%. The nature of the combination is uncertain; at the lower concentrations adsorption probably occurs, whereas at the higher concentrations the formation of alcoholates and cellulose anions may take place.

R-O-Na+, R-O-Na (alcoholate), R-O-Na+ (cellulose anion) The reaction is markedly affected by the temperature, and the same effect

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is produced by a 6.5% solution at -10° as by a 17 to 18% solution at 20° .

Cold water decomposes the alkali cellulose with the formation of hydrate cellulose. Hot water gives a mixture of native and hydrate cellulose.

The preparation of mercerized cotton involves treatment of cotton fibers with strong sodium hydroxide while the fibers are kept under tension to prevent shrinking. The mercerized cellulose obtained by treatment of the alkali cellulose with water has a smooth, lustrous appearance and takes up dyes better than the untreated material.

In the glucose units of the cellulose chain, the hydroxyls of carbons 2 are the most acidic. Thus, in 35% potassium hydroxide solutions, a compound with the formula $C_6H_{10}O_5$.KOH is formed. The potassium seems to be associated with carbon 2 since methylation of the compound and hydrolysis yield 2-methylglucose(139). Similar experiments carried out with the sodium cupricellulose compound gave 2-methyl-and 3-methylglucose. All the free hydroxyls of cellulose are weakly ionizable as is shown by the complete exchange which takes place in deuterium oxide. The exchange is virtually complete in 30 hours at $30^{\circ}C$.

Although the nature of the combination between sodium bydroxide and cellulose in the alkali (soda) cellulose remains undecided, true trisodium alcoholate derivatives have been described. Their preparation involves the reaction of cellulose with a solution of metallic sodium in liquid ammonia. When exposed to air and moisture, these derivatives undergo decomposition and degradation of the molecular chains.

Hydroxides of the other alkali metals (Li, K, Cs, Rb) form alkali celluloses similar to those obtained by the use of sodium hydroxide(140). The maximum swelling effect is produced at a definite concentration for each base and increases with the atomic weight of the alkali metal in-

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volved. The product obtained by use of lithium and potassium hydroxides has a composition averaging that of one mole of alkali for each pair of glucose residues, but that from the action of cesium and rubidium hydroxides averages one mole of base to three glucose residues.

Iron, nickel, cobalt, zinc, and cadmium complexes with ammonia, ethylenediamine, biuret, and tartaric acid have been used to dissolve cellulose. Some of those compounds are merely scientific interest, two of them, iron-tartaric acid complex and cadmium-ethylenediamine complex (Cadoxan), have given a relatively stable solutions towards oxygen under atmospheric conditions.

ACID HYDROLYSIS

Cellulose, like starch, is hydrolyzed by acid solutions; its hydrolysis D-glucose:

 $(C_6H_{10}O_5) + H_2O \longrightarrow C_6H_{12}O_6$

The equation gives only the over-all result of hydrolysis. In actual fact, the hydrolysis of cellulose is a gradual process, which leads to the fomation of simpler and simpler substances.

The action of strong sulphuric acid on cellulose for a short period of time turns it into amyloid, which gives a blue color with iodine. This reaction is often used for the detection of cellulose. Chlorozinciodine, i.e., a solution of iodine and potassium iodide in a saturated solution of zinc chloride, is sometimes used for this purpose instead of sulphuric acid and iodine.

The formation of amyloid is used in the manufacture of parchment; unsized paper is placed for a few seconds in 80% sulphuric acid and then washed with water and an ammonia solution. A layer of amyloid is formed on the surface of the paper, which becomes impenetrable to water.

The action of mineral acids (hydrochloric, sulphuric) upon cellulose causes its partial hydrolization. The product is a brittle substance, which is easily ground to a powder, reduces Fehling's solution, and dissolves partly in alkalis. It is a mixture of unchanged cellulose and the products of its destruction and hydrolysis.

When cellulose impregnated with even dilute acid is dried, especially in a stream of hot air, it disintegrates readily into a powder. This property of cellulose is used to isolate wool from mixed yarn (cotton and wool).

More vigorous acid action causes the further hydrolysis of cellulose, with the formation of simpler and simpler polysaccharides. The ultimate product of the hydrolysis of cellulose is glucose.

In industry the culled wood of woodworking factories is used for the saccharification of cellulose. The culled wood is heated under pressure with an 0.1% solution of sulphuric acid; the syrup obtained is then converted into ethyl alcohol.

According to another method the cellulose is saccharfied in the cold by the action of hydrochloric acid (relative density 1.21). The products of hydrolysis are then heated to remove the bulk of the hydrochloric acid and are neuralized with soda. The neutralized product is used as cattle feed.

Cellulose can also be broken down by microorganisms. Processes of this type are tremendously important in nature; it is in this manner that plant remains on the ground are disintegrated. One such process is the destruction of wooden buildings by dry rot, which oxidizes cellulose by means of the oxygen of the air to CO_2 and H_2O . An important process is the methane fermentation of cellulose, caused by certain types of bacteria at the bottom of stagnant reservoirs; it takes place without access of air and yields methane, carbon dioxide, and fatty acids.

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EXPERIMENTAL

The aim of this work is to study the kinetics of the acid hydrolysis of dextran and cellulose under the effect of ultrasonic waves of different frequencies and intensities, then compare it to the reaction without the effect of sound under the same conditions of acid and carbohydrate concentrations and temperature.

The procedure used to achieve that can be explained as follows:

- A concentration of 0.040 g/ml for dextran and 0.0108 g/ml for cellulose were kept the same for all runs.
- 2. The required temperature for each run was maintained constant by running the reaction in a constant temperature water-bath.
- 3. The viscosity of samples taken in different durations was measured using a Ubbelohedeviscometer.
- 4. Intrinsic viscosity for each sample was calculated using Kraemer's equation,

$$\frac{\ln(n_r)}{c} = [n] + k'' [n]^2 c.$$

Then the weight average molecular weight was calculated by applying the Mark-Houwink-Sakurada equation,

$$[n] = K' M^a.$$

The constants K' and a were determined by measuring the efflux time t required for a specified volume of polymer solution to flow through the capillary tube then comparing it to the corresponding efflux time t_0 for the solvent. The relative viscosity $(n_r = t/t_0)$ and the specific viscosity $(n_{sp} = n_r - 1)$ were then calculated at different polymer

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concentrations. The relations of n_{sp} versus c and $\ln n_r$ versus c were plotted, giving straight lines which were then extrapolated to c = 0 to determine the value of the intrinsic viscosity [n]. Three different known molecular weights were used, then the relation of $\ln [n]$ versus ln M was plotted giving a straight line of solpe = a and intersection = $\ln(K')$.

PREPARTION OF SODIUM CARBONATE PRIMARY-STANDARD (0.10N)

Sodium carbonate $(Na_2 CO_3)$ was used as a primary-standard, because it is stable, nonhygroscopic, and can be obtained in pure form.

- 1. About 10 grams of $\operatorname{Na}_2 \operatorname{CO}_3$ were weighed in a glass weighing bottle.
- 2. The bottle then was placed in an oven at 160°C for two hours.
- 3. The bottle was allowed to cool in a desiccator.
- 4. 5.2995 grams of the cooled dried Na_2CO_3 were weighed on weighing paper, then transferred to a 100 ml. clean dry volumetric flask.
- 5. About 50 ml of distilled water were added, then swirled gently until all salt was dissolved.
- 6. The flask was then filled to the calibration mark with distilled water.
- 7. The flask was labled and used for concentration calibration of the standards.

PREPARATION OF HYDROCHLORIC ACID (DIFFERENT COCENTRATIONS) Since hydrochloric acid is not very stable, a fresh sample of the re-

1. A little less than 500 ml of distilled water was placed into a clean dry 500 ml bottle.

quired concentration was always prepared whenever it was needed.

2. The volume of 36% concentrated hydrochloric acid, needed to prepare hydrochloric acid of the required concentration was calculated, then, measured into a small graduated cylinder, transferred to the bottle and mixed thoroughly

- 50 ml of 0.1 N Na₂CO₃ solution was placed into 200-ml conical (Erlenmeyer) flask, then 4 drops of bromocresol green indicator were added.
- 4. 50 ml buret was filled with the hydrochloric acid which was prepaired before, then it was used to titrate the sodium carbonate solution 0.1N.
- 5. When the color reached an intermediate green color, the titration was stopped, the solution was boiled gently for two minutes.
- 6. The solution then was cooled to room temperature, the flask walls were washed with distilled water, then the titration was continued to the end point.

The pH of the end point of this titration is 4, therefore the following equation represents the neutralization reaction,

$$2HC1 + Na_2CO_3 = H_2CO_3 + 2NaC1$$

the molarity of HCl was obtained by applying the following relation:

$$M(HC1) = \frac{moles HC1}{liter} = \frac{2 \times (moles Na_2C0)}{(ml HC1)/1000}$$

$$= \frac{2 \times 0.1 \text{ ml}(\text{Na}_2\text{CO}_3)}{\text{ml} (\text{HC1})} = \frac{10}{\text{ml}(\text{HC1})}$$

The molarity of HCl was then adjusted to the required one, by adding the nessecary volume of distilled water, or 36% HCl.

PREPATATION OF POTASSIUM HYDROXIDE (DIFFERENT CONCENTRATIONS) Since potassium hydroxide soultion tends to absorb carbon dioxide, the needed sample was always prepared fresh whenever it needed.

- About 800 ml of distilled water was placed in a one liter flask, then boiled gently for about 5 minutes to remove any dissolved carbon dioxide.
- 2. The flask was covered with a watch glass and allowed to cool to room temperature.
- 3. The amount of KOH needed to make the solution in the required concentration was calculated, then weighed into a beaker, enough of the boiled distilled water was added to dissolve KOH.
- 4. The solution was transferred to volumetric flask, more boiled distilled water was used to rinse the beaker then transferred to the flask.
- 5. The flask was then filled to the calibration mark with distilled water.
- 6. 50 ml KOH solution was placed into a conical (Erlenmeyer) flask, two drops of phenolphthalein was added .
- 7. The HCl which was previously standarized was used to fill a buret, then to titrate KOH solution to the end point.

The equation

$$KOH + HC1 = KC1 + H_2O$$

represents the reaction occurs. The molarity of KOH was calculated by applying the following relation:

$$M(KOH) = \frac{\text{moles KOH}}{\text{liter}} = \frac{\text{moles HC1}}{(\text{ml(KOH)}/1000)}$$

DEXTRAN

Since aqueous solutions of dextrans are readily attacked by bacteria, a fresh sample of 0.080 gm/ml concentration was always prepared whenever it was needed.

Hydrochloric acid of concentration twice that required to run the reaction was prepared. Both dextran and acid solutions were brought to the required temperature, then equal volumes were mixed in a constant temperature water-bath, at the same moment a stop watch was started. At different durations a 5 ml sample of the reaction mixture was taken and added immediately to 5 ml of KOH solution of the same acid concentration of the reaction mixture to quench it.

The final dextran solution would containing KCl of concentration equal to half the concentration of the acid in the reaction mixture. Since a salt effect may affect the value of the intrinsic viscosity and consequently the values of K' and a of the Mark-Houwink-Sakurada equation, evaluating these values in solutions contain KCl of concentrations equal to that of the quenched samples is necessary.

Intrinsic viscosity of each sample was determined by measuring the viscosities of different polymer concentrations in a constant KCl concentration (by diluting with KCl solution of concentration same as that of the quenched sample), and then calculating both the relative viscosity n_r and specific viscosity n_{sp} . The Kramer equation,

$$\ln(n_r)/c = [n] + k''[n]^2 c$$

was applied to calculate the intrinsic viscosity. Then, the Mark-Houwink-Sakurada equation was applied using the proper values for K' and a which were evaluated before, to calculate weight average molecular weight of each sample.

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EVALUATING THE CONSTANTS OF MARK-HOUWINK-SAKURADA EQUATION

A solution of pure KCl of the required concentration was prepared. This solution was used to prepare the dextran solution in the needed concentration. It was also used to dilute the dextran solution to lower concentrations.

CHEMICALS

Dextrans T70 $\overline{M}_{y} = 73100$

T40 $\overline{M}_{w} = 42500$

T10 $\bar{M}_{w} = 10500$

Pharmacia Fine Chemicals Co. N.J, U.S.A.

Distilled water

Potassium chloride, food grade

J.T. Baker Chemical Co. Phillipsburg, N.J. U.S.A.

APPARATUS

Ubbelohde viscometer

Fish-Schurman Corp. New Rochelle, N.Y, U.S.A.

Water-bath

Stirrer

Thermowatch, +0.05^oC

Thermometer

Clamps

Suction bulb

Stop-watch



UBBELOHDE VISCOMETER

PROCEDURE

For both equations, Huggin's and Kreamer to be applicable, the viscosity of dextran solutions is restricted to the range that gives relative viscosities (n_r) , between 1.1 and 1.5 It was found (by trial and error) that the concentrations of 0.04, 0.02, and 0.01 gm/ml for dextrans T10, T40, and T70 respectively give relative viscosities which satisfy this range.

- 1. Viscometer was filled with distilled water, then placed into waterbath of temperature $25.00 \pm 0.05^{\circ}$ C for about 2 hours, to allow the temperature to equilibrate.
- 2. The suction bulb was used to raise the level of the water higher then the first calibration mark.
- 3. The time necessary for the water level to flow between the two marks was measured several times, then the average was taken as $t_0 (t_0 = 90.88 \text{ sec.})$

- 4. Prepare KCl solution of the required concentrations (0.25, 0.5, 0.75, 1.0, 1.5, and 2.0 g/ml)
- 5. Prepare dextran solutions in the proper concentration, by dissolving dextran into KCl solution of the required concentration.
- 6. Viscometer was dried in an oven, then allowed to cool to room temperature.
- 7. 10 ml of dextran solution was placed into the viscometer which was then immersed into water-bath for about two hours to allow the temperature to equilibrate.
- 8. The efflux time was measured several times then the average \bar{t} was calculated.
- 9. One ml. of the proper KCl solution was added to the viscometer to dilute the dextran to a lower concentration; with aid of the suction bulb the solution was mixed, then allowed to equilibrate.
- 10. The efflux time was measured several times, then the average was calculated.
- 11. Steps 10 and 11 were repeated after adding 1,2,3,4 and 10 ml of KC1 of the proper concentration.
- 12. $n_r = \bar{t}/t_o$, $n_{sp} = n_r 1$, $\ln(n_r)/c$, and n_{sp}/c were calculated, then $\ln(n_r)/c$ vs c and n_{sp}/c vs c were plotted.
- 13. From the straight lines produced [n], k', and k" were calculated for each molecular weight.
- 14. In [n] vs ln M was plotted, from the straight line produced k' and a were calculated for each KC1 concentration.

HYDROLYSIS OF DEXTRAN

Dextran solution of the concentration of 0.04 g/ml was hydrolysed with hydrochloric acid in different concentrations, and temperature. Each case was considered as a control, then compared to that under the effect of ultrasonic waves of different frequencies and intensities without varying the other conditions of concentration, and temperature.

CHEMICALS

Dextrans Hydrochloric acid J.T. Baker Chemical Co. Potassium hydroxide J.T. Baker Chemical Co. Phillipsburg, N.J. U.S.A. Distilled water **APPARATUS** Two water-baths, model 20967-095 Forma Scientific, Inc. Metietta, Ohio U.S.A. two thermometers Two reaction vessels Two stirrers Pipette 25 ml bottles Sound waves generators, Model G100 MARK I and Oscillator model UO MARK III, variable frequency generator Fibra-Sonics Inc. Chicago, Illinois U.S.A. Hydrophone, Type 8100 Bruel & Kjaer product, Naerum, Denmark Oscilloscope, Type 1222 A Hewlett Packard, Colorado Springs, Colorado, U.S.A. Ubbelhode viscometers Wescan Instruments Inc. Santa Clara, California, U.S.A. Viscosity timer Model 221

Wescan Instruments Inc. Santa Clara, Caifornia, U.S.A. Suction bulb

Stop watchs

PROCEDURE

- 1. Dextran solution of the concentration of 0.08 g/ml was prepared.
- 2. In each of two clean dry conical flasks, 30 ml of dextran solution was measured. Also, 30 ml of HCl of a concentration double that required to run the reaction, was placed into each, the reaction vessels of control and sound. All four solutions were brought to the required tempreature of the reaction.
- 3. 5 ml of KOH solution of a concentration equal to that of HCl in the reaction mixture, was placed in each of 16, 25 ml bottles.
- The dextran solution was transferred into the reaction vessel without the effect of ultrasound (control), and the stop-watch started immediately.
- 5. Two types of reaction vessels under the effect of ultrasound were used, one was a glass cylinder upon which the sound transducer was welded to its bottom. The other was where the transducer was immersed into the reaction mixture.
- 6. When the two solutions were brought together the sound-generator was started immediately and also a stop-watch.
- 7. The reaction was allowed to proceed, and a 5 ml sample was taken at different durations and added immediately to one of the bottles contains 5 ml of KOH solution, then mixed well to quench it.
- Viscosity of each of those samples was measured by same method described before.
- 9. The average efflux time (\tilde{t}) for each sample was calculated.
- 10. Relative viscosity $(n_r = \bar{t}/t_o)$, and inherent viscosity $(n_{inh}=ln(n_r)/c)$ were calculated for each sample at different concentrations as shown

in tables. Using the linear regression method the intrinsic viscosity was calculated for each sample.

11. By substituting into Mark-Houwink-Sakurada equation

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[n]=K' M^a

using the proper values of K' and a, $\overline{M}_{_{\mathbf{W}}}$ was calculated for each sample.

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Evaluating the constants of the molecular weight equation for 0.25 M KCl dextran solution

 $\bar{M}_{w} = 10500$

C(gm/ml)	ī(s)	$n_r = \overline{t} / t_o$	ln(n _r)/C	Curve coefficients	n _{sp}	n _{sp} /C	Curve coefficients
.0400	129.11	1.4207	8.78		.4207	10.52	
.0364	125.73	1.3835	8.82		.3835	10.42	
.0308	119.55	1.3155	8.90	2	.3155	10.24	0
.0250	113.70	1.2511	8.96	r ² = .9960	.2511	10.04	$r^2 = .9985$
.0200	108.91	1.1984	9.05	b =- 13.4545	.1984	9.92	b = 30.0308
.0133	102.63	1.1293	9.14	k"= -0.1550	.1293	9.72	k'= .3685

k'-k"=0.5085

₩ ₩=42500

C(gm/ml)	ī(s)	$n_r = \overline{t}/t_o$	$ln(n_r)/C$	Curve coefficients	n sp	n _{sp} /C	Curve coefficients
.0200 .0182 .0154 .0125 .0100 .0050	129.00 125.54 119.67 113.73 108.85 99.60	1.4195 1.3814 1.1368 1.2514 1.1977 1.0960	17.51 17.75 17.87 17.94 18.04 18.32	r ² = .9562 b =- 48.2084 k''= -0.1400	.4195 .3814 .3168 .2514 .1977 .0960	20.97 20.96 20.57 20.11 19.77 19.19	r ² = .9874 b =126.7770 k'= .3685

k'-k"=0.5085

M_=73100

C(gm/ml)	ī(s)	n _r =ī/t _o	ln(n _r)/C	Curve coefficients	n _{sp}	n _{sp} /C	Curve coefficients
.0100 .0091 .0077 .0063 .0050 .0030	116.70 114.20 110.30 106.70 103.26 98.18	1.2841 1.2566 1.2137 1.1741 1.1362 1.0803	25.01 25.10 25.15 25.47 25.54 25.75	r ² = .9659 b =-109.7942 k''= -0.1610	.2841 .2566 .2137 .1741 .1362 .0802	28.41 28.20 27.75 27.63 27.24 26.78	r^2 .9883 b =228.7403 k'= .3360

k'-k"=0.497

M w	[n]	K	a	r ²
10500 42500 73100	9.31 18.56 26.10	0.0723	0.5237	.9968



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Evaluating the constants of the molecular weight equation for 0.5 M KCl dextran solution

 $\bar{M}_{1} = 10500$

C(gm/m1)	ī(s)	$n_r = \bar{t}/t_o$	ln(n _r)/C	Curve coefficients	n _{sp}	n _{sp} /C	Curve coefficients
.0400 .0364 .0308 .0250 .0200 .0133	129.84 125.87 120.07 113.95 108.97 102.65	1.4287 1.3850 1.3212 1.2539 1.1991 1.1295	8.92 8.95 9.04 9.05 9.08 9.16	r^{2} .9567 b =- 8.4762 k''= -0.0990	.4287 .3850 .3212 .2539 .1991 .1295	10.72 10.58 10.43 10.16 9.96 9.74	$r^2 = .9957$ b = 37.3015 k' = .4370

k'-k''=0.5080

M	=4	2	5	00
W				

C(gm/ml)	ī(s)	n _r =ī/t _o	ln(n _r)/C	Curve coefficients	n sp	n _{sp} /C	Curve coefficients
.0200 .0182 .0154 .0125 .0100 .0050	133.30 128.90 122.33 115.80 110.39 100.24	1.4668 1.4184 1.3461 1.2742 1.2147 1.1030	19.15 19.20 19.30 19.39 19.45 19.61	r^2 .9983 b =- 30.6292 k"= -0.0780	.4668 .4184 .3461 .2742 .2147 .1030	23.34 22.99 22.47 21.94 21.47 20.60	r^2 = .9997 b =182.8466 k'= .5030

k'-k"=0.5030

₩ w=73100

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C(gm/ml)	ī(s)	n _r =ī/t _o	ln(n _r)/C	Curve coefficients	n _{sp}	n _{sp} /C	Curve coefficients
.0100 .0091 .0077 .0063 .0050 .0033	117.14 114.59 110.71 106.91 103.46 99.06	1.2890 1.2609 1.2182 1.1764 1.1384 1.0900	25.38 25.47 25.63 25.79 25.93 26.12	r ² = .9998 b =-111.0868 k''= -0.1590	.2890 .2609 .2182 .1764 .1384 .0900	28.90 28.67 28.00 28.00 27.68 27.28	r^{2} = .9999 b =241.5990 k'= .5040

k'-k"=0.504

м w	[n]	K	а	r ²
10500 42500 73100	9.25 19.77 26.48	.061	.542	.9999

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Evaluating the constants of the molecular wight equation for 0.75 M KCl dextran solution

M_w=10500

6	C(gm/ml)	ī(s)	n _r =t/t _o	$\ln(n_r)/C$	Curve coefficients	n sp	n _{sp} /C	Curve coefficients
	.0400 .0364 .0308 .0250 .0200 .0133	129.07 125.28 119.47 113.73 108.89 102.60	1.4202 1.3786 1.3146 1.2514 1.1982 1.1290	8.77 8.82 8.88 8.97 9.04 9.12	r^{2} = .9980 b =- 13.2602 k''= -0.1530	.4202 .3786 .3146 .2514 .1982 .1290	10.51 10.40 10.21 10.06 9.91 9.70	$r^2 = .9990$ b = 30.0661 k'= 0.3480

k'-k"=0.501

₩ ₩	42	50	0

C(gm/ml)	ī(s)	$n_r = \bar{t}/t_o$	ln(n _r)/C	Curve coefficients	n sp	n _{sp} /C	Curve coefficients
.0200 .0182 .0154 .0125 .0100 .0050	129.25 125.33 119.61 113.81 108.94 99.64	1.4222 1.3791 1.3162 1.2523 1.1988 1.064	17.61 17.66 17.84 18.00 18.13 18.40	r^{2} = .9974 b =- 53.9986 k''= -0.1550	.4222 .3791 .3162 .2523 .1988 .0964	21.11 20.83 20.53 20.19 19.88 19.27	r^2 .9990 b =120.7431 k'= 0.3460

k'-k"=0.51C

M_w=73100

C(gm/ml)	ī(s)	n _r =ī/t _o	ln(n _r)/C	Curve cofficients	n _{sp}	n _{sp} /C	Curve coefficients
.0100 .0091 .0071 .0063 .0050 .0030	117.36 114.78 110.85 107.04 103.56 98.35	1.2914 1.2630 1.2198 1.1778 1.1395 1.0822	25.57 25.30 25.80 25.98 26.12 26.34	r^{2} = .9990 b =-111.2100 k''= -0.1560	.2914 .2630 .2198 .1778 .1395 .0822	29.14 28.90 28.54 28.23 27.90 27.41	r^2 .9996 b =245.3656 k'= 0.3450

k'k"=0.5010

M _w	[n]	K	а	r ²
10500 42500 73100	9.30 18.67 26.67	.0655	.5341	.9958



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Evaluating the constants of the molecular weight equation for 1.0 M KC1 dextran solution

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M._=10500

C(gm/m1)	ī(s)	$n_r = \bar{t}/t_o$	ln(n _r)/C	Curve coefficients	n sp	n _{sp} /C	Curve coefficients
.0400 .0364 .0308 .0250 .0200 .0133	129.22 125.42 119.61 113.81 108.93 102.65	1.4219 1.3801 1.13162 1.2523 1.1987 1.1296	8.80 8.85 8.92 9.00 9.06 9.16	r^{2} = .9992 b =- 13.3285 k''= -0.1530	.4219 .3801 .3162 .2523 .1987 .1296	10.55 10.44 10.27 10.09 9.93 9.74	$r^2 = .9998$ b = 30.5398 k'= .3510

k'-k"=0.504

₩ w=42500

C(gm/ml)	ī(s)	$n_r = \bar{t}/t_o$	$\ln(n_r)/C$	Curve coefficients	nsp	n _{sp} /C	Curve coefficients
.0200 .0182 .0154 .0125 .0100 .0050	129.56 125.76 119.89 114.00 109.12 99.73	1.4256 1.3839 1.3192 1.2544 1.2007 1.0974	17.73 17.85 17.99 18.13 18.29 18.58	r^{2} = .9982 b =- 55.8071 k''= -0.1570	.4256 .3839 .3192 .2544 .2007 .0974	21.28 21.09 20.73 20.35 20.07 19.47	r ² = .9995 b =121.8010 k'= .3430

k'-k''=0.500

₩ ₩

C _(gm/m1)	ī(s)	n _r =t/t _o	$ln(n_r)/C$	Curve coefficients	n _{sp}	n _{sp} /C	Curve coefficients
.0100 .0091 .0077 .0063 .0050 .0030	117.14 114.62 110.72 106.91 103.45 98.30	1.2889 1.2612 1.2183 1.1764 1.1383 1.0817	25.38 25.50 25.64 25.79 25.91 26.17	r^{2} = .9973 b =-109.6628 k''= -0.1560	.2889 .2612 .2183 .1764 .1383 .0817	28.89 28.70 28.35 28.00 27.66 27.22	r ² = .9992 b =242.5339 k'= .3460

k'-k"=0.502

м w	[n]	K	а	r ²
10500 42500 73100	9.33 18.85 26.48	.0679	.5307	.9974

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Evaluating the constants of the molecular weight equation for 1.5 M KCl dextran solution

₩ ₩=10500

C(gm/ml)	ī(s)	n _r =ī/t _o	$\ln(n_r)/C$	Curve coefficients	n _{sp}	n _{sp} /C	Curve coefficients
.0400 .0364 .0308 .0250 .0200 .0133	125.96 122.50 117.23 111.94 107.49 101.72	1.3860 1.3479 1.2899 1.2317 1.1828 1.1193	8.16 8.20 8.27 8.34 8.39 8.47	r ² = .9993 b =- 11.6182 k''= -0.1560	.3860 .3479 .2899 .2317 .1828 .1193	9.65 9.56 9.41 9.27 9.14 8.97	r^2 .9990 b = 25.4606 k' = .3420

k'-k"=0.498

₩ ₩ ₩

C(gm/ml)	ī(s)	n _r =ī/t _o	ln(n _r)/C	Curve coefficients	n _{sp}	n _{sp} /C	Curve coefficients
.0200	130.65	1.4376	18.15		.4376	21.88	
.0182	126.55	1.3925	18.19		.3925	21.57	
.0154	120.40	1.3248	18.26	2	.3248	21.09	2
.0125	114.28	1.2575	18.33	r ² = .9962	.2575	21.60	$r^2 = .9541$
.0100	109.26	1.2022	18.42	b =- 25.9001	.2022	20.22	b =151.6444
.0050	99.70	1.0971	18.53	k"= -0.0740	.0971	19.41	k'= .4350

k'-k''=0.090

M_w=73100

C(gm/m1)	ī(s)	$n_r = \bar{t}/t_o$	ln(n _r)/C	Curve coefficients	nsp	n _{sp} /C	Curve coefficients
.0100 .0091 .0077 .0063 .0050 .0030	113.74 111.54 108.18 104.88 101.88 98.05	1.2515 1.2273 1.1904 1.1540 1.1210 1.0789	22.44 22.51 22.63 22.74 22.85 23.01	r^{2} = .9990 b =- 84.4900 k''= -0.1560	.2515 .2273 .1904 .1540 .1210 .0789	25.15 24.98 24.72 24.45 24.21 23.91	r^{2} = .9985 b =185.8888 k'= .3430

k'-k"=0.499

м w	[n]	K	a	r ²
10500 42500 73100	8.63 18.66 23.28	0.0711	0.5194	.9964

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Evaluating the constants of the molecular weight equation for 2.0 M KCl dextran solution

 $\bar{M}_{w} = 10500$

Ī	C(gm/m1)	ī(s)	n _r =ī/t _o	ln(n _r)/C	Curve coefficients	n _{sp}	n _{sp} /C	Curve coefficients
	.0400 .0364 .0308 .0250 .0200 .0133	131.99 127.86 121.70 115.39 110.18 103.45	1.4524 1.4070 1.3391 1.2697 1.2124 1.1383	9.33 9.38 9.48 9.55 9.63 9.74	r^{2} = .9981 b =- 15.2340 k''= -0.1540	.4524 .4070 .3391 .2697 .2124 .1383	11.31 11.18 11.01 10.79 10.62 10.40	r^{2} = .9994 b = 34.2101 k'= .3460

k'-k"=0.500

₩ _w =42500

C(gm/m1)	t(s)	$n_r = \bar{t}/t_o$	ln(n _r)/C	Curve coefficients	n _{sp}	n _{sp} /C	Curve coefficients
.0200 .0182 .0154 .0125 .0100 .0050	133.03 128.82 122.45 115.99 110.67 100.45	1.4637 1.4175 1.3474 1.2763 1.2177 1.1053	19.05 19.17 19.36 19.52 19.70 20.02	r^{2} = .9994 b =- 64.3800 k''= -0.1560	.4637 .4175 .3474 .2763 .2177 .1053	23.19 22.94 22.56 22.11 21.77 21.06	r^{2} = .9998 b =142.5550 k'= .3440

k'-k"=0.500

₩_=73100

n _r =t/to	ln(n _r)/C	Curve coefficients	n _{sp}	n _{sp} /C	Curve coefficients
1.3098	26.99		.3098	30.98	
1.2799	27.12		.2799	30.76	
1.2337	27.28	2	.2337	30.36	2
1.1886	27.42	$r^2 = .9970$.1886	29.93	$r^2 = .9991$
1.1480	27.61	b =-124.6825	.1480	29.61	b =274.5585
1.0872	27.88	k"= -0.1560	.0872	29.08	k'= .3440
	n _r =t/t _o 1.3098 1.2799 1.2337 1.1886 1.1480 1.0872	$\begin{array}{c c c c c c c c c c c c c c c c c c c $	$\begin{array}{c c c c c c c c c c c c c c c c c c c $	$\begin{array}{ c c c c c c c c c c c c c c c c c c c$	$\begin{array}{ c c c c c c c c c c c c c c c c c c c$

k'-k"=0.5000

м w	[n] K		a	r ²
10500	9.94			
42500	20.34			
73100	28.24	.0711	.5290	.9986



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C(KC1)	M w	k'	k"	k'-k"	[n]	k	а
.25	10500 42500 73100	.347 .369 .336	-0.155 -0.140 -0.161	.502 .509 .497	9.31 18.56 26.10	.0723	.5237
.50	10500 42500 73100	.429 .346 .345	-0.079 -0.155 -0.156	.508 .501 .501	9.25 18.67 26.67	.0655	.5341
.75	10500 42500 73100	.348 .346 .345	-0.154 -0.155 -0.156	.501 .501 .501	9.30 18.67 26.67	.0655	.5341
1.00	10500 42500 73100	.351 .343 .346	-0.153 -0.157 -0.156	.504 .500 .502	9.33 18.85 26.48	.0679	.5307
1.50	10500 42500 73100	.342 .435 .343	-0.156 -0.074 -0.156	.498 .509 .499	8.63 18.66 23.28	.0711	.5194
2.00	10500 42500 73100	.346 .344 .344	-0.154 -0.156 -0.156	.500 .500 .500	9.94 20.34 28.24	.0711	.5329

Values of the constants of molecular weight equation for dextran solution in different KC1 concentrations

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Hydrolysis	of Dextra	n
Acid	$\Omega n 1 v$	

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:=45 [°] C	C(HC1)=0.5 M						C(Dextran)=.04gm/m1			
T(min)	C(gm/ml)	ī(s)	n r	ln(n _r)/C	Curve coefficients	[n]	<u>M</u> w			
0							73100	2.392x10		
30	.0200 .0182 .0154 .0125	144.83 139.35 131.07 122.74	1.594 1.533 1.442 1.351	23.30 23.49 23.78 24.04	r ² = .9985 b =- 98.9335 k''= -0.1550	25.29	72000	2.404x10		
60	.0200 .0182 .0154 .0125	144.44 139.00 130.72 122.53	1.589 1.529 1.438 1.348	23.17 23.35 23.61 23.91	r ² = .9995 b =- 98.0601 k"= -0.1550	25.13	71100	2.414x10 ⁻		
90	.0200 .0182 .0154 .0125	143.87 138.46 130.28 122.20	1.583 1.524 1.434 1.345	22.97 23.13 23.39 23.69	r^2 .9989 b =- 95.9116 k''= -0.1550	24.88	69800	2.429x10 ⁻		
120	.0200 .0182 .0154 .0125	143.39 138.10 129.91 121.95	1.578 1.520 1.429 1.342	22.80 22.99 23.20 23.53	r^2 .9931 b =- 94.9069 k''= -0.1560	24.70	68800	2.441x10 ⁻		
150	.0200 .0182 .0154 .0125	142.71 137.55 129.49 121.56	1.570 1.514 1.425 1.338	22.56 22.77 22.99 23.27	r^{2} = .9959 b =- 92.4260 k''= -0.1550	24.42	67400	2.457x10 ⁻		
180	.0200 .0182 .0154 .0125	142.39 137.20 129.35 121.35	1.567 1.510 1.433 1.335	22.45 22.63 22.92 23.13	r ² = .9933 b =- 91.6377 k''= -0.1550	24.30	66700	2.466x10 ⁻		
240	.0200 .0182 .0154 .0125	141.43 136.46 128.61 120.84	1.556 1.502 1.415 1.330	22.11 22.33 22.55 22.79	r^{2} = .9921 b =- 88.5231 k''= -0.1550	23.91	64700	2.491x10 ⁻¹		
360	.0200 .0182 .0154 .0125	139.87 134.78 127.37 119.90	1.539 1.483 1.402 1.319	21.56 21.65 21.92 22.17	r^2 .9915 b =- 83.7263 k''= -0.1550	23.21	61100	2.539x10 ⁻¹		
	$r^2 = 0.998$	8		1	· · · · · · · · · · · · · · · · · · ·	b =4.	111x10	6		
	a =2.392	×10 ⁻²				$k_{45}^{C} = 6$.723x10	5		

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Hydrolysis of Dextran Acid and Ultrasound C(HC1)=0.5 M

T=45⁰C Frequency=17kHz

C(Dextran)=.04gm/m1 Power =200w/cm²

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T(min)	C(gm/m1)	ī(s)	n _r	ln(n _r)/c	Curve coefficients	[n]	M _w	
0							73100	2.392×10^{-2}
30	.0200 .0182 .0154 .0125	144.72 139.23 130.92 122.69	1.592 1.532 1.441 1.350	23.26 23.44 23.70 24.01	r ² = .9991 b =- 99.3044 k"= -0.1560	25.24	71700	2.407×10 ⁻²
60	.0200 .0182 .0154 .0125	144.17 138.78 130.49 122.39	1.586 1.527 1.436 1.347	23.07 23.26 23.49 23.81	r ² = .9965 b =- 96.8467 k"= -0.1550	25.01	70500	2.421×10 ⁻²
90	.0200 .0182 .0154 .0125	143.51 138.20 130.07 122.00	1.579 1.521 1.431 1.342	22.84 23.03 23.28 23.56	r^{2} = .9993 b =- 95.0537 k''= -0.1550	24.75	69100	2.437x10 ⁻²
120	.0200 .0182 .0154 .0125	143.00 137.69 129.65 121.71	1.574 1.515 1.427 1.339	22.67 22.83 23.07 23.37	r^2 .9980 b =- 92.7274 k''= -0.1540	24.52	67900	2.451x10 ⁻²
150	.0200 .0182 .0154 .0125	142.34 137.08 129.27 121.31	1.566 1.508 1.422 1.335	22.43 22.58 22.88 23.10	r ² = .9951 b =- 91.2513 k''= -0.1550	24.26	66500	2.468x10 ⁻²
180	.0200 .0182 .0154 .0125	141.91 136.66 128.88 121.07	1.562 1.504 1.418 1.332	22.28 22.42 22.68 22.95	r ² = .9989 b =- 90.0301 k''= -0.1550	24.07	65500	2.481x10 ⁻²
240	.0200 .0182 .0154 .0125	140.66 135.75 128.01 120.41	1.548 1.494 1.409 1.325	21.84 22.05 22.24 22.51	r^{2} = .9922 b =- 86.4054 k''= -0.1550	23.59	63000	2.513x10 ⁻²
360	.0200 .0182 .0154 .0125	138.65 133.79 126.43 119.24	1.526 1.472 1.391 1.312	22.12 21.25 21.44 21.73	r^{2} = .9909 b =- 80.2999 k''= -0.1560	22.71	58600	2.574x10 ⁻²
r	r ² =0.9998	3	**********************			b =5.0	0607x10	-6
	a =2.391	3x10 ⁻²				$4^{k_{45}^{s}} = 8.2$	2764x10	-5

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Hydrolysis of Dextran Acid Only C(HCl)=1.0 M

T=45⁰C

C(Dextran)=.04gm/m1

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T(min)	C(gm/ml)	Ē(s)	n _r	$ln(n_r)/C$	Curve coefficients	[n]	M _w	$\overline{M}_{w}^{-1/3}$
0		[73100	2.392×10^{-2}
30	.0200 .0182 .0154 .0125	149.71 143.36 134.01 124.76	1.647 1.577 1.475 1.373	24.96 25.04 25.22 25.35	r^2 .9942 b =- 53.4276 k''= -0.0790	26.03	71000	2.415×10 ⁻²
60	.0200 .0182 .0154 .0125	148.84 142.61 133.34 124.31	1.638 1.569 1.367 1.368	24.67 24.76 24.89 25.06	r ² = .9972 b =- 51.5187 k"= -0.0780	25.70	69400	2.433x10 ⁻²
90	.0200 .0182 .0154 .0125	147.53 141.54 132.45 123.62	1.623 1.557 1.457 1.360	24.22 24.34 24.46 24.61	r^2 .9946 b =- 50.6608 k''= -0.0800	25.24	67100	2.461x10 ⁻²
120	.0200 .0182 .0154 .0125	146.56 140.61 131.77 123.07	1.613 1.547 1.450 1.354	23.89 23.98 24.12 24.26	r^2 = .9999 b =- 49.3778 k''= -0.0800	24.88	65300	2.483x10 ⁻²
150	.0200 .0182 .0154 .0125	145.29 139.49 130.82 122.40	1.599 1.535 1.439 1.347	23.46 23.54 23.65 23.82	r^2 .9914 b =- 47.2602 k''= -0.0790	24.40	63000	2.513x10 ⁻²
180	.0200 .0182 .0154 .0125	144.62 138.86 130.37 122.01	1.591 1.528 1.435 1.343	23.23 23.29 23.43 23.57	r^2 .9958 b =- 46.1550 k''= -0.0790	24.14	61800	2.529x10 ⁻²
210	.0200 .0182 .0154 .0125	143.69 138.08 129.75 121.51	1.581 1.519 1.428 1.337	22.91 22.98 23.12 23.24	r^2 .9981 b =- 44.7207 k''= -0.0790	23.00	60200	2.552x10 ⁻²
240	.0200 .0182 .0154 .0125	142.92 137.34 129.16 121.09	1.573 1.511 1.421 1.332	22.64 22.69 22.83 22.96	r^2 .9930 b =- 43.8365 k"= -0.0790	23.50	58800	2.572x10 ⁻²
	r ² =0.9976	6				b =7.	6389x10	-6
	a =2.3917	7x10 ⁻²				$k_{45}^{c} = 1$.	249x10 ⁻	4

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Hydrolysis of Dextran Acid and Ultrasound C(HC1)=1.0 M

T=45[°]C Frequency=17kHz

C(Dextran) = .04gm/m1Power = 200w/cm²

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T(min)	C(gm/m1)	t(s)	n r	ln(n _r)/C	Curve coefficients	[n]	M _w	M
0							73100	2.392×10^{-2}
30	.0200 .0182 .0154 .0125	149.44 140.14 133.77 124.64	1.644 1.575 1.472 1.371	24.87 24.96 25.10 25.27	r ² = .9983 b =- 53.1108 k"= -0.0790	25.93	70500	2.421x10 ⁻²
60	.0200 .0182 .0154 .0125	147.96 141.94 132.78 123.85	1.628 1.562 1.461 1.363	24.37 24.50 24.62 24.78	r ² = .9903 b =- 50.4908 k''= -0.0780	25.40	67900	2.451x10 ⁻²
90	.0200 .0182 .0154 .0125	146.50 140.57 131.74 123.04	1.612 1.547 1.450 1.354	23.87 23.97 24.11 24.24	r^{2} = .9981 b =- 49.2078 k''= -0.0800	24.86	65200	2.484x10 ⁻²
120	.0200 .0182 .0154 .0125	145.41 139.55 130.94 122.44	1.600 1.536 1.441 1.347	23.50 23.57 23.71 23.85	r^2 .9983 b =- 47.2293 k''= -0.0790	24.44	63200	2.511x10 ⁻²
150	.0200 .0182 .0154 .0125	143.98 138.34 129.92 121.68	1.584 1.522 1.430 1.339	23.01 23.09 23.21 23.35	r ² = .9993 b =- 45.1194 k''= -0.0790	23.91	60700	2.545x10 ⁻²
180	.0200 .0182 .0154 .0125	142.95 137.45 129.17 121.12	1.573 1.512 1.421 1.333	22.65 22.73 22.83 22.98	r ² = .9940 b =- 43.1795 k"= -0.0780	23.51	58900	2.570x10 ⁻²
210	.0200 .0182 .0154 .0125	141.51 136.19 128.15 120.34	1.557 1.499 1.410 1.324	22.14 22.23 22.32 22.46	r^2 .9931 b =- 41.4174 k''= -0.0780	22.97	56400	2.607x10 ⁻²
240	.0200 .0182 .0154 .0125	140.36 135.23 127.40 119.71	1.544 1.488 1.402 1.317	21.73 21.88 21.93 22.04	r^2 = .9851 b =- 39.8331 k''= -0.0780	22.54	54500	2.637x10 ⁻²
	r ² =0.9994	4				b =1.	0206x10	-5
	a =2.3906	5×10^{-2}				$_{\rm H}^{\rm k_{45}^{\rm S}} = 1.$	669x10 ⁻²	, +

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Hydeolysis of Dextran Acid Only C(HCl)=1.5 M

T=45⁰C

C(Dextran)=.04gm/m1

T(min)	C(gm/ml)	ī(s)	nr	ln(n _r)/C	Curve coefficients	[n]	M _w	$\overline{M}_{w}^{-1/3}$
0							73100	2.392×10^{-2}
30	.0200 .0182 .0154 .0125	144.86 139.34 131.01 122.75	1.494 1.533 1.442 1.351	23.31 23.48 23.75 24.05	r ² = .9996 b =- 98.5779 k"= -0.1540	25.28	69600	2.431x10 ⁻²
60	.0200 .0182 .0154 .0125	143.27 137.98 129.82 121.87	1.576 1.518 1.428 1.341	22.76 22.94 23.16 23.47	r^{2} = .9961 b =- 92.9361 k''= -0.1530	24.62	66300	2.471x10 ⁻²
90	.0200 .0182 .0154 .0125	141.82 136.53 128.79 121.00	1.561 1.502 1.417 1.331	22.25 22.36 22.64 22.90	r ² = .9949 b =- 88.7472 k"= -0.1540	24.00	63200	2.511x10 ⁻²
120	.0200 .0182 .0154 .0125	140.49 135.56 127.87 120.29	1.546 1.492 1.407 1.324	21.78 21.97 22.17 22.43	r ² = .9960 b =- 84.6047 k"= -0.1530	23.49	60700	2.545x10 ⁻²
150	.0200 .0182 .0154 .0125	138.95 134.14 126.76 119.40	1.529 1.476 1.395 1.314	21.23 21.39 21.61 21.84	r^2 .9994 b =- 80.8331 k"= -0.1550	22.85	57600	2.589x10 ⁻²
180	.0200 .0182 .0154 .0125	137.70 132.95 125.87 118.66	1.515 1.463 1.385 1.306	20.78 20.90 21.15 21.34	r ² = .9959 b =- 76.3351 k"= -0.1540	22.30	55100	2.628x10 ⁻²
210	.0200 .0182 .0154 .0125	136.49 131.87 124.87 118.00	1.502 1.451 1.374 1.298	20.34 20.45 20.63 20.89	r^2 = .9913 b =- 72.8263 k''= -0.1540	21.78	52700	2.667x10 ⁻²
2400	.0200 .0182 .0154 .0125	135.02 130.72 123.92 117.18	1.486 1.438 1.364 1.289	19.79 19.97 20.14 20.33	r^2 = .9902 b =- 70.0441 k''= -0.1560	21.21	50100	2.713x10 ⁻²
	r ² =0.999	5	b =1.	324x10 ⁻¹	5			
	a =2.391	×10 ⁻²		$k_{45}^{c} = 2$.	166x10 ⁻	4		

Hydrolysis of Dextran Acid and Ultrasound C(HCl) = 1.5 M

C(Dextran)=.04gm/m1 Power = 200w/cm^2

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T(min)	C(gm/m1)	t(s)	n r	$\ln(n_r)/C$	Curve coefficients	[n]	Mw	_M −1/3 w
0							73100	2.392×10^{-2}
30	.0200 .0182 .0154 .0125	144.45 139.01 130.71 122.52	1.589 1.530 1.438 1.348	23.17 23.35 23.60 23.90	r^{2} = .9991 b =- 96.4680 k''= -0.1530	25.10	68700	2.442x10 ⁻²
60	.0200 .0182 .0154 .0125	142.17 136.95 129.04 121.23	1.564 1.507 1.420 1.334	22.37 22.53 22.77 23.05	r^{2} = .9993 b =- 90.2388 k''= -0.1540	24.17	64000	2.500×10 ⁻²
90	.0200 :0182 .0154 .0125	140.21 135.31 127.69 120.12	1.543 1.489 1.405 1.322	21.68 21.87 22.08 22.32	r^{2} = .9964 b =- 83.7082 k''= -0.1530	23.37	60100	2.553x10 ⁻²
120	.0200 .0182 .0154 .0125	138.30 133.49 126.32 119.02	1.522 1.469 1.390 1.310	20.99 21.13 21.38 21.58	r^2 .9972 b =- 79.7280 k''= -0.1560	22.59	56400	2.608x10 ⁻²
150	.0200 .0182 .0154 .0125	136.61 132.03 125.02 118.08	1.503 1.453 1.376 1.299	20.38 20.52 20.71 20.95	r^2 .9985 b =- 75.1526 k''= -0.1570	21.88	53100	2.661x10 ⁻²
180	.0200 .0182 .0154 .0125	135.13 130.73 123.97 117.23	1.487 1.438 1.364 1.290	19.83 19.98 20.16 20.37	r^2 .9982 b =- 70.9019 k"= -0.1570	21.26	50300	2.709x10 ⁻²
210	.0200 .0182 .0154 .0125	133.41 129.18 122.71 116.24	1.468 1.421 1.350 1.279	19.19 19.32 19.50 19.69	r^2 .9996 b =- 66.2648 k''= -0.1570	20.52	47100	2.769x10 ⁻²
240	.0200 .0182 .0154 .0125	132.01 127.90 121.70 115.43	1.453 1.407 1.339 1.270	18.67 18.78 18.96 19.13	r^2 .9996 b =- 61.6276 k''= -0.1560	19.90	44500	2.822x10 ⁻²
	r ² =0.999	8			ین پر پر بین به بین بر از این پر پر پر پر اور این اور این پر پر پر پر اور این اور این پر پر پر پر پر	b =1.	793x10 ⁻	5
	a =2.391;	к10 ⁻²				$k_{45}^{s} = 2$.	937x10	4

 $T=45^{\circ}C$

Frequency=17kHz

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Hydrolysis of Dextran Acid Only C(HC1)=3.0 M

T=45⁰C

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C(Dextran)=.04gm/ml

T(min)	C(mg/ml)	īt(s)	n _r	ln(n _r)/C	Curve coefficients	[n]	M w	$\bar{M}_{w}^{-1/3}$
0							73100	2.392×10^{-2}
15	.0200 .0182 .0154 .0125	139.32 134.41 126.98 119.62	1.533 1.479 1.397 1.316	21.36 21.50 21.72 21.98	r^2 .9988 b =- 82.4175 k''= -0.1560	23.00	68000	2450x10 ⁻²
30	.0200 .0182 .0154 .0125	137.48 132.77 125.72 118.56	1.513 1.461 1.383 1.305	20.70 20.83 21.07 21.27	r^2 = .9980 b =- 77.0616 k''= -0.1560	22.24	63700	2.504x10 ⁻²
45	.0200 .0182 .0154 .0125	135.52 131.02 124.28 117.44	1.491 1.442 1.368 1.292	19.98 20.10 20.32 20.51	r^2 .9986 b =- 71.5589 k''= -0.1560	21.41	59200	2.566x10 ⁻²
60	.0200 .0182 .0154 .0125	133.85 129.48 123.02 116.47	1.473 1.425 1.354 1.282	19.36 19.45 19.66 19.85	r^2 .9965 b =- 66.7440 k''= -0.1560	20.68	55400	2.623x10 ⁻²
90	.0200 .0182 .0154 .0125	132.16 127.84 121.47 115.13	1.454 1.407 1.337 1.267	18.72 18.75 18.84 18.92	r^2 = .9918 b =- 27.5060 k''= -0.0740	19.26	48300	2.746x10 ⁻²
120	.0200 .0182 .0154 .0125	129.22 125.33 119.39 113.51	1.422 1.379 1.314 1.249	17.60 17.66 17.72 17.79	r^{2} = .9936 b =- 24.7082 k''= -0.0750	18.10	42800	2.859x10 ⁻²
150	.0200 .0182 .0154 .0125	126.79 123.12 117.64 112.12	1.395 1.355 1.294 1.234	16.65 16.68 16.76 16.80	r^2 .9796 b =- 20.9367 k''= -0.0720	17.07	38300	2.967x10 ⁻²
180	.0200 .0182 .0154 .0125	124.26 120.90 115.81 110.70	1.367 1.330 1.274 1.218	15.64 15.68 15.74 15.78	r^2 = .9884 b =- 18.8268 k''= -0.0730	16.02	33900	3.090x10 ⁻²
	r ² =0.999	8		b =3	.8748x10	-5		

 $a = 2.3915 \times 10^{-2}$

 $k_{45}^{c} = 6.337 \times 10^{-4}$

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Hydeolysis of Dextran Acid and Ultrasound C(HC1)=3.0 M

T=45[°]C Frequency=17kHz

C(Dextran)=.04gm/ml Power =200w/cm²

T(min)	C(gm/m1)	īt(s)	n r	ln(n _r)/C	Curve coefficients	[n]	M _w	
0							73100	2.392×10^{-2}
15	.0200 .0182 .0154 .0125	139.02 134.15 126.77 119.45	1.430 1.476 1.395 1.314	21.25 21.40 21.61 21.87	r ² = .9985 b =- 81.8997 k''= -0.1560	22.89	67300	2.458x10 ⁻²
30	.0200 .0182 .0154 .0125	136.94 132.26 123.27 118.25	1.507 1.455 1.378 1.301	20.50 20.62 20.84 21.06	r ² = .9993 b =- 75.2718 k''= -0.1560	22.00	62400	2.521×10 ⁻²
45	.0200 .0182 .0154 .0125	134.64 130.34 123.62 116.96	1.482 1.434 1.360 1.287	19.65 19.81 19.98 20.18	r ² =	21.05	57300	2.594x10 ⁻²
60	.0200 .0182 .0154 .0125	132.78 128.61 122.21 115.89	1.461 1.425 1.345 1.275	18.96 19.08 19.23 19.45	$r^{2}=$.9948 b =- 64.1472 k''= -0.1570	20.24	53100	2.661x10 ⁻²
90	.0200 .0182 .0154 .0125	129.20 125.38 119.58 113.81	1.422 1.380 1.316 1.252	17.59 17.68 17.82 18.00	r^{2} = .9968 b =- 54.3551 k''= -0.1560	18.67	45500	2.801x10 ⁻²
120	.0200 .0182 .0154 .0125	127.45 123.71 118.08 112.51	1.402 1.361 1.299 1.238	16.91 16.95 17.00 17.08	r^{2} = .9913 b =- 22.2119 k''= -0.0740	17.35	39500	2.936x10 ⁻²
150	.0200 .0182 .0154 .0125	124.63 12.19 116.05 110.91	1.371 1.334 1.277 1.220	15.79 15.81 15.88 15.93	r^2 .9875 b =- 19.5146 k''= -0.0750	16.17	34500	3.072x10 ⁻²
180	.0200 .0182 .0154 .0125	121.49 118.55 113.94 109.34	1.337 1.304 1.254 1.203	14.51 14.60 14.68 14.79	r^2 .9915 b =- 36.0924 k''= -0.1550	15.24	30800	3.190x10 ⁻²
	r ² =0.999	6		b =4	.4923x10	-5		
	a =2.391	7x10 ⁻²			I	$k_{45}^{s} = 7$.347x10 ⁻⁴	4

Hydrolysis of Dextran Acid Only C(HCl)=4.0 M

I-45 0		·····			· · · · · · · · · · · · · · · · · · ·		U (DEXCI	an)=0.04g/m3
T(min)	C(gm/ml)	ī(s)	n _r	$\ln(n_r)/C$	Curve coefficients	[n]	M _w	M _w ^{1/3}
0							73100	2.392×10^{-2}
10	.0200 .0182 .0154 .0125	148.13 142.22 133.49 124.57	1.630 1.565 1.469 1.371	24.42 24.60 24.96 25.22	r^2 .9947 b =-109.0038 k''= -0.1540	26.60	67300	2.458x10 ⁻²
20	.0200 .0182 .0154 .0125	145.53 139.92 131.44 123.13	1.601 1.540 1.446 1.355	23.54 23.71 23.96 24.29	$r^{2}=9967$ b =- 99.1267 k''= -0.1520	25.51	62200	2.524x10 ⁻²
30	.0200 .0182 .0154 .0125	143.01 137.81 129.73 121.72	1.574 1.516 1.427 1.339	22.66 22.87 23.11 23.77	r^{2} = .9966 b =- 93.1216 k''= -0.1550	24.54	57800	2.586x10 ⁻²
40	.0200 .0182 .0154 .0125	140.44 135.44 127.80 120.25	1.545 1.490 1.406 1.325	21.76 21.92 22.13 22.40	r^{2} = .9981 b =- 84.2183 k"= -0.1530			
50	.0200 .0182 .0154 .0125	137.95 133.27 126.03 118.85	1.518 1.466 1.387 1.308	20.86 21.03 21.23 21.46	r^{2} .9979 b =- 78.7232 k''= -0.1560	22.44	48900	2.735x10 ⁻²
60	.0200 .0182 .0154 .0125	136.19 131.61 124.67 117.84	1.499 1.448 1.372 1.297	20.22 20.34 20.52 20.78	r^2 = .9930 b =- 73.9006 k''= -0.1570	21.68	45800	2.795x10 ⁻²
70	.0200 .0182 .0154 .0125	134.23 129.85 123.31 116.72	1.478 1.429 1.356 1.284	19.51 19.60 19.81 20.01	r^2 .9963 b =- 67.9883 k''= -0.1560	20.85	42600	2.863x10 ⁻²
80	.0200 .0182 .0154 .0125	132.55 128.46 122.08 115.76	1.459 1.414 1.343 1.274	18.87 19.01 19.16 19.35	r^2 .9964 b = 62.5628 k''= -0.1540	20.13	39900	2.926x10 ⁻²
	r ² =0.9990	6			**************************************	b =6	.7367x10) ⁻⁵
	a =2.390	5×10^{-2}				$k_{45}^{c} = 1$.102x10	-3

T=45⁰C

C(Dextran)=0.04g/m1

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Hydrolysis of Dextran Acid and Ultrasound C(HC1)=4.0 M

Frequency=17kHz T=45⁰C Power = 200w/cm^2

C(Dextran)=.04gm/m1

T(min)	C(gm/m1)	t(s)	n r	$ln(n_r)/C$	Curve coefficients	[n]	м w	™
0							73100	2.392x10 ⁻²
10	.0200 .0182 .0154 .0125	148.03 142.12 133.42 142	1.629 1.564 1.468 1.370	24.39 24.56 24.93 25.18	r ² = .9925 b =-108.2773 k"= -0.1540	26.55	67100	2.461x10 ⁻²
20	.0200 .0182 .0154 .0125	144.78 193.25 130.89 122.71	1.593 1.532 1.440 1.350	23.28 23.44 23.68 24.02	r^{2} = .9939 b =- 97.7046 k''= -0.1540	25.21	60800	2.543x10 ⁻²
30	.0200 .0182 .0154 .0125	142.67 137.52 129.45 121.53	1.570 1.513 1.425 1.337	22.54 22.75 22.99 23.24	r^{2} = .9958 b =- 91.8773 k''= -0.1540	24.39	57200	2.595x10 ⁻²
40	.0200 .0182 .0154 .0125	140.10 135.10 127.61 120.03	1.542 1.487 1.404 1.321	21.64 21.78 22.04 22.25	r^2 .9974 b =- 82.5643 k"= -0.1520	23.29	52400	2.672x10 ⁻²
50	.0200 .0182 .0154 .0125	137.59 132.98 125.77 118.65	1.514 1.463 1.384 1.306	20.73 20.91 21.09 21.33	r^2 .9948 b =- 77.8576 k''= -0.1570	22.30	48300	2.746x10 ⁻²
60	.0200 .0182 .0154 .0125	135.77 131.24 124.37 117.59	1.494 1.444 1.369 1.294	20.00 20.19 20.37 20.61	r ² = .9961 b =- 71.4120 k" -0.1550	21.49	45100	2.809x10 ⁻²
70	.0200 .0182 .0154 .0125	133.41 129.23 122.73 116.25	1.468 1.422 1.350 1.279	19.19 19.34 19.50 19.69	r^2 .9959 b =- 65.2292 k''= -0.1550	20.50	41300	2.893x10 ⁻²
80	.0200 .0182 .0154 .0125	132.21 128.10 121.80 115.55	1.455 1.410 1.340 1.271	18.74 18.86 19.01 19.21	r^2 = .9974 b =- 61.6586 k''= -0.1550	19.97	39300	2.941x10 ⁻²
<u> </u>	r ² =0.998	5		<u> </u>		b =6	.9583x10	-5
	a =2.394	×10 ⁻²				$k_{45}^{s} = 1$.138x10 ⁻	3

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т=50⁰с

Hydrolysis of Dextran Acid Only C(HCl)=0.5 M

C(Dextran)=.04gm/m1

T(min)	C(gm/m1)	ī(s)	nr	ln(n _r)/C	Curve coefficients	[n]	M w	
0							73100	2.392×10^{-2}
30	.0200 .0182 .0154 .0125	144.68 139.19 130.88 122.66	1.592 1.532 1.440 1.350	23.25 23.42 23.68 23.99	r^{2} = .9988 b =- 98.2302 k''= -0.1550	25.21	71600	2.408x10 ⁻²
60	.0200 .0182 .0154 .0125	143.44 138.05 130.09 121.93	1.578 1.519 1.431 1.342	22.82 22.97 23.29 23.51	r ² = .9931 b =- 94.4354 k"= -0.1550	24.71	68900	2.439x10 ⁻²
90	.0200 .0182 .0154 .0125	142.64 137.40 129.48 121.50	1.570 1.512 1.425 1.337	22.54 22.71 22.99 23.23	r^{2} = .9983 b =- 92.7042 k''= -0.1560	24.40	67200	2.460x10 ⁻²
120	.0200 .0182 .0154 .0125	142.65 136.48 128.66 120.94	1.559 1.502 1.416 1.331	22.19 22.34 22.57 22.86	r ² = .9975 b =- 88.8168 k''= -0.1550	23.96	65000	2.487x10 ⁻²
150	.0200 .0182 .0154 .0125	140.66 135.61 127.96 120.38	1.548 1.492 1.408 1.325	21.89 21.99 22.22 22.49	r^2 .9991 b =- 86.3282 k''= -0.1560	23.56	62900	2.513x10 ⁻²
180	.0200 .0182 .0154 .0125	139.95 134.96 127.51 119.96	1.540 1.485 1.403 1.320	21.59 21.73 21.99 22.21	r^2 .9983 b =- 83.8086 k''= -0.1550	23.26	61400	2.534x10 ⁻²
210	.0200 .0182 .0154 .0125	139.08 134.35 126.86 119.51	1.530 1.478 1.396 1.315	21.28 21.48 21.66 21.91	r^2 .9920 b =- 81.2505 k"= -0.1550	23.26	61400	2.534x10 ⁻²
240	.0200 .0182 .0154 .0125	138.60 133.75 126.39 119.21	1.525 1.472 1.391 1.312	21.10 21.23 21.42 21.71	$r^2 = .9909$ b =- 80.2999 k''= -0.1560	22.69	58500	2.576x10 ⁻²
,	r ² =0.997	6	b =7.	9389x10	-6			
	a =2.390	0×10^{-2}				$k_{50}^{c} = 1$.	298x10	4

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Hydrolysis of Dextran Acid and Ultrasound C(HC1)=0.5 M

T=50⁰C Frequency=17kHz

C(Dextran)=.0gm/m1 Power =200w/cm²

T(min)	C(gm/m1)	ī(s)	n r	ln(n _r)/C	Curve coefficients	[n]	M w	
0							73100	2.392x10 ⁻²
30	.0200 .0182 .0154 .0200	144.09 138.74 130.51 122.35	1.585 1.527 1.436 1.346	23.04 23.25 23.50 23.78	r^{2} = .9979 b =- 97.2023 k" -0.1560	25.00	70400	2.422x10 ⁻²
60	.0200 .0182 .0154 .0125	142.92 137.65 129.67 121.66	1.573 1.515 1.427 1.339	22.64 22.81 23.08 23.34	$r^{2}=$.9997 b =- 93.6007 k''= -0.1560	24.51	67900	2.452x10 ⁻²
90	.0200 .0182 .0154 .0125	141.64 136.47 128.74 120.92	1.559 1.502 1.417 1.33	22.19 22.34 22.61 22.58	r ² = .9990 b =- 88.9636 k" =- 1550	23.97	65000	2.487x10 ⁻²
120	.0200 .0182 .0154 .0125	140.92 135.77 128.17 120.50	1.551 1.494 1.410 1.326	21.93 22.06 22.33 22.57	r ² = .9980 b =- 86.8151 k"= -0.1550	23.66	63400	2.503x10 ⁻²
150	.0200 .0182 .0154 .0125	139.78 134.82 127.30 119.88	1.538 1.483 1.401 1.319	21.54 21.67 21.88 22.16	$r^{2}=$.9961 b =- 83.3140 k''= -0.1550	23.19	61000	2.540x10 ⁻²
180	.0200 .0182 .0154 .0125	138.80 133.98 126.62 119.32	1.527 1.474 1.393 1.313	21.17 21.33 21.54 21.78	r ² = .9993 b =- 80.4854 k"= -0.1550	22.79	59000	2.569x10 ⁻²
210	.0200 .0128 .0154 .0125	137.78 133.05 125.92 118.69	1.516 1.464 1.386 1.306	20.81 20.94 21.18 21.36	r^2 = .9956 b =- 74.5730 k''= -0.1500	23.30	56600	2.604x10 ⁻²
240	.0200 .0182 .0154 .0125	136.82 132.26 125.18 118.17	1.506 1.455 1.377 1.300	20.46 20.62 20.79 20.01	r^{2} = .9962 b =- 71.6284 k''= -0.1490	21.90	54700	2.635×10 ⁻²
	r ² =0.998	8	<u></u>	b =1.0028x10 ⁻⁵				
	a =2.391	8x10 ⁻²				$H^{k_{50}^{s}} = 1$.640x10 ⁻	4

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Hydrolysis of Dextran Acid Only

г=50 ⁰ С			.0 M	C(Dextran)=.04gm/m1				
T(min)	C(gm/ml)	$C(gm/m1)$ $\overline{t}(s)$ n_r $ln(n_r)/C$ Curve coefficient				[n]	M . w	
0							73100	2.392x10 ⁻²
30	.0200 .0182 .0154 .0125	149.10 142.84 133.54 124.44	1.641 1.572 1.469 1.369	24.75 24.85 25.00 25.14	r^{2} = .9990 b =- 52.0442 k''= -0.0782	25.79	7000	2.426x10 ⁻²
60	.0200 .0182 .0154 .0125	146.43 140.50 131.66 123.00	1.611 1.546 1.449 1.353	23.85 23.94 24.07 24.21	r ² = .9999 b =- 47.7858 k''= -0.0777	24.81	65200	2.485x10 ⁻²
120	.0200 .0182 .0154 .0125	142.58 137.11 128.94 120.91	1.569 1.509 1.419 1.330	22.52 22.60 22.71 22.84	r^{2} = .9993 b =- 42.2830 k''= -0.0774	23.37	58400	2.577x10 ⁻²
180	.0200 .0182 .0154 .0125	139.15 134.08 126.50 119.03	1.531 1.475 1.392 1.310	21.30 21.37 21.48 21.59	r ² = .9994 b =- 38.7201 k"= -0.0795	22.06	52500	2.671x10 ⁻²
240	.0200 .0182 .0154 .0125	136.10 131.38 124.32 117.34	1.498 1.446 1.368 1.291	20.19 20.25 20.35 20.45	r ² = .9997 b =- 34.8095 k"= -0.0798	20.87	47400	2.763×10 ⁻²
300	.0200 .0182 .0154 .0125	133.39 129.00 122.39 115.85	1.468 1.419 1.347 1.275	19.19 19.24 19.33 19.42	r ² = .9995 b =- 30.8988 k"= -0.0788	19.80	43000	2.854x10 ⁻²
360	.0200 .0182 .0154 .0125	130.91 126.80 120.61 114.46	1.440 1.395 1.327 1.259	18.25 18.30 18.38 18.46	r^2 = .9999 b =- 28.0624 k''= -0.0793	18.80	39000	2.949x10 ⁻²
420	.0200 .0182 .0154 .0125	128.73 124.86 119.04 113.24	1.417 1.374 1.310 1.246	17.41 17.46 17.53 17.60	r^2 .9992 b =- 25.2261 k''= -0.0786	17.91	35700	3.037x10 ⁻²
	r ² =0.999	7		b =1	.5508x10	-5		
	$a = 2.3891 \times 10^{-2}$.536x10 ⁻²	ŧ.

Hydrolysis of Dextran Acid and Ultrasound C(HC1)=1.0 M

T=50⁰C Frequency=25kHz

C(Dextran)=.04gm/m1 Power =.4w/cm²

T(min)	C(gm/m1)	ī(s)	n r	ln(n _r)/C	Curve coefficients	[n]	м w	$\overline{M}_{w}^{-1/3}$
0							73100	2.392×10^{-2}
30	.0200 .0182 .0154 .0125	147.76 141.67 132.60 123.72	1.626 1.559 1.459 1.361	24.30 24.39 24.53 24.68	r^{2} = .9999 b =- 50.6222 k''= -0.0790	25.30	67600	2.455x10 ⁻²
30	.0200 .0182 .0154 .0125	145.08 139.31 130.71 122.27	1.596 1.533 1.438 1.345	23.39 23.47 23.60 23.73	$r^{2}=.99999$ b =- 45.4672 k''= -0.0770	24.31	62800	2.516x10 ⁻²
120	.0200 .0182 .0154 .0125	140.40 135.19 127.39 119.71	1.545 1.488 1.402 1.317	21.75 21.82 21.93 22.05	r^2 = .9998 b =- 39.9644 k''= -0.0786	22.54	54600	2.636x10 ⁻²
180	.0200 .182 .0154 .0125	136.40 131.65 124.54 117.51	1.501 1.449 1.370 1.293	20.30 20.37 20.46 20.56	r^{2} .9990 b =- 34.2917 k''= -0.0778	20.99	47900	2.754x10 ⁻²
240	.0200 .0182 .0154 .0125	133.02 128.66 122.12 115.64	1.464 1.416 1.344 1.272	19.05 19.10 19.19 19.27	r^2 = .9990 b =- 29.6545 k''= -0.0769	19.65	42400	2.868×10 ⁻²
300	.0200 .0182 .0154 .0125	129.66 125.69 119.70 113.76	1.427 1.383 1.317 1.252	17.77 17.82 17.89 17.96	r^2 .9992 b =- 25.2261 k''= -0.0755	18.29	37100	2.998×10 ⁻²
360	.0200 .0182 .0154 .0125	127.18 123.49 117.92 112.37	1.399 1.359 1.298 1.236	16.81 16.85 16.91 16.98	r ² = .9993 b =- 22.5597 k''= -0.0757	17.27	33400	3.105x10 ⁻²
420	.0200 .0182 .0154 .0125	142.70 121.28 116.12 110.96	1.372 1.335 1.278 1.221	15.82 15.86 15.91 15.97	r^2 = .9987 b =- 19.7233 k''= -0.0750	16.23	29800	3.225x10 ⁻²
	r ² =0.999	8				b =1.	.9798x10	-5
	a =2.396	×10 ⁻²				$k_{50}^{s} = 3$.	238x10	4

Hydrolysis of Dextran Acid Only C(HC1)=2.0 M

T(min)	C(gm/ml)	ī(s)	n _r	ln(n _r)/C	Curve coefficients	[n]	M w		
0							73100	2.392x10 ⁻²	
30	.0200 .0182 .0154 .0125	142.35 137.10 129.17 121.32	1.566 1.509 1.421 1.335	22.44 22.59 22.83 23.11	r ² = .9988 b =- 89.1645 k"= -0.152	24.22	64500	2.494x10 ⁻²	
60	.0200 .0182 .0154 .0125	138.12 133.32 126.18 118.90	1.520 1.467 1.388 1.308	20.93 21.06 21.31 21.50	r^{2} = .9961 b =- 77.4094 k''= -0.1530	22.48	56000	2.614x10 ⁻²	
90	.0200 .0182 .0154 .0125	134.47 130.14 123.48 116.84	1.480 1.432 1.359 1.286	19.59 19.73 19.91 20.10	r^2 .9987 b =- 67.3391 k"= -0.1530	20.95	49000	2.732x10 ⁻²	
120	.0200 .0182 .0154 .0125	131.47 127.38 121.27 115.70	1.447 1.402 1.334 1.267	18.46 18.55 18.73 18.90	r ² = .9986 b =- 59.4791 k''= -0.1540	19.64	43400	2.845x10 ⁻²	
150	.0200 .0182 .0154 .0125	128.66 124.91 119.23 113.50	1.416 1.374 1.312 1.249	17.38 17.48 17.63 17.78	r ² = .9998 b =- 53.2885 k"= -0.1570	18.45	38600	2.959x10 ⁻²	
180	.0200 .0182 .0154 .0125	126.24 122.74 117.46 112.09	1.389 1.351 1.292 1.233	16.43 16.51 16.66 16.78	r^{2} = .9972 b =- 47.4071 k''= -0.1570	17.38	34500	3.072×10 ⁻²	
210	.0200 .0182 .0154 .0125	124.00 120.81 115.82 110.81	1.364 1.329 1.274 1.219	15.54 15.64 15.75 15.86	r ² = .9936 b =- 41.9430 k" -0.1560	16.39	30900	3.186x10 ⁻²	
240	.0200 .0182 .0154 .0125	122.17 119.12 114.48 109.72	1.344 1.311 1.260 1.207	14.79 14.87 14.99 15.07	r^2 .9884 b =- 37.6536 k''= -0.1560	15.55	28000	3.293x10 ⁻²	
$r^2 = 0.9998$ b $= 3.7906 \times 10^{-5}$									

т=50⁰С

C(Dextran)=.04gm/m1

 $k_{50}^{c} = 6.199 \times 10^{-4}$

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 $a = 2.388 \times 10^{-2}$

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Hydrolysis of Dextran Acid and Ultrasound C(HC1)=2.0 M

T=50[°]C Frequency=25kHz

C(Dextran)=.04gm/ml Power =.4w/cm²

T(min)	C(gm/ml)	t(s)	nr	ln(n _r)/C	Curve coefficients	[n]	M w	M
0							73100	2.392×10^{-2}
30	.0200 .0182 .0154 .0125	143.08 137.58 129.30 121.23	1.574 1.514 1.423 1.334	22.69 22.78 22.90 23.05	$r^{2}=.9985$ b =- 47.4380 k''= -0.0850	23.64	61600	2.532×10 ⁻²
60	.0200 .0182 .0154 .0125	138.72 133.70 126.19 118.84	1.526 1.471 1.389 1.308	12.15 21.21 21.31 21.46	r^2 .9888 b =- 41.0310 k''= -0.0850	21.96	53600	2.652x10 ⁻²
90	.0200 .0182 .0154 .0125	132.37 128.31 121.98 115.66	1.457 1.412 1.342 1.273	18.80 18.95 19.11 19.29	r^2 = .9952 b =- 63.9859 k''= -0.1580	20.09	45300	2.805×10 ⁻²
120	.0200 .0182 .0154 .0125	129.15 125.37 119.60 113.78	1.424 1.380 1.316 1.252	1757 17.68 17.84 17.98	r^2 .9974 b =- 54.7106 k''= -0.1570	18.67	39500	2.936×10 ⁻²
150	.0200 .0182 .0154 .0125	126.23 122.75 117.56 112.09	1.389 1.351 1.292 1.233	16.43 16.52 16.66 16.78	r^2 .9978 b =- 46.8892 k''= -0.1550	17.37	34500	3.072x10 ⁻²
180	.0200 .0182 .0154 .0152	123.83 120.62 115.68 110.70	1.363 1.327 1.273 1.218	15.47 15.56 15.67 15.78	r^2 .9968 b =- 40.8687 k''= -0.1540	16.30	30600	3.197x10 ⁻²
210	.0200 .0182 .0154 .0125	121.31 118.38 113.81 109.24	1.335 1.303 1.252 1.202	14.44 14.53 14.61 14.72	r ² = .9915 b =- 36.0924 k"= -0.1570	15.17	26700	3.345x10 ⁻²
240	.0200 .0182 .0154 .0125	119.22 116.49 112.26 108.01	1.312 1.282 1.235 1.188	13.57 13.64 13.72 13.81	r^2 .9971 b =- 31.4553 k''= -0.1560	14.20	23600	3.486x10 ⁻²
<u></u>	r ² =0.999	7	L	u la		b =4.	5400x10	-5
	a =2.3904	4x10 ⁻²				${}_{\rm H}^{\rm k_{50}^{\rm s}} = 7.$	425x10	4

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Hydrolysis of Dextran Acid and Ultrasound C(HC1)=2.0 M

T=50⁰C Frequency=17kHz

C(Dextran)=.04gm/m1Power $=200w/cm^2$

T(min)	C(gm/ml)	ī(s)	n r	ln(n _r)/C	Curve coefficients	[n]	M _w	M _w ^{−1/3}
0							73100	2.392×10^{-2}
30	.0200 .0182 .0154 .0125	140.74 135.64 128.04 20.40	1.549 1.493 1.409 1.325	21.87 22.00 22.26 22.50	r ² = .9986 b =- 85.2230 k" -0.1530	23.57	61200	2.538x10 ⁻²
60	.0200 .0182 .0154 .0125	135.66 131.15 124.32 117.51	1.493 1.443 1.368 1.293	20.03 20.15 20.35 20.56	r ² = .9998 b =- 70.8633 k"= -0.1540	21.44	51200	2.693x10 ⁻²
90	.0200 .0182 .0154 .0125	131.61 127.53 121.41 115.18	1.448 1.403 1.336 1.267	18.52 18.62 18.81 18.96	r ² = .9970 b =- 59.6569 k"= -0.1540	19.17	43700	2.839x10 ⁻²
120	.0200 .0182 .0154 .0125	127.84 124.17 118.64 113.02	1.407 1.366 1.305 1.244	17.06 17.15 17.31 17.44	r ² = .9975 b =- 51.3177 k"= -0.1570	18.09	37200	2.995x10 ⁻²
150	.0200 .0182 .0154 .0125	124.79 121.44 116.36 111.25	1.373 1.336 1.280 1.224	15.85 15.93 16.05 16.18	r ² = .9999 b =- 43.8751 k''= -0.1570	16.73	32100	3.146x10 ⁻²
180	.0200 .0182 .0154 .0125	122.14 119.06 114.37 109.72	1.344 1.310 1.257 1.207	14.78 14.84 14.93 15.07	r ² = .9893 b =- 38.1946 k"= -0.1580	15.54	27900	3.297x10 ⁻²
210	.0200 .0182 .0154 .0125	119.51 116.74 112.44 108.18	1.315 1.285 1.237 1.119	13.69 13.76 13.82 13.94	r^2 = .9839 b =- 32.0040 k''= -0.1560	14.33	14000	3.467x10 ⁻²
240	.0200 .0182 .0154 .0125	117.97 115.33 111.30 107.27	1.297 1.269 1.225 1.180	13.04 13.09 13.16 13.26	r^2 .9946 b =- 28.9590 k''= -0.1560	13.62	21800	3.580x10 ⁻²
•	r ² =0.999	5	+			b =5.	0300x10	-5
	a =2.390	5x10 ⁻²				${}_{\rm H}^{\rm k}{}_{50}^{\rm s} = 8.1$	226x1 ⁻⁴	

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Hydrolysis of Dextran Acid Only C(HC1)=3.0 M

т=50⁰с

C(Dextran)=.04gm/ml

T(min)	C(gm/m1)	īt(s)	nr	ln(n _r)/C	Curve coefficients	[n]	M _w	M
0							73100	2.92×10^{-2}
15	.0200 .0182 .0154 .0125	137.67 132.92 125.87 118.65	1.515 1.463 1.385 1.306	20.76 20.89 21.14 21.33	r ² = .9961 b =- 77.4094 k"= -0.1560	22.30	64000	2.500x10 ⁻²
30	.0200 .0182 .0154 .0125	133.62 129.32 122.80 116.36	1.470 1.423 1.351 1.280	19.27 19.38 19.54 19.77	r ² = .9938 b =- 65.9093 k"= -0.1560	257	54800	2.633x10 ⁻²
45	.0200 .0182 .0154 .0125	131.00 127.05 120.94 114.83	1.441 1.398 1.331 1.264	18.28 18.40 18.55 18.71	r ² = .9983 b =- 56.6814 k''= -0.1500	19.42	49000	2.733x10 ⁻²
60	.0200 .0182 .0154 .0125	128.43 124.75 119.05 113.37	1.413 1.373 1.310 1.247	17.29 17.40 17.53 17.68	r ² = .9980 b =- 51.1786 k''= -0.1520	18.32	43800	2.837x10 ⁻²
75	.0200 .0182 .0154 .0125	125.97 122.51 117.20 111.92	1.386 1.348 1.290 1.232	16.32 16.40 16.51 16.65	r^{2} = .9982 b =- 43.5273 k''= -0.1470	17.18	38700	2.956x10 ⁻²
90	.0200 .0182 .0154 .0125	123.50 120.33 115.41 110.49	1.359 1.324 1.270 1.216	15.33 15.42 15.51 15.63	r^2 .9948 b =- 38.9288 k''= -0.1500	16.11	34200	3.081x10 ⁻²
105	.0200 .0182 .0154 .0125	121.69 118.66 114.05 109.45	1.339 1.306 1.255 1.204	14.59 14.65 14.74 14.87	r ² = .9930 b =- 36.9503 k"= -0.1570	15.32	31000	3.183x10 ⁻²
120	.0200 .0182 .0154 .0125	119.87 117.09 112.75 108.39	1.319 1.288 1.241 1.193	13.84 13.92 14.00 14.09	r ² = .9929 b =- 32.5296 k"= -0.1550	14.50	27900	3.297x10 ⁻²
	r ² =0.9995	5				b =7.	5378x10	-5

 $a = 2.3934 \times 10^{-2}$

 $k_{50}^{c} = 1.233 \times 10^{-3}$

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Hydrolysis of Dextran Acid and Ultrasound C(HC1)=3.0 M

T=50[°]C Frequency=25kHz

C(Dextran)=.04gm/m1Power = $.4w/cm^2$

T(min)	C(gm/m1)	Ē(s)	n r	$ln(n_r)/C$	Curve coefficients	[n]	M w	M
0							73100	2.392×10^{-2}
15	.0200 .0182 .054 .0125	136.74 132.15 125.11 118.16	1.505 1.454 1.377 1.300	20.43 20.57 20.76 21.00	r^2 .9983 b =- 75.1526 k''= -0.1560	21.93	62000	2.527×10 ⁻²
30	.0200 .0182 .0154 .0125	133.89 129.57 123.01 116.52	1.473 1.426 1.354 1.282	19.37 19.49 19.66 19.88	r^{2} = .9976 b =- 67.3313 k''= -0.1570	20.71	55500	2.622×10 ⁻²
45	.0200 .0182 .0154 .0125	130.36 126.50 120.49 114.49	1.434 1.392 1.326 1.260	18.04 18.17 18.31 18.48	r^{2} = .9963 b =- 57.4078 k''= -0.1560	19.20	48000	2.752×10 ⁻²
60	.0200 .0182 .0154 .0125	132.01 127.56 120.87 114.42	1.453 1.404 1.330 1.259	18.67 18.63 18.52 18.43	r^{2} = .9935 b =- 33.0087 k''= -0.1020	18.02	42500	2.866x10 ⁻²
75	.0200 .0182 .0154 .0125	1278 124.69 118.63 112.70	1.417 1.372 1.305 1.240	17.43 17.38 17.30 17.22	r^{2} = .9999 b =- 28.0624 k''= -0.0990	16.87	37400	2.990×10 ⁻²
90	.0200 .0182 .0154 .0125	122.74 119.60 114.88 110.05	1.351 1.316 1.264 1.211	15.03 15.09 15.22 15.31	r ² = .9933 b =- 38.3414 k"= -0.1540	15.80	33000	3.118x10 ⁻²
105	.0200 .0182 .0154 .0125	120.99 118.06 113.59 109.03	1.331 1.299 1.250 1.200	14.31 14.38 14.48 14.57	r ² = .9978 b =- 34.6395 k"= -0.1540	15.01	29900	3.222x10 ⁻²
120	.0200 .0182 .0154 .0125	118.96 116.19 112.06 107.84	1.309 1.278 1.233 1.187	13.46 13.50 13.60 13.69	r ² = .9954 b =- 31.4166 k"= -0.1580	14.08	26400	3.358×10 ⁻²
<u>*************************************</u>	r ² =0.999 a =2.393	4 3x10 ⁻⁵	L	L		b =7 $L^{k_{50}^{S}} = 1$.9767x10 .305x10	-5 3

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Hydrolysis of Dextran Acid and Ultrasound C(HC1)=3.0 M

T=50[°]C Frequency=17kHz

C(Dextran)=.04gm/m1power =200w/cm²

T(min)	C(gm/m1)	ī(s)	n r	<u>l</u> n(n _r)/C	Curve coefficients	[n]	M. w	
0							73100	2.392×10^{-2}
15	.0200 .0128 .0154 .0125	136.50 131.39 124.94 118.03	1.502 1.452 1.375 1.299	20.35 20.48 20.67 20.91	r^{2} = .9983 b =- 75.1526 k''= -0.1580	21.84	61500	2.533×10 ⁻²
30	.0200 .0182 .0154 .0125	132.60 128.40 122.13 115.76	1.459 1.413 1.344 1.274	18.89 18.99 19.19 19.36	r^{2} = .9980 b =- 63.7375 k''= -0.1570	20.16	52700	2.667x10 ⁻²
45	.0200 .0182 .0154 .0125	129.38 125.63 119.76 113.97	1.425 1.382 1.318 1.254	17.70 17.79 17.97 18.11	$r^{2}=9932$ b =- 54.0073 k"= -0.1530	18.77	46000	2.791×10 ⁻²
60	.0200 .0182 .0154 .0125	126.79 132.16 117.80 112.37	1.395 1.355 1.296 1.236	16.65 16.70 16.85 16.98	r^2 .9919 b =- 45.4285 k''= -0.1480	17.55	10100	2.914x10 ⁻²
75	.0200 .0182 .0154 .0125	124,03 120.74 115.77 110.79	1.365 1.329 1.274 1.219	15.55 15.61 15.72 15.85	r^2 = .9967 b =- 40.1345 k''= -0.1500	16.35	35200	3.051x10 ⁻²
90	.0200 .0182 .0154 .0125	121.67 118.67 114.07 109.45	1.339 1.306 1.255 1.204	14.59 14.66 14.76 14.86	r ² = .9994 b =- 35.8838 k''= -0.1530	15.31	31000	3.183x10 ⁻²
105	.0200 .0182 .0154 .0125	119.35 116.58 112.32 108.07	1.313 1.283 1.236 1.189	13.63 13.68 12.75 13.86	r^2 .9902 b =- 30.2033 k''= -0.1490	14.23	27000	3.333x10 ⁻⁵
120	.0200 .0182 .0154 .0125	117.77 115.18 111.18 107.14	1.296 1.267 1.223 1.179	12.96 13.02 13.09 13.17	r^2 .9977 b =- 27.54410 k''= -0.1510	13.52	24400	3.448x10 ⁻²
	r ² =0.999	6				b =8.	7956x10	-5
	a =2.395	8x10 ⁻²				$H^{k_{50}^{s}} = 1.$	438x10 ⁻³	3

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Hydrolysis of Dextran Acid Only C(HCl)=4.0 M

т=50⁰С

C(Dextran)=.04gm/ml

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T(min)	C(gm/n1)	ī(s)	nr	ln(n _r)/C	Curve coefficients	[n]	м _w	w ^{−1/3}
0							73100	2.392x10 ⁻²
10	.0200 .0182 .0154 .0125	145.60 139.99 131.62 123.16	1.602 1.540 1.448 1.355	23.57 23.74 24.05 24.32	r ² = .9987 b =-101.2134 k''= -0.1550	25.59	62600	2.518x10 ⁻²
20	.0200 .0182 .0154 .0125	139.75 134.89 127.33 119.87	1.538 1.484 1.401 1.319	21.52 21.70 21.90 22.15	r ² = .9970 b =- 82.28610 k''= -0.1530	23.18	52000	2.679x10 ⁻²
30	.0200 .0182 .0154 .0125	136.80 132.08 125.14 118.15	1.505 1.453 1.377 1.300	20.45 20.54 20.77 20.99	r^2 .9946 b =- 73.6610 k" = -0.1540	21.90	46800	2.775x10 ⁻²
40	.0200 .0182 .0154 .0125	132.92 128.73 122.40 115.94	1.463 1.416 1.347 1.276	19.01 19.13 19.33 19.48	r ² = .9949 b =- 63.3975 k''= -0.1540	20.29	40500	2.912x10 ⁻²
50	.0200 .0182 .0154 .0125	129.60 152.82 119.93 114.05	1.426 1.384 1.320 1.255	17.75 17.87 18.01 18.17	r ² = .9977 b =- 55.0893 k''= -0.1550	18.86	35300	3.084x10 ⁻²
60	.0200 .0182 .0154 .0125	127.04 123.44 118.05 112.55	1.398 1.358 1.299 1.238	16.75 16.83 16.98 17.10	r^2 .9972 b =- 47.4071 k"= -0.1510	17.70	31400	3.170x10 ⁻²
70	.0200 .0182 .0154 .0125	124.22 120.96 115.92 110.93	1.367 1.331 1.276 1.221	15.63 15.71 15.80 15.95	r^2 .9906 b =- 41.5874 k''= -0.1540	16.46	27400	3.317x10 ⁻²
80	.0200 .0182 .0154 .0125	123.31 119.27 114.55 109.82	1.346 1.312 1.260 1.208	14.85 14.94 15.03 15.14	r ² = .9943 b =- 37.6845 k"= -0.1550	15.61	24800	3.429x10 ⁻²
\$	r ² =0.999	1				b =1	.2995x10	-4 .
	a =2.396	$x 10^{-3}$				$k_{50}^{c} = 2$.125x10	.3

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Hydrolusis of Dextran Acid and Ultrasound C(HCl)=4.0 M

T=50⁰C Frequency=25kHz

C(Dextran)=.04gm/m1Power =.4w/cm²

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T(min)	C(gm/m1)	ī(s)	n r	$\ln(n_r)/C$	Curve coefficients	[n]	M _w	<u>M</u> _w ^{−1/3}
0							73100	2.392×10^{-2}
10	.0200 .0182 .0154 .0125	145.07 139.57 131.14 122.89	1.596 1.536 1.443 1.352	23.38 23.57 23.81 24.14	r^{2} = .9967 b =- 99.6831 k''= -0.1550	25.37	61600	2.532x10 ⁻²
20	.0200 .0182 .0154 .0125	140.58 135.58 128.02 120.31	1.547 1.492 1.409 1.324	21.81 21.98 22.25 22.44	r^{2} = .9920 b =- 84.8906 k"= -0.1530	23.52	53500	2.654x10 ⁻²
30	.0200 .0182 .0154 .0125	136.55 131.87 124.98 118.00	1.503 1.451 1.375 1.298	20.36 20.45 20.69 20.89	$r^{2}=$.9942 b =- 72.7645 k''= -0.1530	21.80	46400	2.783x10 ⁻²
40	.0200 .0182 .0154 .0125	132.98 128.79 122.44 115.97	1.463 1.417 1.347 1.276	19.03 19.16 19.36 19.50	r^2 = .9911 b =- 63.2275 k''= -0.1530	20.31	40600	2.910x10 ⁻²
50	.0200 .0182 .0154 .0125	129.67 125.87 119.98 114.08	1.427 1.385 1.320 1.255	17.77 17.90 18.04 18.19	r^2 = .9945 b =- 54,9192 k''= -0.1540	18.88	35400	3.045x10 ⁻²
60	.0200 .0182 .0154 .0125	126.75 123.24 117.81 112.39	1.395 1.356 1.296 1.237	16.63 16.74 16.85 16.99	r^2 = .9947 b =- 46.7501 k''= -0.1510	17.58	31000	3.183x10 ⁻²
70	.0200 .0182 .0154 .0125	124.43 121.12 116.12 111.04	1.369 1.333 1.278 1.222	15.71 15.78 15.91 16.03	r ² .9992 b =- 43.1486 k"= -0.1570	16.56	27700	3.305×10 ⁻²
80	.0200 .0182 .0154 .0125	122.13 119.02 114.39 109.69	1.344 1.310 1.259 1.207	14.78 14.82 14.94 15.05	r^2 .9916 b =- 37.0894 k''= -0.1540	15.51	24500	3.443×10 ⁻²
	r ² =0.999	8		·····		b =1.	3072x10	-3
	a =2.393	5x10 ⁻²				$L_{50}^{k_{50}^{s}=2}$.	138x10 ⁻¹	3

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Hydrolysis of Dextran Acid and Ultrasound C(HC1)=4.0 M

T=50⁰C Frequency=17kHz

C(Dextran)=.04gm/m1 Power =200w/cm²

T(min)	C(gm/m1)	ī(s)	nr	ln(n _r)/C	Curve coefficients	[n]	M _w	$\overline{M}_{w}^{-1/3}$
0		1					73100	2.392×10^{-2}
10	.0200 .0182 .0154 .0125	145.92 140.35 131.75 123.38	1.606 1.544 1.450 1.358	23.68 23.88 24.11 24.46	r^{2} = .9940 b =-101.6539 k''= -0.1540	25.71	63200	2.511x10 ⁻²
20	.0200 .0182 .0154 .0125	140.14 135.08 127.60 120.05	1.542 1.486 1.404 1.321	21.66 21.78 22.04 22.27	r^{2} = .9975 b =- 82.9044 k''= -0.1530	23.31	52600	2.669x10 ⁻²
30	.0200 .0182 .0154 .0125	136.45 131.87 124.94 117.96	1.501 1.451 1.375 1.298	20.32 20.45 20.67 20.86	$r^{2}=$.9985 b =- 72.6331 k''= -0.1530	21.78	46300	2.785x10 ⁻²
40	.0200 .0182 .0159 .0125	132.46 128.31 122.20 115.69	1.458 1.412 1.343 1.273	18.84 18.95 19.13 19.31	r^2 .9999 b =- 62.8719 k''= -0.1560	20.10	39800	2.92×10 ⁻²
50	.0200 .0182 .0154 .0125	129.20 125.38 119.66 113.80	1.422 1.380 1.317 1.252	17.59 17.68 17.86 17.99	r^2 .9947 b =- 54.5019 k''= -0.1560	18.68	34700	3.066x10 ⁻²
60	.0200 .0182 .0154 .0125	126 122.59 117.28 111.99	1.387 1.349 1.290 1.232	16.35 16.45 16.56 16.71	r ² = .9963 b =- 46.9202 k''= -0.1570	17.29	30000	3.218x10 ⁻²
70	.0200 .0182 .0154 .0125	123.91 120.71 115.73 110.75	1.363 1.328 1.273 1.219	15.50 15.60 15.70 15.82	r ² = .9941 b =- 41.5952 k''= -0.1560	16.34	27000	3.333x10 ⁻²
80	.0200 .0182 .0154 .0125	122.02 118.89 114.36 109.63	1.343 1.309 1.258 1.206	14.73 14.80 14.92 15.01	r^2 .9952 b =- 37.8236 k''= -0.1580	15.49	24400	3.448x10 ⁻²
	r ² =0.998	9	//	la en ancara de entre e reserva en reserva	k	b =1.	3458x10	-4
	a =2.389	3×10^{-4}				$H^{k_{50}^{s}} = 2$.	201x10 ⁻³	3

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Hydrolysis of Dextran Acid Only C(HC1)=0.5 M

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т=60 ⁰ С				U(HUI)=(J.5 M		C(Dextra	an)=.04gm/m1
T(min)	C(gm/m1)	īt(s)	n _r	$ln(n_r)/C$	Curve coefficients	[n]	M _w	$\overline{M}_{w}^{-1/3}$
0							73100	2.392x10 ⁻²
30	.0200 .0182 .0154 .0125	141.73 136.68 128.78 121.01	1.560 1.504 1.417 1.332	22.22 22.42 22.63 22.91	r^2 .9959 b =- 89.7596 k''= -0.155	24.03	65300	2.483x10 ⁻²
60	.0200 .0182 .0154 .0125	138.20 133.36 126.18 118.96	1.521 1.467 1.388 1.309	20.96 21.07 21.31 21.54	r^{2} = .9974 b =- 78.6460 k''= -0.1550	22.25	57700	2.588x10 ⁻²
90	.0200 .0182 .0154 .0125	135.65 131.19 124.29 117.54	1.493 1.444 1.368 1.293	20.03 20.17 20.33 20.58	r^{2} = .9931 b =- 71.6207 k''= -0.1560	21.46	52600	2.669x10 ⁻²
120	.0200 .0182 .0154 .0125	132.79 128.68 122.28 115.89	1.461 1.416 1.346 1.275	18.96 19.11 19.27 19.45	r^{2} = .9952 b =- 63.9849 k"= -0.1560	20.25	47100	2.770×10 ⁻²
150	.0200 .0182 .0154 .0125	130.72 126.73 120.70 114.61	1.438 1.394 1.328 1.261	18.18 18.27 18.43 18.56	r^2 .9975 b =- 51.3177 k''= -0.1390	19.21	42600	2.864x10 ⁻²
180	.0200 .0182 .0154 .0125	128.27 124.53 118.84 113.22	1.411 1.370 1.308 1.246	17.23 17.31 17.42 17.58	r^2 .9941 b =- 46.0159 k''= -0.1400	18.15	18200	2.969x10 ⁻²
240	.0200 .0182 .0154 .0125	124.66 121.34 116.27 111.20	1.372 1.335 1.279 1.224	15.80 15.88 16.00 16.14	r^{2} = .9993 b =- 45.1194 k''= -0.1620	16.70	32600	3.130x10 ⁻²
360	.0200 .0182 .0154 .0125	118.35 115.68 111.59 107.51	1.302 1.273 1.228 1.183	13.21 13.26 13.33 13.44	r^{2} = .9902 b =- 30.2033 k''= -0.1580	13.81	22700	3.532x10 ⁻²
	r ² =0.9994	+				b =3.	1505x10	-5

a =2.3913x10⁻²

 $k_{60}^{c} = 5.152 \times 10^{-4}$

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Hydrolusis of Dextran Acid and Ultrasound C(HC1)=0.5 M

T=60⁰C

Frequency=25kHz

C(Dextran) = .04gm/mlPower = $.4w/cm^2$

<u>м</u> -1/3 [n] м

T(min)	C(gm/ml)	ī(s)	n r	ln(n _r)/C	Curve coefficients	[n]	м _w	M
0							73100	2.392×10^{-2}
30	.0200 .0182 .0154 .0125	140.99 135.88 128.28 120.54	1.551 1.495 1.412 1.326	21.96 22.10 22.38 22.60	r^{2} = .9967 b =- 86.9928 k''= -0.1550	23.70	63600	2.505×10 ⁻²
60	.0200 .0182 .0154 .0125	137.39 132.60 125.57 118.49	1.512 1.459 1.382 1.304	20.66 20.76 21.00 21.22	r ² = .9960 b =- 76.3274 k''= -0.1550	22.17	5600	2.614x10 ⁻²
90	.0200 .0182 .0154 .0125	133.85 129.48 123.01 116.47	1.473 1.425 1.354 1.282	19.36 19.45 19.66 19.85	r ² = .9965 b =- 66.7440 k"= -0.1560	20.68	49000	2.733x10 ⁻²
120	.0200 .0182 .0154 .0125	130.94 127.03 120.90 114.83	1.441 1.398 1.330 1.264	18.26 18.40 18.53 18.71	r^{2} = .9929 b =- 58.1343 k''= -0.1540	19.44	43600	2.841x10 ⁻²
150	.0200 .0182 .0154 .0125	128.41 124.69 119.01 113.29	1.413 1.372 1.310 1.247	17.28 17.38 17.51 17.63	r^{2} = .9965 b =- 46.3714 k''= -0.1400	18.22	38500	2.962x10 ⁻²
180	.0200 .0182 .0154 .0125	125.96 122.49 117.23 111.87	1.386 1.348 1.290 1.231	16.32 16.40 16.53 16.62	r^2 .9917 b =- 40.4900 k" = -0.1380	17.14	34300	3.078x10 ⁻²
240	.0200 .0182 .0154 .0125	121.25 118.30 113.80 109.20	1.334 1.302 1.252 1.202	14.42 14.49 14.69 14.69	r^2 = .9968 b =- 36.2315 k''= -0.1580	15.15	27100	3.329x10 ⁻²
360	.0200 .0182 .0154 .0125	115.80 113.36 109.71 105.99	1.274 1.247 1.207 1.166	12.12 12.14 12.23 12.30	r^2 = .9831 b =- 25.1874 k''= -0.1580	12.61	19100	3.741x10 ⁻²
1	r ² =0.999	3				b =3.	.7917	
	a =2.392	4				$L^{k_{60}^{s}} = 6$.	201x10 ⁻⁴	4

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Hydrolusis of Dextran Acid and Ultrasound C(HC1)=0.5 M

T=60⁰C Frequency=17kHz

C(Dextran)=.04gm/m1 Power =200w/cm²

	·)					t	I OWCL	2000,000	
T(min)	C(gm/ml)	ī(s)	n _r	ln(n _r)/C	Curve coefficients	[n]	M w		
0							73100	2.392×10^{-2}	
30	.0200 .0182 .0154 .0125	141.25 163.12 128.35 120.72	1.554 1.498 1.412 1.328	22.05 22.20 22.42 22.71	r^{2} = .9968 b =- 87.2247 k''= -0.1540	23.79	64100	2.499x10 ⁻²	
30	.0200 .0182 .0154 .0125	137.24 132.69 125.52 118.45	1.510 1.460 1.381 1.303	20.61 20.80 20.97 21.20	r ² = .9916 b =- 76.0955 k"= -0.1550	22.15	55900	2.61510 ⁻²	
90	.0200 .0182 .0154 .0125	133.86 129.48 123.00 116.47	1.473 1.425 1.353 1.282	19.36 19.45 19.65 19.85	r^2 .9967 b =- 66.3962 k"= -0.1550	20.67	49000	2.733×10 ⁻²	
120	.0200 .0182 .0154 .0125	130.70 126.74 120.74 114.67	1.438 1.395 1.329 1.262	18.17 18.27 18.45 18.60	r^{2} = .9980 b =- 58.0648 k"= -0.1550	19.33	43100	2.852x10 ⁻²	
150	.0200 .0182 .0154 .0125	128.11 124.45 118.78 113.13	1.410 1.369 1.307 1.245	17.17 17.27 17.39 17.52	r^{2} = .9977 b =- 46.0236 k''= -0.1400	18.10	38000	2.974x10 ⁻²	
180	.0200 .0182 .0154 .0125	125.90 122.44 117.19 111.84	1.385 1.347 1.290 1.231	16.30 16.38 16.51 16.60	r^2 .9917 b =- 40.4900 k''= -0.1380	17.12	34200	3.081x10 ⁻²	
240	.0200 .0182 .0154 .0125	121.62 118.61 114.00 109.36	1.338 1.305 1.254 1.203	14.57 14.63 14.72 14.81	$r^{2}_{=}$.9998 b =- 31.9731 k''= -0.1380	15.21	27300	3.321x10 ⁻²	
360	.0200 .0182 .0154 .0125	115.56 113.18 109.55 105.85	1.272 1.245 1.205 1.165	12.01 12.06 12.13 12.20	r^2 .9992 b =- 25.2261 k''= -0.1610	12.52	18800	3.761x10 ⁻²	
	r ² =0.999	8		le 1999 - 29 - 20 - 20 - 20 - 20 - 20 - 20 -	$b = 3.8343 \times 10^{-5}$				
	a =2.390	2x10 ⁻²				$H^{k_{60}^{s}} = 6$.271x10 ⁻⁴	4	

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Hydrolysis of Dextran Acid Only C(HC1)=1.0 M

T=60 ⁻ C	

C(Dextran)=.04gm/m1

T(min)	C(gm/ml)	t(s)	n _r	ln(n _r)/C	coefficients	[n]	M W	$\overline{M}_{w}^{-1/3}$
0							73100	2.392×10^{-2}
30	.0200 .0182 .0154 .0125	142.53 137.06 128.90 120.88	1.568 1.508 1.418 1.330	22.50 22.58 22.70 22.82	r^{2} = .9998 b =- 42.6308 k''= -0.0782	23.35	58300	2.5792x10 ⁻²
60	.0200 .0182 .0154 .0125	135.87 131.18 124.16 117.22	1.495 1.443 1.366 1.290	20.11 20.17 20.26 20.36	r ² = .9998 b =- 33.2171 k''= -0.0770	20.78	47000	2.771x10 ⁻²
90	.0200 .0182 .0154 .0125	130.96 126.84 120.64 114.49	1.441 1.396 1.327 1.260	18.27 18.32 18.40 18.48	r^{2} = .9999 b =- 28.0624 k''= -0.0791	18.82	39100	2.946x10 ⁻²
120	.0200 .0182 .0154 .0125	126.22 122.64 117.22 111.83	1.389 1.349 1.290 1.230	16.43 16.57 16.53 16.59	r ² = .9998 b =- 21.3154 k"= -0.0750	16.87	32000	3.150x10 ⁻²
150	.0200 .0182 .0154 .0125	122.59 119.40 114.58 109.76	1.349 1.314 1.261 1.208	14.96 15.00 15.05 15.10	r^2 .9974 b =- 18.4790 k''= -0.0787	15.33	26800	3.342x10 ⁻²
180	.0200 .0182 .0154 .0125	119.31 116.48 112.19 107.88	1.313 1.282 1.234 1.187	13.61 13.64 13.68 13.72	r ² = .9986 b =- 14.5684 k''= -0.0754	13.91	22400	3.548x10 ⁻²
210	.0200 .0182 .0154 .0125	117.13 114.54 110.59 106.63	1.289 1.260 1.217 1.173	12.69 12.71 12.75 12.79	r^2 .9983 b =- 13.4941 k''= -0.0804	12.95	19600	3.709x10 ⁻²
240	.0200 .0182 .0154 .0125	114.86 112.50 108.92 105.31	1.264 1.238 1.199 1.159	11.71 11.73 11.76 11.79	r^2 = .9998 b =- 10.6577 k''= -0.0750	11.93	16800	3.904x10 ⁻²
	r ² =0.9997	7		b =6.3	267x10	5		
	a =2.3898	3×10^{-2}	$k_{c}^{c} = 1.0$	35×10^{-3}				

 $k_{60}^{c} = 1.035 \times 10^{-3}$

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Hydrolysis of Dextran Acid and Ultrasound C(HCl)=1.0 M

T=60⁰C Frequency=25kHz

C(Dextran)=.04gm/ml Power =.4w/cm²

T(min)	C(gm/m1)	ī(s)	n r	$\ln(n_r)/C$	Curve coefficients	[n]	M w		
0							73100	2.392x10 ⁻²	
30	.0200 .0182 .0154 .0125	140.27 135.07 127.30 119.64	1.543 1.486 1.401 1.316	21.70 21.77 21.88 22.00	r ² = .9998 b =- 39.9644 k''= -0.0790	22.49	54400	2.639x10 ⁻²	
60	.0200 .0182 .0154 .0125	132.57 128.27 121.80 115.39	1.459 1.411 1.340 1.270	18.88 18.98 19.02 19.10	r ² = .9990 b =- 29.6545 k''= -0.0782	19.47	41700	2.884x10 ⁻²	
90	.0200 .0182 .0154 .0125	126.68 123.13 117.62 112.14	1.395 1.355 1.294 1.234	16.64 16.69 16.75 16.82	r^2 = .9982 b =- 23.6340 k''= -0.0807	17.10	32800	3.124x10 ⁻²	
120	.0200 .0182 .0154 .0125	122.35 119.19 114.41 109.63	1.346 1.312 1.259 1.206	14.87 14.90 14.95 15.00	r^2 = .9999 b = - 17.4047 k''= -0.0752	15.23	26500	3.354x10 ⁻²	
150	.0200 .0182 .0154 .0125	118.40 115.67 111.52 107	1.303 1.273 1.227 1.181	13.23 13.25 13.29 13.33	r^2 = .9983 b =- 13.4941 k''= -0.0741	13.51	21200	3.613x10 ⁻²	
180	.0200 .0182 .0154 .0125	115.59 113.16 109.46 105.74	1.272 1.245 1.204 1.163	12.03 12.05 12.08 12.11	r^{2} = .9998 b =- 10.6577 k''= -0.0711	12.26	17700	3.837x10 ⁻²	
210	.0200 .0182 .0154 .0125	112.88 110.74 107.46 104.16	1.242 1.218 1.182 1.146	10.84 10.86 10.88 10.91	r^2 = .9938 b =- 9.0656 k''= -0.0746	11.03	14500	4.101x10 ⁻²	
240	.0200 .0182 .0154 .0125	110.98 109.03 106.05 103.04	1.221 1.200 1.167 1.134	9.99 10.00 10.03 10.05	r^{2} = .9888 b =- 8.3391 k''= -0.0809	10.15	12400	4.320x10 ⁻²	
	r ² =0.999	8	L	L		ь =8	.052x10	5	

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Hydrolysis of Dextran Acid and Ultrasound C(HC1)=1.0 M

T=60[°]C Frequency=60kHz

C(Dextran)=.04gm/ml Power =.4w/cm²

T(min)	C(gm/ml)	ī(s)	n r	$\ln(n_r)/C$	Curve coefficients	[n]	м _w	
0							73100	2.392x10 ⁻²
30	.0200 .0182 .0154 .0125	140.27 135.07 127.30 119.64	1.543 1.485 1.401 1.316	21.70 21.77 21.88 22.00	r ² = .9998 b =- 39.9644 k"= -0.0790	22.49	54500	2.639x10 ⁻²
60	.0200 .0182 .0154 .0125	132.77 128.44 121.94 115.50	1.461 1.413 1.342 1.271	18.95 19.01 19.09 19.18	r^{2} = .9994 b =- 30.3810 k''= -0.0790	19.55	42000	2.877x10 ⁻²
90	.0200 .0182 .0154 .0200	126.73 123 117.69 112.11	1.394 1.354 1.294 1.234	16.63 16.67 16.73 16.80	r^2 = .9993 b =- 22.5597 k''= -0.0770	17.08	32900	3.121x10 ⁻²
120	.0200 .0182 .0154 .0125	122.61 119.42 114.60 109.77	1.349 1314 1.261 1.203	14.97 15.01 15.06 15.11	r^2 = .9973 b =- 18.4790 k''= -0.0790	15.34	27000	3.333x10 ⁻²
150	.0200 .0182 .0154 .0125	118.38 115.65 111.51 107.35	1.303 1.273 ,1.227 1.181	13.22 13.24 13.28 13.32	r ² = .9983 b =- 13.4941 k''= -0.0742	13.50	21300	3.608x10 ⁻²
180	.0200 .0182 .0154 .0125	115.44 113.02 109.34 105.65	1.270 1.244 1.203 1.162	11.96 11.98 12.01 12.05	r^2 .9961 b =- 11.9020 k''= -0.0800	12.19	17600	3.844x10 ⁻²
210	.0200 .182 .0154 .0125	113.08 110.91 107.61 104.28	1.244 1.220 1.184 1.147	10.93 10.94 10.97 11.00	r^2 .9903 b =- 9.5834 k''= -0.0775	11.12	14800	4.073x10 ⁻²
240	.0200 .0182 .0154 .0125	110.83 108.89 105.94 102.96	1.219 1.198 1.166 1.133	9.92 9.94 9.69 9.98	r^{2} = .9894 b =- 7.8213 k''= -0.0770	10.08	12300	4.332x10 ⁻²
f	r ² =0.999	8				b =8.	044x10 ⁻	5
	a =2.391;	к10 ⁻²				$_{L}^{k_{60}^{s}} = 1.1$	316x10 ⁻¹	3

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Hydrolysis of Dextran Acid and Ultrasound C(HC1)=1.0 M

T=60⁰C Frequency=150kHz

C(Dextran)=.04gm/ml Power =.4w/cm²

T(min)	C(gm/m1)	ī(s)	n _r	ln(n _r)/C	Curve coefficients	[n]	м w	_M ^{−1/3}
0							73100	2.392×10^{-2}
30	.0200 .0182 .0154 .0125	140.56 135.32 127.50 119.80	1.547 1.489 1.403 1.318	21.81 21.87 21.99 22.10	r ² = .9986 b =- 39.2380 k''= -0.0769	22.49	54400	2.631x10 ⁻²
60	.0200 .0182 .0154 .0125	132.94 128.60 122.07 115.60	1.463 1.415 1.343 1.272	19.02 19.08 19.16 19.25	r ² = .9994 b =- 30.3810 k''= -0.0788	19.62	42300	2.87×10 ⁻²
90	.0200 .0182 .0154 .0125	126.99 123.32 117.78 112.26	1.397 1.357 1.296 1.235	16.73 16.77 16.84 16.90	r ² = .9985 b =- 22.9075 k''= -0.0775	17.19	33300	3.108×10 ⁻²
120	.0200 .0182 .0154 .0125	122.33 119.17 114.39 109.61	1.346 1.311 1.259 1.206	14.86 14.89 14.94 14.99	r^2 = .9999 b =- 17.4047 k''= -0.0753	15.22	26600	3.350x10 ⁻²
150	.0200 .0182 .0154 .0125	118.69 115.93 111.74 107.53	1.306 1.276 1.230 1.183	13.35 13.38 13.42 13.46	r ² = .9986 b =- 14.5684 k''= -0.0783	13.64	21700	3.585x10 ⁻²
180	.0200 .0182 .0154 .0125	115.61 113.18 109.48 105.75	1.272 1.245 1.205 1.164	12.03 12.06 12.09 12.12	r^2 = .9894 b =- 11.7320 k''= -0.0779	12.27	17800	3.830x10 ⁻²
210	.0200 .0182 .0154 .0125	112.82 110.70 107.36 104.06	1.240 1.216 1.179 1.136	10.83 10.85 10.87 10.91	r^2 = .9824 b =- 10.3099 k''= -0.0847	11.03	14500	4.101x10 ⁻²
240	.0200 .0182 .0154 .0125	111.02 109.07 106.09 103.07	1.222 1.200 1.167 1.134	10.01 10.03 10.05 10.07	r ² = .9894 b =- 7.8213 k''= -0.7560	10.17	12500	4.303×10 ⁻²
,	r ² =0.999	7			,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,	b =8.0	283x10	5

 $a = 2.388 \times 10^{-2}$

 $k_{60}^{s} = 1.313 \times 10^{-3}$
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Hydrolysis of Dextran Acid Only C(HC1)=1.5 M

T=60⁰C

C(Dextran)=.04gm/ml

T(min)	C(gm/m1)	Ē(s)	n _r	$\ln(n_r)/C$	Curve coefficients	[n]	м w	$\bar{M}_{w}^{-1/3}$
0							73100	2.392x10 ⁻²
15	.0200 .0154 .0154 .0125	139.93 127.94 127.49 119.94	1.240 1.485 1.403 1.320	21.58 21.72 21.98 22.20	r^{2} = .9983 b =- 83.8086 k''= -0.1550	23.25	59500	2.562x10 ⁻²
30	.0200 .0182 .0154 .0125	134.58 130.17 123.50 116.90	1.481 1.432 1.359 1.286	19.63 19.74 19.92 20.14	r^{2} = .9976 b =- 67.8491 k''= -0.1540	20.98	49100	2.732x10 ⁻²
45	.0200 .0182 .0154 .0125	129.38 125.61 119.75 113.92	1.424 1.382 1.318 1.254	17.66 17.78 17.91 18.08	r ² = .9965 b =- 54.7415 k"= -0.1560	18.76	39800	2.929x10 ⁻²
60	.0200 .0182 .0154 .0125	126.22 122.73 117.43 112.08	1.389 1.351 1.292 1.233	16.43 16.51 16.64 16.78	r ² = .9997 b =- 46.7115 k''= -0.1550	17.36	34500	3.071x10 ⁻²
90	.0200 .0182 .0154 .0125	120.27 117.41 113.03 108.62	1.323 1.292 1.244 1.195	14.01 14.07 14.17 14.26	r^2 .9991 b =- 33.5652 k''= -0.1557	14.68	25200	3.411x10 ⁻²
120	.0200 .0182 .0154 .0125	115.82 113.41 109.73 106.00	1.274 1.248 1.207 1.166	12.13 12.17 12.24 12.31	r^{2} = .9997 b =- 24.1518 k''= -0.1520	12.62	19000	3.750×10 ⁻²
150	.0200 .0182 .0154 .0125	112.65 110.56 107.37 104.12	1.240 1.217 1.181 1.146	10.74 10.77 10.82 10.88	r^{2} = .9978 b =- 18.6490 k''= -0.1511	11.12	15000	4.055x10 ⁻²
180	.0200 .0182 .0154 .0125	109.59 107.81 105.08 102.30	1.206 1.186 1.156 1.126	9.36 9.39 9.43 9.47	$r^{2}=$.9983 b =- 14.4947 k''= -0.1560	9.65	11500	4.429x10 ⁻²
	r ² =0.999	6				b =1.	.1207x10	-4
	a =2.399	8x10 ⁻²				k ^c ₆₀ =1.	833x10	3

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Hydrolysis of Dextran Acid and Ultrasound C(HC1)=1.5 M

T=60⁰C Frequency=25kHz

C(Dextran)=.04gm/ml Power =.4w/cm²

T(min)	C(gm/m1)	īt(s)	n r	ln(n _r)/C	Curve coefficients	[n]	M w	
0							73100	2.392x10 ⁻²
15	.0200 .0182 .0154 .0125	138.42 133.71 126.39 119.11	1.523 1.471 1.391 1.311	21.04 21.22 21.42 21.64	r^{2} = .9960 b =- 78.5532 k''= -0.1530	22.63	56600	2.604x10 ⁻²
30	.0200 .0182 .0154 .0125	132.30 128.14 121.82 115.59	1.456 1.410 1.340 1.272	18.78 18.88 19.03 19.24	r^{2} = .9944 b =- 60.7543 k"= -0.1520	19.99	44900	2.814x10 ⁻²
45	.0200 .0182 .0154 .0125	127.18 123.58 118.11 112.64	1.399 1.360 1.300 1.239	16.80 16.89 17.02 17.17	r^{2} = .9995 b =- 49.0301 k''= -0.1550	17.78	36000	3.028x10 ⁻²
60	.0200 .0182 .0154 .0125	123.09 119.91 115.14 110.24	1.354 1.319 1.267 1.213	15.17 15.23 15.36 15.45	r^{2} = .9933 b =- 38.3414 k''= -0.1510	15.94	29400	3.241x10 ⁻²
90	.0200 .0182 .0154 .0125	116.60 114.12 110.31 106.46	1.283 1.256 1.214 1.171	12.46 12.51 12.58 12.66	r^2 .9996 b = 26.4704 k''= -0.1570	12.99	20000	3.684x10 ⁻²
120	.0200 .0182 .0154 .0125	112.34 110.30 107.14 103.94	1.236 1.214 1.179 1.144	10.60 10.64 10.69 10.74	r^{2} = .9974 b =- 18.4790 k''= -0.1540	10.97	14600	4.089x10 ⁻²
150	.0200 .0182 .0154 .0125	109.06 107.33 104.67 101.98	1.200 1.181 1.152 1.122	9.12 9.14 9.17 9.22	r ² = .9851 b =- 13.1463 k"= -0.1490	9.38	10900	4.513x10 ⁻²
180	.0200 .0182 .0154 .0125	106.67 105.18 102.88 100.55	1.174 1.157 1.132 1.106	8.01 8.03 8.05 8.09	r^2 .9824 b =- 10.3099 k''= -0.1530	8.22	8500	4.900x10 ⁻²
1	r ² =0.999	8	,	*******	ni di kata da kata da kata da kata kata kata	b =1.	4029x10	-4
	a =2.398	3x10 ⁻²			1	$k_{60}^{s} = 2$.	2943x10	-3

Hydrolysis of Dextran Acid and Ultrasound C(HC1)=1.5 M

T=60⁰C Frequency=25kHz

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C(Dextran)=.04gm/m1 Power =1.93w/cm²

							A commence of the second se	A second s	
T(min)	C(gm/ml)	ī(s)	nr	ln(n _r)/C	Curve coefficients	[n]	M w	™_w ^{-1/3}	
0							73100	2.392x10 ⁻²	
15	.0200 .0182 .0154 .0125	138.49 133.74 126.43 119.14	1.524 1.472 1.391 1.311	21.06 21.23 21.44 21.66	r^{2} = .9979 b =- 79.0710 k''= -0.1540	22.65	56700	2.603x10 ⁻²	
30	.0200 .0182 .0154 .0125	132.90 128.68 122.27 115.94	1.462 1.416 1.345 1.272	19.00 19.11 19.27 19.48	r ² = .9970 b =- 63.4207 k"= -0.1550	20.26	46000	2.791x10 ⁻²	
45	.0200 .0182 .0154 .0125	127.45 123.81 118.36 112.78	1.402 1.362 1.302 1.241	16.91 16.99 17.16 17.27	r^2 .9911 b =- 49.3469 k"= -0.1540	17.90	36500	3.015x10 ⁻²	
60	.0200 .0182 .0154 .0125	123.34 120.14 115.28 110.41	1.357 1.322 1.268 1.215	15.27 15.34 15.44 15.57	$r^{2}=$.9974 b =- 39.6167 k''= -0.1540	16.06	29800	3.225x10 ⁻²	
90	.0200 .0182 .0154 .0125	117.20 114.64 110.75 106.81	1.290 1.261 1.219 1.175	12.72 12.76 12.84 12.92	r^2 .9983 b =- 26.9882 k''= -0.1530	13.26	20800	3.636x10 ⁻²	
120	.0200 .0182 .0154 .0125	112.67 110.58 107.40 104.13	1.240 1.217 1.182 1.146	10.75 10.78 10.85 10.89	r^2 .9861 b =- 19.3446 k''= -0.1560	11.14	15000	4.055x10 ⁻²	
150	.0200 .0182 .0154 .0125	109.15 107.41 104.74 102.04	1.201 1.182 1.153 1.123	9.16 9.18 9.22 9.27	r ² = .9931 b =- 14.7384 k"= -0.1650	9.45	11000	4.496x10 ⁻²	
180	.0200 .0182 .0154 .0125	106.77 105.29 102.97 100.61	1.175 1.159 1.133 1.107	8.06 8.09 8.11 8.14	r^2 .9782 b =- 10.1399 k''= -0.1480	8.27	8600	4.881x10 ⁻²	
$r^2 = 0.9998$ b $= 1.3931 \times 10^{-4}$									
$a = 2.3862 \times 10^{-2}$ $k_{10}^{5} = 2.2783 \times 10^{-3}$									

 $k_{60}^{s} = 2.2783 \times 10^{-3}$

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Hydrolysis	of	Dextran
Acid	0n.	1y
C(HC1)=	=2.0	ว ัท

r=60 ⁰ C				C(HC1)=2	C(Dextran)=.04gm/m1					
T(min)	C(gm/ml)	īt(s)	nr	ln(n _r)/C	Curve coefficients	[n]	M. W			
0							73100	2.392×10^{-2}		
10	.0200 .0182 .0154 .0125	140.16 135.14 127.55 120.08	1.542 1.487 1.403 1.321	21.66 21.80 22.01 22.29	r^{2} = .9961 b =- 83.3140 k''= -0.153	23.32	6000	2.554x10 ⁻²		
20	.0200 .0182 .0154 .0125	135.13 130.69 123.93 117.21	1.487 1.438 1.364 1.290	19.83 19.96 20.14 20.35	r^2 .9994 b =- 68.7534 k"= -0.1530	21.21	50200	2.711x10 ⁻²		
30	.0200 .0182 .0154 .0125	130.89 126.89 120.81 114.79	1.440 1.396 1.329 1.263	18.24 18.34 18.49 18.69	r ² = .9961 b =- 59.5100 k"= -0.1580	19.42	42500	2.866x10 ⁻²		
40	.0200 .0182 .0154 .0125	127.02 123.44 118.03 112.55	1.398 1.358 1.299 1.238	16.74 16.83 16.97 17.11	r ² = .9999 b =- 49.3778 k"= -0.1570	17.73	35800	3.034x10 ⁻²		
50	.0200 .0182 .0154 .0125	123.89 120.68 115.72 110.74	1.363 1.328 1.273 1.219	15.49 15.58 15.69 15.81	r^2 .9981 b =- 42.1130 k''= -0.1580	16.34	30700	3.194x10 ⁻²		
60	.0200 .0182 .0154 .0125	121.18 118.26 113.71 109.16	1.333 1.301 1.251 1.201	14.39 14.47 14.55 14.66	r^2 .9948 b =- 35.0182 k''= -0.1540	15.10	26500	3.355x10 ⁻²		
70	.0200 .0182 .0154 .0125	118.94 116.24 112.05 107.84	1.309 1.279 1.233 1.187	13.45 13.52 13.60 13.69	r^{2} .9971 b =- 31.4553 k''= -0.1590	14.08	23200	3.506x10 ⁻²		
80	.0200 .0182 .0154 .0125	117.03 114.49 110.60 106.72	1.288 1.260 1.217 1.174	12.64 12.69 12.75 12.85	r^2 .9898 b =- 27.3669 k''= -0.1580	13.18	20500	3.654x10 ⁻²		
	$r^2 = 0.9998$ b = 1.5867x10 ⁻⁴									

 $a = 2.3949 \times 10^{-2}$

 $k_{60}^{c} = 2.5948 \times 10^{-3}$

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Hydrolysis of Dextran Acid and Ultrasound C(HC1)=2.0 M

T=60 ⁰ C
Frequency=17kHz

C(Dextran)=.04gm/ml Power =200w/cm²

T(min)	C(gm/m1)	ī(s)	n _r	ln(n _r)/C	Curve coefficients	[n]	M _w	${{\rm M}_{\rm w}}^{-1/3}$	
0							73100	2.392×10^{-2}	
10	.0200 .0182 .0154 .0125	138.58 133.86 126.50 119.20	1.525 1.473 1.392 1.312	21.10 21.28 21.47 21.70	r^{2} = .9958 b =- 78.2054 k''= -0.1520	22.68	5700	2.598x10 ⁻²	
20	.0200 .0182 .0154 .0125	132.22 128.10 121.80 115.55	1.455 1.410 1.340 1.271	18.75 18.86 19.02 19.21	r^{2} = .9991 b =- 60.9321 k''= -0.1530	19.97	44800	2.816x10 ⁻²	
30	.0200 .0182 .0154 .0125	127.14 123.56 118.09 112.63	1.399 1.360 1.299 1.239	16.79 16.88 17.01 17.17	r^2 .9986 b =- 50.2744 k''= -0.1590	17.79	36000	3.028x10 ⁻²	
40	.0200 .0182 .0154 .0125	123.22 120.04 115.19 110.35	1.356 1.321 1.267 1.214	15.22 15.29 15.39 15.53	r^2 = .9951 b =- 40.8610 k''= -0.1590	16.03	19600	3.233x10 ⁻²	
50	.0200 .0182 .0154 .0125	119.69 116.93 112.62 108.29	1.317 1.287 1.239 1.192	13.77 13.85 13.93 14.02	r ² = .9929 b =- 32.5296 k''= -0.1560	14.43	24300	3.453x10 ⁻²	
60	.0200 .0182 .0154 .0125	116.63 114.18 110.35 106.49	1.283 1.256 1.214 1.172	12.47 12.54 12.61 12.68	r^2 = .9994 b =- 27.3746 k''= -0.1610	13.03	20000	3.684x10 ⁻²	
70	.0200 .0182 .0154 .0125	114.75 112.45 108.95 105.36	1.263 1.237 1.199 1.159	11.66 11.70 11.78 11.88	r^2 .9897 b =- 23.2553 k''= -0.1580	12.13	17500	3.852x10 ⁻²	
80	.0200 .0182 .0154 .0125	112.43 110.33 107.19 103.99	1.237 1.214 1.179 1.144	10.64 10.66 10.72 10.78	r^2 .9903 b =- 19.1669 k''= -0.1580	11.02	14600	4.089x10 ⁻²	
,	r ² =0.999	6	<u></u>		<u>+ </u>	b =2.1	185x10	4	
	a =0.023	9x10 ⁻²			$H^{k_{60}^{s}=3.465\times10^{-3}}$				

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Hydrolysis of Dextran Acid Only C(HCl)=3.0 M

Т=60 ⁰ С

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C(Dextran)=.04gm/m1

T(min)	C(gm/ml)	t(s)	nr	$\ln(n_r)/C$	Curve coefficients	[n]	M w	_M ^{−1/3}
0							73100	2.392x10 ⁻²
10	.0200 .0182 .0154 .0125	132.08 127.99 121.71 115.48	1.453 1.408 1.339 1.271	18.69 18.81 18.97 19.16	r^{2} = .9992 b =- 62.0063 k''= -0.1560	19.93	51600	2.686x10 ⁻²
20	.0200 .0182 .0154 .0125	124.92 121.51 116.45 111.32	1.375 1.337 1.281 1.225	15.91 15.96 16.10 16.23	r^{2} = .9930 b =- 43.8365 k''= -0.1560	16.77	37000	3.001x10 ⁻²
30	.0200 .0182 .0154 .0125	120.00 117.20 112.84 108.46	1.320 1.290 1.242 1.193	13.90 13.97 14.05 14.15	r^{2} = .9975 b =- 32.6996 k''= -0.1540	14.56	28200	3.285x10 ⁻²
40	.0200 .0182 .0154 .0125	116.84 114.72 110.36 106.45	1.286 1.257 1.214 1.171	12.56 12.58 12.61 12.65	r ² = .9961 b =- 11.9020 k" -0.0730	12.80	22000	3.569x10 ⁻²
50	.0200 .0182 .0154 .0125	113.35 111.15 107.80 104.43	1.247 1.223 1.186 1.149	11.05 11.06 11.09 11.12	r^2 .9903 b =- 9.5834 k''= -0.7600	11.24	17100	3.882x10 ⁻²
60	.0200 .0182 .0182 .0125	109.78 107.98 107.98 102.41	1.208 1.188 1.188 1.127	9.45 9.47 9.51 9.56	$r^{2}=$.9931 b =- 14.7384 k''= -0.1550	9.74	13000	4.253x10 ⁻²
70	.0200 .0182 .0154 .0125	108.28 106.64 104.10 101.52	1.191 1.173 1.145 1.117	8.76 8.79 8.82 8.86	r^2 .9948 b =- 12.7763 k''= -0.1590	9.02	11200	4.470x10 ⁻²
80	.0200 .0182 .0154 .0125	106.69 105.20 102.91 100.56	1.174 1.158 1.132 1.107	8.02 8.04 8.07 8.10	r^{2} = .9998 b =- 10.6577 k''= -0.1570	8.23	9400	4.738x10 ⁻²
1	r ² =0.998	7			1 1 · · · · · · · · · · · · · · · · · ·	b =2.	9728x10	-4
	a =2.397	1×10^{-2}				$k_{60}^{c} = 4$.	862x10 ⁻³	}

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Hydrolysis of Dextran Acid and Ultrasound C(HCl)=3.0 M

T=60[°]C Frequency=25kHz

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C(Dextran)=.04gm/m1 Power =.4w/cm²

T(min)	C(gm/ml)	t(s)	n r	ln(n _r)/C	Curve coefficients	[n]	М w	
0							73100	2.392×10^{-2}
10	.0200 .0182 .0154 .0125	131.51 127.47 121.34 115.14	1.447 1.403 1.335 1.267	18.48 18.59 18.77 18.93	r ² = .9989 b =- 60.3833 k''= -0.1560	19.69	50400	2.707x10 ⁻²
20	.0200 .0182 .0154 .0125	124.34 121.10 116.06 111.00	1.368 1.333 1.277 1.221	15.67 15.77 15.88 16.00	r ² = .9956 b =- 43.1873 k"= -0.1580	16.54	36000	3.030×10 ⁻²
30	.0200 .0182 .0154 .0125	119.12 116.38 112.20 107.94	1.311 1.281 1.235 1.188	13.53 13.59 13.68 13.76	r ² = .9982 b =- 30.7288 k"= -0.1530	14.15	26700	3.349x10 ⁻²
40	.0200 .0182 .0154 .0125	115.65 113.23 109.51 102.77	1.273 1.246 1.205 1.164	12.05 12.08 12.11 12.14	r^{2} = .9894 b =- 11.7320 k''= -0.0780	12.29	20300	3.666x10 ⁻²
50	.0200 .0182 .0154 .0125	112.43 110.34 107.13 103.90	1.237 1.214 1.179 1.143	10.64 10.66 10.68 10.71	r^2 = .9938 b =- 9.0656 k''= -0.0770	10.82	15900	3.997x10 ⁻²
60	.0200 .0182 .0154 .0125	109.29 107.54 104.86 102.12	1.203 1.183 1.154 1.124	9.22 9.25 9.29 9.33	r^2 = .9986 b =- 14.5684 k''= -0.1610	9.51	12400	4.320x10 ⁻²
70	.0200 .0182 .0154 .0125	107.51 105.92 103.52 101.05	1.183 1.165 1.139 1.112	8.40 8.41 8.46 8.49	r ² = .9765 b =- 12.7676 k"= -0.1710	8.65	10300	4.596x10 ⁻²
80	.0200 .0182 .0154 .0125	105.55 104.17 102.05 99.88	1.161 1.146 1.123 1.099	7.48 7.50 7.53 7.55	r^2 = .9884 b =- 9.4134 k''= -0.1600	7.67	8200	4.959x10 ⁻²
	r ² =0.999	8	I <u></u>			b =3.	.1905x10	-4
	a =2.390	0x10 ⁻²				$L^{k_{60}^{s}} = 5$.218x10 ⁻³	3

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Hydrolysis of Dextran Acid and Ultrasound C(HC1)=3.0 M

T=60⁰C

Frequency=17kHz

C(Dextran)=.04gm/m1 Power =200w/cm²

					1			,
T(min)	C(gm/ml)	ī(s)	n r	ln(n _r)/C	Curve coefficients	[n]	м _w	
0							73100	2.392x10 ⁻²
10	.0200 .0182 .0154 .0125	130.66 126.72 120.72 114.65	1.438 1.394 1.328 1.262	18.15 18.27 18.44 18.59	$r^{2}=$.9972 b =- 58.6212 k''= -0.1570	19.33	48600	2.740x10 ⁻²
20	,0200 .0182 .0154 .0125	123.12 119.97 115.13 110.29	1.355 1.320 1.267 1.214	15.18 15.26 15.36 15.49	$r^{2}=.9978$ b =- 40.6909 k"= -0.1590	15.99	33700	3.096x10 ⁻²
30	.0200 .0182 .0154 .0125	177.79 115.17 111.19 107.16	1.296 1.267 1.223 1.179	12.97 13.01 13.10 13.18	r^2 .9971 b =- 28.5803 k"= -0.1560	13.54	24500	3.443×10 ⁻²
40	.0200 .0182 .0154 .0125	113.73 111.53 108.17 104.76	1.251 1.227 1.190 1.153	11.21 11.25 11.31 11.37	r^2 .9998 b =- 21.3154 k''= -0.1570	11.64	18300	3.794x10 ⁻²
50	.0200 .0182 .0154 .025	110.65 108.75 105.87 102.93	1.218 1.197 1.165 1.133	9.84 9.86 9.91 9.96	r^{2} = .9944 b =- 16.3305 k''= -0.1580	10.16	14100	4.139x10 ⁻²
60	.0200 .0182 .0154 .0125	107.94 106.32 103.85 101.31	1.188 1.170 1.143 1.115	8.60 8.62 8.66 8.69	r^2 = .9957 b =- 12.2498 k''= -0.1570	8.84	10800	4.524x10 ⁻²
70	.0200 .0182 .0154 .0125	106.22 104.86 102.62 100.35	1.170 1.154 1.129 1.104	7.85 7.86 7.89 7.90	r^{2} = .9903 b =- 9.5834 k''= -0.1480	8.04	9000	4.807x10 ⁻²
80	.0200 .0182 .0154 .0125	104.34 1.3.09 101.14 99.15	1.148 1.134 1.113 1.091	6.91 6.93 6.95 6.97	r^2 .9894 b =- 7.8213 k''= -0.1560	7.07	7000	5.228×10 ⁻²
	r ² =0.999	6			L	b =3.	5162x10	-4
	a =2.3894	4x10 ⁻²			1	$k_{60}^{s} = 5.2$	750x10 ⁻³	3

Hydrolysis of Dextran Acid Only C(HC1)=4.0 M

r=60 ⁰ C					C(Dextra	n)=.04gm/m1		
T(min)	C(gm/m1)	ī(s)	n r	ln(n _r)/C	Curve coefficients	[n]	м w	
0							73100	2.392x10 ⁻²
5	.0200 .0182 .0154 .0125	140.61 135.59 127.93 120.35	1.547 1.492 1.408 1.324	21.82 21.98 22.20 22.47	r^2 .9988 b =- 85.8103 k''= -0.1550	23.54	53500	2.654x10 ⁻²
10	.0200 .0182 .0154 .0125	133.51 129.23 122.74 116.28	1.469 1.422 1.351 1.279	19.23 19.34 19.41 19.72	r^2 .9980 b =- 65.0128 k''= -0.1540	20.52	41400	2.891x10 ⁻²
15	.0200 .0182 .0154 .0125	127.43 123.83 118.32 112.78	1.402 1.363 1.302 1.241	16.90 17.00 17.13 17.27	r^2 = .9990 b =- 48.8600 k"= -0.1530	17.88	32000	3.150x10 ⁻²
20	.0200 .0182 .0154 .0125	122.72 119.62 114.84 110.05	1.350 1.316 1.264 1.211	15.02 15.10 15.78 15.31	r^2 .9968 b =- 37.8545 k''= -0.1520	15.78	25300	3.406x10 ⁻²
25	.0200 .0182 .0154 .0125	119.01 116.31 112.11 107.88	1.310 1.280 1.234 1.187	13.48 13.56 13.63 13.72	r^2 .9899 b =- 30.9375 k''= -0.1550	14.11	20500	3.654x10 ⁻²
30	.0200 .0182 .0152 .0125	115.62 113.25 109.58 105.88	1.272 1.246 1.206 1.165	12.04 12.09 12.15 12.22	r^2 .9982 b =- 23.6340 k''= -0.1510	12.52	16400	3.93×10 ⁻²
35	.0200 .0182 .0154 .0125	133.48 111.31 107.98 104.62	1.249 1.225 1.188 1.151	11.10 11.14 11.20 11.26	r^2 = .9998 b =- 21.3154 k''= -0.1600	11.53	14000	4.149x10 ⁻²
40	.0200 .0182 .0154 .0125	111.07 109.16 106.19 103.19	1.222 1.201 1.168 1.135	10.03 10.07 10.11 10.16	r^2 .9946 b =- 16.8869 k''= -0.1570	10.37	11500	4430x10 ⁻²
	r ² =0.999	7				b =5	.0770x10	-4
$a = 2.3915 \times 10^{-2}$.303x10 ⁻³	3

T=60⁰C

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Hydrolysis of Dextran Acid and Ultrasound C(HCl)=4.0 M

T=60⁰C Frequency=25kHz

C(Dextran)=.04gm/ml Power =.4w/cm²

T(min)	C(gm/m1)	t(s)	n _r	$\ln(n_r)/C$	Curve coefficients	[n]	M w	$\overline{M}_{w}^{-1/3}$
0							73100	2.392×10^{-2}
5	.0200 .0182 .0154 .0125	140.45 135.45 127.80 120.26	1.545 1.490 1.406 1.323	21.77 21.93 22.14 22.41	r^2 .9981 b =- 84.2183 k''= -0.1530	23.45	53200	2.659x10 ⁻²
10	.0200 .0182 .0154 .0125	133.36 129.14 122.67 116.20	1.467 1.421 1.350 1.279	19.18 19.31 19.48 19.66	r^2 .9990 b =- 63.4284 k''= -0.1520	20.46	41200	2.895×10 ⁻²
15	.0200 .0182 .0154 .0125	127.49 123.91 118.37 112.82	1.403 1.363 1.302 1.241	16.92 17.03 17.16 17.30	r^{2} = .9973 b =-499.3430 k''= -0.1550	17.93	32100	3.147x10 ⁻²
20	.0200 .0182 .0154 .0125	122.58 119.45 114.73 109.96	1.349 1.314 1.262 1.210	14.96 15.02 15.13 15.25	$r^{2}=9984$ b =- 38.8902 k''= -0.1570	15.73	25100	3.415x10 ⁻²
25	.0200 .0182 .0154 .0125	118.88 116.13 111.99 107.80	1.308 1.278 1.232 1.186	13.43 13.47 13.56 13.66	r^{2} = .9944 b =- 31.0689 k''= -0.1580	14.04	20300	3.666x10 ⁻²
30	.0200 .0182 .0154 .0125	115.45 113.08 109.45 105.78	1.270 1.244 1.204 1.164	11.96 12.01 12.07 12.15	r^2 .9973 b =- 24.8783 k''= -0.1600	12.46	16200	3.952×10 ⁻²
35	.0200. .0182 .0154 .0125	113.29 111.14 107.85 104.50	1.247 1.223 1.187 1.150	11.02 11.06 11.12 11.17	r^2 .9966 b =- 20.0711 k''= -0.1540	11.42	13800	4.169x10 ⁻²
40	.0200 .0182 .0154 .0125	110.99 109.05 106.12 103.13	1.221 1.200 1.168 1.135	10.00 10.01 10.07 10.12	r^2 .9768 b =- 16.8483 k''= -0.1580	10.33	11400	4.443x10 ⁻²
]	r ² =0.999	7	<u> </u>	Anna 2007		ь =5.	1223x10	-4
	a =2.390	9x10 ⁻²				$L^{k_{60}^{s}} = 8.$	377x10 ⁻¹	3

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Hydrolysis of Dextran Acid and Ultrasound C(HC1)=4.0 M

т=60⁰С

Frequency=17kHz

C(Dextran)=.04gm/m1Power =200w/cm²

T(min)	C(gm/m1)	īt(s)	n r	ln(n _r)/C	Curve coefficients	[n]	M _w	
0							73100	2.392×10^{-2}
5	.0200 .0182 .0154 .0125	140.52 135.58 127.90 120.31	1.546 1.492 1.407 1324	21.79 21.98 22.19 22.44	r^{2} = .9968 b =- 84.9525 k"= -0.1540	23.50	53400	2.656x10 ⁻²
10	.0200 .0182 .0154 .0125	132.82 128.61 122.28 115.88	1.461 1.415 1.346 1.275	18.97 19.08 19.27 19.44	r^{2} = .9991 b =- 63.2197 k''= -0.1540	20.23	40300	2.917x10 ⁻²
15	.0200 .0182 .0154 .0125	126.88 123.37 117.91 112.47	1.396 1.358 1.297 1.238	16.69 16.79 16.91 17.05	r^2 .9982 b =- 47.2679 k"= -0.1520	17.64	31200	3.176x10 ⁻²
20	.0200 .0182 .0154 .0125	121.89 118.87 114.26 109.56	1.341 1.308 1.257 1.206	14.68 14.75 14.87 14.95	r^2 = .9910 b =- 36.5793 k''= -0.1540	15.42	24200	3.457x10 ⁻²
25	.0200 .0182 .0154 .0125	118.22 115.56 111.53 107.41	1.301 1.272 1.227 1.182	13.15 13.20 13.30 13.37	r^2 .9938 b =- 30.0023 k''= -0.1590	13.75	19.500	3.715x10 ⁻²
30	.0200 .0182 .0154 .0125	114.83 112.53 109.00 105.41	1.264 1.238 1.199 1.160	11.70 11.74 11.81 11.87	r^2 .9985 b =- 22.9075 k''= -0.1550	12.16	15500	4.011x10 ⁻²
35	.0200 .0182 .0154 .0125	112.63 110.56 107.36 104.11	1.239 1.217 1.181 1.146	10.73 10.77 10.82 10.87	r^2 .9974 b =- 18.4790 k''= -0.1500	11.10	13100	4.242x10 ⁻²
40	.0200 .0182 .0154 .0125	110.47 108.62 105.74 102.83	1.216 1.195 1.164 1.131	9.76 9.80 9.83 9.88	r^2 .9859 b =- 15.2948 k''= -0.1510	10.07	10900	4.510x10 ⁻²
·[r ² =0.999	8			<u> </u>	b =5.	3190x10	-4
	a =2.389	1×10^{-2}				$H^{k_{60}^{s}} = 8$	699x10	3

-	1	4	5	-
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Hydrolysis of Dextran Acid Only C(HCl)=1.0 M

T=70⁰C

.

C(Dextran)=.04gm/ml

T(min)	C(gm/ml)	īt(s)	n _r	$\ln(n_r)/C$	Curve coefficients	[n]	M _w	
0							73100	2.392×10^{-2}
15	.0200 .0182 .0125 .0125	136.40 131.65 117.51 117.51	1.501 1.449 1.293 1.293	20.30 20.37 20.56 20.56	r^{2} = .9990 b =- 34.2917 k''= -0.0778	20.99	47900	2.754x10 ⁻²
30	.0200 .0182 .0154 .0125	126.92 123.25 117.73 112.22	1.397 1.356 1.295 1.235	16.70 16.74 16.81 16.87	$r^{2}=$.9985 b =- 22.9075 k''= -0.0778	17.16	33000	3.118x10 ⁻²
45	.0200 .0182 .0154 .0125	120.29 117.36 112.91 108.45	1.324 1.291 1.242 1.193	14.02 14.05 14.09 14.14	r^{2} = .9985 b =- 15.8127 k''= -0.0769	14.34	23700	3.381×10 ⁻²
60	.0200 .0182 .0154 .0125	115.86 113.40 109.66 105.89	1.275 1.248 1.207 1.165	12.14 12.16 12.20 12.23	r^{2} = .9957 b =- 12.2498 k''= -0.0799	12.38	18000	3.826x10 ⁻²
75	.0200 .0182 .0154 .0125	112.08 110.02 106.87 103.69	1.233 1.211 1.176 1.141	10.48 10.50 10.52 10.55	r^2 = .9938 b =- 9.0656 k''= -0.0797	10.66	13600	4.189x10 ⁻²
90	.0200 .0182 .0154 .0125	108.97 107.23 104.57 101.86	1.199 1.180 1.151 1.121	9.08 9.09 9.11 9.13	r^{3} = .9983 b =- 6.7470 k''= -0.0795	9.21	10300	4.596x10 ⁻²
105	.0200 .0182 .0154 .0125	107.00 105.46 103.09 100.69	1.177 1.160 1.134 1.108	8.16 8.17 8.19 8.20	r^2 = .9795 b = - 5.5027 k''= -0.0804	8.27	8400	4.919x10 ⁻²
120	.0200 .0182 .0154 .0125	105.44 104.06 101.93 99.77	1.160 1.145 1.122 1.098	7.43 7.44 7.45 7.47	r^{2} = .9824 b =- 5.1550 k''= -0.0909	7.52	7000	5.228x10 ⁻²
	r ² =0.999	5			And Support to the second s	b =2.	.389x10 ⁻¹	4
	a =2.399	×10 ⁻²				$k_{70}^{c} = 3$.907x10 ⁻³	3

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Hydrolysis of Dextran Acid and Ultrasound C(HC1)=1.0 M

T=70⁰C

Frequency=25kHz

C(Dextran)=.04gm/m1 Power =.4w/cm²

· · · · · · · · · · · · · · · · · · ·			+					
T(min)	C(gm/ml)	ī(s)	n r	$ln(n_r)/C$	Curve coefficients	[n]	м w	
0							73100	2.392×10^{-2}
15	.0200 .0182 .0154 .0125	133.60 129.17 122.53 115.96	1.470 1.421 1.348 1.276	19.26 19.32 19.41 19.50	r^2 .9998 b =- 31.9731 k''= -0.0807	19.88	43300	2.848x10 ⁻²
30	.0200 .0182 .0154 .0125	123.15 119.90 114.99 110.08	1.355 1.313 1.265 1.211	15.19 15.23 15.28 15.33	r^{2} = .9974 b =- 18.4790 k''= -0.0763			
45	.0200 .0182 .0154 .0125	116.51 113.98 110.13 106.27	1.282 1.254 1.212 1.169	12.42 12.44 12.48 12.51	r^{2} = .9957 b =- 12.2498 k''= -0.0764	12.67	18800	3.761x10 ⁻²
60	.0200 .0182 .0154 .0125	111.91 109.89 106.74 103.59	1.231 1.209 1.175 1.140	10.41 10.42 10.45 10.47	r^2 = .9888 b = - 8.3391 k''= -0.0746	10.58	13400	4.210x10 ⁻²
75	.0200 .0182 .0154 .0125	108.47 106.77 104.19 101.56	1.193 1.175 1.146 1.118	8.84 8.86 8.87 8.89	r^2 = .9655 b = - 6.2292 k''= -0.0775	8.97	9800	4.673x10 ⁻²
90	.0200 .0182 .0154 .0125	105.67 104.26 102.10 99.90	1.163 1.146 1.123 1.099	7.54 7.55 7.56 7.57	r^2 = .9894 b =- 3.9107 k''= -0.0674	7.63	7200	5.179x10 ⁻²
105	.0200 .0182 .0154 .0125	103.89 102.66 100.77 98.84	1.143 1.130 1.109 1.088	6.69 6.70 6.71 6.72	r^2 = .9894 b =- 3.9107 k''= -0.0853	6.76	5700	5.598x10 ⁻²
120	.0200 .0182 .0154 .0125	102.45 10.36 99.69 97.98	1.127 1.115 1.097 1.078	5.99 6.00 6.01 6.01	r^2 .8363 b =- 2.6664 k''= -0.0729	6.05	4600	6.013x10 ⁻²
.	r ² =0.9997	7		l _{en} , mannen an	.	b =3.	0429x10	-4
	a =2.395;	×10 ⁻²				$L^{k_{70}^{s}} = 4.$	976x10 ⁻³	3

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Hydrolysis of Dextran Acid Only C(HC1) = 2.0 M

C(Dextran)=.04gm/m1

T(min)	C(gm/m1)	t(s)	nr	ln(n _r)/C	Curve coefficients	[n]	м _w	™_w ^{-1/3}
0							73100	2.392×10^{-2}
5	.0200 .0182 .0154 .0125	136.32 131.75 124.85 117.88	1.500 1.450 1.374 1.297	20.27 20.40 20.62 20.81	r ² = .9985 b =- 72.6331 k"= -0.1540	21.73	52500	2.671x10 ⁻²
10	.0200 .0182 .0154 .0125	128.38 124.65 119.02 113.32	1.413 1.372 1.310 1.247	17.27 17.36 17.52 17.65	r^{2} = .9975 b =- 51.3177 k''= -0.1530	18.30	38000	2.974x10 ⁻²
15	.0200 .0182 .0154 .0125	122.58 119.45 114.74 109.96	1.349 1.314 1.263 1.210	14.96 15.02 15.14 15.25	r^{2} = .9986 b =- 39.2380 k''= -0.1580	15.74	28600	3.270x10 ⁻²
20	.0200 .0182 .0154 .0125	118.18 115.54 111.47 107.39	1.300 1.271 1.227 1.182	13.13 13.19 13.26 13.35	r^2 .9976 b =- 28.7889 k"= -0.1530	13.71	22100	3.563x10 ⁻²
25	.0200 .0182 .0154 .0125	114.67 112.37 108.88 105.32	1.262 1.237 1.198 1.159	11.63 11.67 11.73 11.80	r ² = .9993 b =- 22.5597 k"= -0.1550	12.08	17400	3.859x10 ⁻²
30	.0200 .0182 .0154 .0125	111.74 109.75 106.68 103.58	1.230 1.208 1.174 1.140	10.33 10.37 10.41 10.46	r^2 .9946 b =- 16.8869 k''= -0.1480	10.67	13800	4.169x10 ⁻²
35	.0200 .0182 .0154 .0125	109.70 107.90 105.17 102.36	1.207 1.187 1.157 1.126	9.41 9.43 9.48 9.52	r^2 = .9949 b =- 15.0862 k''= -0.1600	9.71	11500	4.430x10 ⁻²
40	.0200 .0182 .0154 .0125	107.77 106.19 103.72 101.21	1.186 1.168 1.141 1.114	8.52 8.55 8.58 8.61	r^2 .9894 b =- 11.7320 k''= -0.1530	8.76	9500	4.722x10 ⁻²
1	r ² =0.9998	3		1	ummening	b =5.	4587x10	-4
	a =2.3894	4x10 ⁻²				$k_{70}^{c} = 9$	581x10 ⁻³	3

T=70⁰C

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Hydrolysis of Dextran Acid and Ultrasound C(HC1)=2.0 M

.

T=70⁰C Frequency=17kHz

C(Dextran)=.04gm/m1 Power = 200w/cm²

T(min)	C(gm/m1)	īt(s)	n r	$\ln(n_r)/C$	Curve coefficients	[ŋ]	M _w	₩ _w ^{-1/3}
0							73100	2.392x10 ⁻²
5	.0200 .0182 .0154 .0125	133.86 129.54 122.99 116.48	1.473 1.425 1.353 1.282	19.36 19.48 19.65 19.85	r^{2} = .9993 b =- 64.8427 k''= -0.1520	20.66	47800	2.755x10 ⁻²
10	.0200 .0182 .0154 .0125	124.70 121.41 116.31 111.21	1.372 1.336 1.280 1.224	15.82 15.91 16.02 16.15	r ² = .9985 b =- 43.3573 k''= -0.1560	16.69	32000	3.150x10 ⁻²
15	.0200 .0182 .0154 .0125	117.82 115.20 111.22 107.18	1.296 1.268 1.224 1.179	12.98 13.03 13.11 13.20	r ² = .9994 b =- 29.3067 k"= -0.1590	13.56	21600	3.591x10 ⁻²
20	.0200 .0182 .0154 .0125	113.65 111.45 108.11 104.72	1.251 1.226 1.190 1.152	11.18 11.21 11.27 11.34	r ² = .9955 b =- 21.4854 k''= -0.1590	11.61	16100	3.960×10 ⁻²
25	.0200 .0182 .0154 .0125	110.42 108.56 105.69 102.80	1.215 1.195 1.163 1.131	9.74 9.77 9.80 9.86	r ² = .9824 b =- 15.4649 k''= -0.1530	10.05	12300	4.332×10 ⁻²
30	.0200 .0182 .0154 .0125	107.57 105.99 103.58 101.09	1.184 1.166 1.140 1.112	8.43 8.45 8.49 8.52	$r^{2}=$.9957 b =- 12.2498 k''= -0.1630	8.67	9300	4.755x10 ⁻²
35	.0200 .0182 .0154 .0125	105.13 103.78 101.73 99.62	1.157 1.142 1.119 1.096	7.28 7.29 7.32 7.35	$r^{2}=$.9903 b =- 9.5834 k''= -0.1720	7.47	7000	5.228x10 ⁻²
40	.0200 .0182 .0154 .0125	104.20 102.94 101.03 99.06	1.147 1.133 1.112 1.090	6.84 6.85 6.88 6.89	r^2 .9578 b =- 7.0948 k''= -0.1460	6.98	6200	5.443x10 ⁻²
	$r^2 = 0.998$	1				b=7.858	3x10 ⁻⁴	

 $a = 2.3846 \times 10^{-2}$

 $H^{k_{70}^{s}=1.285\times10^{-2}}$

CELLULOSE

Cellulose is insoluble in water, but it is soluble in solution of some metal complexing agents. Most of those compounds are readily attacked by acids, therefore, studying the kinetics of acid hydrolysis of cellulose in a homogeneous solution can not be achieved. This kinetic study was done in a heterogeneous system, where fine powder of purified cellulose was suspended in water, then the acid or acid of the desired concentration was added. This system is more difficult to study since many variables could affect the result, such as particle size, crystallinity, speed of agitation, volume of reaction mixture and the medium of suspension. All necessary precautions to keep all those variables the same for all the different runs, were taken.

To determine the weight average molecular weight of each sample collected at different reaction durations, viscosity has to be evaluated first. It was found that cupriethylene diamine of copper content 1.00 ± 0.02 M can dissolve the cellulose even in the presence of KCl in the highest concentration expected after quenching the sample with KOH.

After the sample was quenched and just before running the viscosity cupriethylene diamine $(1.00 \pm 0.02 \text{ M copper})$ was added to dissolve the cellulose. The viscosity was measured by applying the same procedure used in dextran. To dilute the sample to lower concentration a fresh solution containing KCl and cupriethylene diamine of the same concentration as the original sample was used.

EVALUATING THE MOLECULAR WEIGHT OF CELLULOSE

The molecular weight of the sample of cellulose used in this study was unknown, therefore it had to be evaluated experimentally. The constants K' and a of the Mark-Houwink-Sakurada equation of cellulose solution in

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cupriethylene diamine at 25°C publishe by Elias (141) were used for this evaluation.

CHEMICALS

Cellulose, Sigmacell type 100 noncrystalline, highly prurified powder Sigma Chemical Co. St. Louis Mo. U.S.A.

Cupriethylene diamine, 1.00 ± 0.02 M copper content, ratio of ethylene diamine to copper is 2.00 ± 0.04 (Cu(En)₂)

G. Frederick Smith Chemical Co.

Columbus, Ohio, U.S.A.

Distilled water

APPARATUS

Water-bath

Ubbelohde viscometer

Viscosity timer

Suction bulb

Thermo-watch

Analytical balance

Beakers

Stirrer

Pipette

PROCEDURE

- 1. Viscometer was cleaned thoroughly with chromic acid, then rinsed copiously with distilled water.
- 2. Viscometer was dried with acetone and air.
- 3. Viscometer was immersed in a 25°C thermostat bath to equilibrate

- 4. 100 ml of 2.0M KCl was mixed with 50 ml of cupriethylene diamine. This was used as the solvent for cellulose. The reason of adding KCl is to determine \overline{M}_{W} under KCl concentration equal to the average of that would produce during the hydrolysis runs.
- 5. 10.0 ml of this solvent was placed into the viscometer then allowed to equilibrate.
- 6. The efflux time of the solvent was evaluated several times. An average was calculated and considered as t_0 ($t_0 = 106.61$ s).
- 7. 0.20 gm of cellulose was dissolved into 120.0 ml of the previous solvent mixture (c = 1.667×10^{-3} g/ml).
- 8. Viscometer was cleaned, dried, and allowed to equilibrate into water-bath.
- 9. 10.0 ml of cellulose solution was placed into viscometer, then allowed to equilibrate
- 10. Efflux time was measured sevaral times, the average was then taken
- 11. 1, 2, 3, 10, and 20. ml of solvent was added, mixed then the efflux time was determined after each addition.
- 12. $n_r = \bar{t}/t_0$, $\ln(n_r)/c$, $n_{sp} = n_r 1$, and n_{sp}/c were calculated.
- 13. Plot of $ln(n_r)/c$ vs c and n_{sp}/c vs c were made, then [n] was evaluated.
- 14. Mark-Houwink-Sakurada equation was applied to calculate $\overline{\vec{M}}_{_{W}}$ of cellulose.

Evaluating the intrinsic

viscosity of cellulose

C(gm/ml)	ī(s)	n _r =t/t _o	ln(n _r)/C	Curve coefficients	n _{sp}	n _{sp} /C	Curve coefficients
1.6667×10^{-3} 1.5152 \text{x10}^{-3} 1.2821 \text{x10}^{-3} 1.0417 \text{x10}^{-3} 8.3333 \text{x10}^{-4} 5.5556 \text{x10}^{-4}	163.51 157.85 149.10 140.35 133.13 123.92	1.5337 1.4806 1.3986 1.3165 1.2488 1.1624	256.61 259.02 261.63 263.96 266.58 270.82	r^{2} = .9942 b =-12253.4505 n = 277.1838 k''= -0.1601	.5337 .4806 .3986 .3165 .2488 .1624	320.23 317.21 310.86 303.81 298.51 292.26	r^2 = .9979 b =25897.1209 r_1 = 277.3883 k'= .3373

k'-k"=.4974



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HYDROLYSIS

The acid hydrolysis of cellulose was carried out in a heterogeneous system. Cellulose powder was suspended into water under continuous agitation.

APPARATUS

Same as used in hydrolysis of dextran, except, only high frequency was used, since cellulose is expected to be more difficult to hydrolyse than dextran. It was proven in case of dextran that changing ultrasound frequencies in the range available does not affect the hydrolysis rate, therefore only a single ferequency of 17 kHz was applied.

PROCEDURE

- 1. Acid and KOH solutions were prepared in the desired concentration as described before.
- 2. 5.0 ml of KOH was placed into a number of 25 c.c. bottles.
- 3. 0.65 g of cellulose was weighed into the control reaction vessel, and 2.1667 g was weighed into the ultrasound reaction vessel.
- 4. Both vessels were brought to the reaction temperature.
- 5. About 300.0 ml of hydrochloric acid was placed into a conical flask then immersed into the water bath at the reaction mixture then was allowed to equilibrate.
- 6. 60.0 ml of HCl was added to the control reaction vessel, and the stop watch (timer) was started immediately.
- 7. 200.0 ml of HCl was added to the ultrasound reaction vessel, and a timer was immediately started.
- 8. After the desired time, 5.0 ml sample was taken out with a pipette, and placed immediately into 25 ml bottle contain 5.0 ml of KOH of

The same molarity as that of the acid in the reaction vessel.

9. To evaluate the viscosity of each of those samples, 5.0 ml of cupriethylene diamine was added to dissolve cellulose, then 10.0 ml of this solution was placed into viscometer and ran as described before.

10. To dilute the concentration in the viscometer, a solution of cupriethylene and KCl of concentration equal to that in those samples used.

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Computer values of coefficient of determination (r^2) at different orders

	RUN		REACTION ORDER (n)															
тос	C _{HCL} (M)	Type	0	1	2	3	3.5	3.6	3.7	3.8	3.9	4	4.1	4.2	4.3	4.4	4.5	5
40	2	C	.6878	.8224	.9281	.9852	.9968	.9980	.9989	.9994	.9997	.9997	.9994	.9989	.9981	.9972	.9960	.9874
	2	S	.6560	.8045	.9235	.9857	.9974	.9985	.9992	.9996	.9997	.9995	.9991	.9983	.9973	.9961	.9947	.9850
	3	C	.6006	.7634	.9030	.9786	.9938	.9955	.9967	.9976	.9981	.9983	.9982	.9977	.9971	.9961	.9950	.9863
	3	S	.5725	.7429	.8933	.9749	.9918	.9938	.9953	.9965	.9973	.9979	.9981	.9980	.9977	.9972	.9964	.9901
	4	C	.5812	.7576	.9099	.9858	.9981	.9990	.9995	.9997	.9994	.9988	.9979	.9968	.9954	.9937	.9918	.9798
	4	S	.5587	.7403	.9025	.9839	.9972	.9983	.9989	.9991	.9989	.9984	.9975	.9964	.9950	.9933	.9915	.9793
50	2	C	.5966	.7596	.9002	.9773	.9935	.9953	.9967	.9978	.9985	.9988	.9989	.9987	.9982	.9975	.9965	.9888
	2	S	.5718	.7450	.8973	.9780	.9939	.9957	.9970	.9980	.9986	.9989	.9989	.9987	.9981	.9974	.9965	.9891
	3	C	.6013	.7612	.8985	.9749	.9919	.9940	.9957	.9970	.9980	.9987	.9992	.9993	.9992	.9989	.9983	.9929
	3	S	.5717	.7403	.8886	.9691	.9860	.9881	.9897	.9909	.9919	.9925	.9928	.9929	.9927	.9923	.9918	.9864
	4	C	.5421	.7179	.8814	.9719	.9912	.9935	.9954	.9969	.9980	.9987	.9992	.9993	.9992	.9988	.9982	.9925
	4	S	.5278	.7097	.8805	.9716	.9897	.9918	.9934	.9946	.9955	.9960	.9962	.9961	.9958	.9953	.9945	.9882
60	2	C	.5352	.7197	.8918	.9792	.9929	.9935	.9939	.9938	.9933	.9924	.9911	.9895	.9876	.9854	.9830	.9675
	2	S	.5149	.7044	.8862	.9795	.9958	.9973	.9984	.9990	.9993	.9992	.9988	.9980	.9970	.9957	.9942	.9840
	3	C	.4840	.6751	.8693	.9718	.9913	.9935	.9952	.9965	.9974	.9980	.9982	.9981	.9978	.9972	.9964	.9897
	3	S	.4625	.6553	.8625	.9716	.9909	.9928	.9942	.9952	.9957	.9958	.9955	.9949	.9941	.9929	.9915	.9816
	4	C	.4495	.6461	.8632	.9753	.9945	.9964	.9977	.9987	.9992	.9993	.9990	.9985	.9977	.9966	.9953	.9860
	4	S	.4383	.6347	.8555	.9681	.9878	.9899	.9914	.9926	.9933	.9937	.9938	.9936	.9931	.9924	.9915	.9843

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Hydrolysis of Cellulose Acid Only C(HCl)= 2.0 M

т=40⁰с

C((cellulose)=.0108gm/m1

T(min)	C(gm/m1)	Ē(s)	nr	ln(n _r)/C	Curve coefficients	[n]	Mw	
0							59200	4.820x10 ⁻¹⁵
120	.0036 .0033 .0028 .0023	216.57 203.06 183.00 165.09	2.031 1.905 1.717 1.549	196.87 195.25 192.97 190.14	r^2 .9980 b =-5107.1430 k''= -0.1600	178.49	36400	2.073x10 ⁻¹⁴
240	.0036 .0033 .0028 .0023	191.61 181.78 166.74 153.41	1.797 1.705 1.564 1.439	162.86 161.70 159.74 158.23	r ² = .9962 b =-3588.7760 k''= -0.1600	149.87	30000	2.704x10 ⁻¹⁴
360	.0036 .0033 .0028 .0025	179.52 171.47 158.88 147.26	1.684 1.608 1.490 1.383	144.75 144.01 142.49 141.03	r^2 = .9990 b =-2891.2400 k''= -0.1600			
480	.0036 .0033 .0028 .0023	161.52 156.40 148.06 140.06	1.515 1.467 1.389 1.314	115.40 116.13 117.30 118.65	r^2 = .9989 b =-2485.7143 k''= -0.1610	124.23	24400	6.884x10 ⁻¹⁴
600	.0036 .0033 .0028 .0023	157.85 153.07 145.42 137.87	1.481 1.436 1.364 1.293	109.02 109.61 110.87 111.80	r ² = .9961 b =-2182.6500 k" -0.1600	116.87	22800	8.437x10 ⁻¹⁴
720	.0036 .0033 .0028 .0023	154.87 150.47 143.17 136.14	1.453 1.411 1.343 1.277	103.72 104.42 105.31 106.31	r^{2} = .9981 b =-1960.2000 k''= -0.1600	110.82	21500	1.006x10 ⁻¹³
840	.0036 .0033 .0028 .0023	152.58 148.45 141.50 134.80	1.431 1.392 1.327 1.264	99.59 100.32 101.12 102.01	r ² = .9945 b =-1817.4500 k''= -0.1610	106.21	20500	1.161x10 ⁻¹³
960	.0036 .0033 .0028 .0023	150.35 146.36 139.85 133.45	1.410 1.373 1.312 1.252	95.50 96.03 96.93 97.63	r ² = .9965 b =-1651.0204 k''= -0.1600	101.48	19500	1.349x10 ⁻¹³

r²=0.9945

a =1.286 $\times 10^{-15}$

b =1.38 $\times 10^{-16}$ k^c₄₀ =1.955 $\times 10^{-10}$

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Hydrolysis of Cellulose Acid and Ultrasound C(HC1)=2.0 M

T=40⁰C Frequency=17kHg

C'(Cellulose)=.0108gm/ml Power =

T(min)	C(gm/ml)	ī(s)	n _r	ln(n _r)/C	Curve coefficients	[n]	M _w	<u>M</u> ^{−3} w
0							59200	4.820x10 ⁻¹⁵
120	.0036 .0033 .0028 .0023	183.67 176.47 164.46 152.98	1.723 1.655 1.543 1.435	151.10 152.72 144.82 157.01	r ² = .9980 b =-4484.6939 k''= -0.1600	167.37	33900	2.567x10 ⁻¹⁴
240	.0036 .0033 .0028 .0023	169.11 163.30 153.71 144.51	1.586 1.532 1.442 1.356	128.16 129.22 130.68 132.25	r ² .9991 b =-3111.2245 k"= -0.1610	139.41	27700	4.705x10 ⁻¹⁴
360	.0036 .0033 .0028 .0023	16200 156.81 148.38 140.34	1.520 1.471 1.392 1.316	116.23 116.93 118.07 119.52	$r^{2}=9964$ b =-2511.2245 k''= -0.1600	125.22	24600	6.717x10 ⁻¹⁴
480	.0036 .0033 .0028 .0023	157.16 152.46 144.90 137.47	1.474 1.430 1.359 1.289	107.80 108.40 109.60 110.53	r^2 = .9973 b =-2133.6735 k"= -0.1600	115.48	22500	8.779x10 ⁻¹⁴
600	.0036 .0033 .0028 .0023	153.33 148.97 142.01 135.21	1.438 1.397 1.332 1.268	100.95 101.38 102.40 103.33	r^2 = .9974 b =-1864.2857 k''= -0.1610	107.61	20800	1.111×10 ⁻¹³
720	.0036 .0033 .0028 .0023	150.82 146.79 140.12 133.75	1.415 1.377 1.314 1.255	96.36 96.92 97.61 98.61	r^2 .9943 b =-1690.8163 k''= -0.1610	102.45	19700	1.308x10 ⁻¹³
840	.0036 .0033 .0028 .0023	148.56 144.74 138.51 132.38	1.393 1.358 1.299 1.242	92.17 92.66 93.49 94.13	r ² = .9963 b =-1519.3878 k"= -0.1590	97.67	18700	1.529x10 ⁻¹³
960	.0036 .0033 .0028 .0023	146.54 142.94 136.97 131.19	1.375 1.341 1.285 1.231	88.37 88.86 89.49 90.20	r^2 = .9983 b =-1385.7143 k''= -0.1590	93.39	17800	1.773×10 ⁻¹³
	r ² =0.999	5				b =1.	782x10	16
	a =3.864:	×10 ⁻¹⁵				$k_{40}^{s} = 2.$	525x10	10

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Hydrolysis of Cellulose Acid Only C(HCl)=3.0 M

T(min)	C(gm/ml)	ī(s)	n r	ln(n _r)/C	Curve coefficients	[ŋ]	M w	™_w^-3
0							59200	4.820x10 ⁻¹⁵
120	.0036 .0033 .0028 .0023	174.78 168.30 157.81 147.80	1.639 1.579 1.480 1.386	137.32 138.35 140.08 142.04	r ² = .9989 b =-3619.3878 k"= -0.1600	150.31	30100	3.667x10 ⁻¹⁴
240	.0036 .0033 .0028 .0023	162.21 157.02 148.57 140.46	1.522 1.473 1.394 1.318	116.59 117.33 118.53 119.89	r^2 = .9991 b =-2526.5306 k''= -0.1600	125.66	24700	6.636x10 ⁻¹⁴
360	.0036 .0033 .0028 .0023	155.57 151.03 143.72 136.53	1.459 1.417 1.348 1.281	104.98 105.55 106.67 107.55	b =-2006.1224 k''= -0.1590	112.21	21800	9.652x10 ⁻¹⁴
480	.0036 .0033 .0028 .0023	150.79 146.80 140.16 133.73	1.414 1.377 1.315 1.254	96.31 96.94 97.72 98.54	r^2 = .9971 b =-1687.7551 k''= -0.1610	102.44	19700	1.308x10 ⁻¹³
600	.0036 .0033 .0028 .0023	148.10 144.36 138.14 132.13	1.389 1.354 1.296 1.239	91.31 91.86 92.53 93.31	r^2 = .9975 b =-1509.1837 k''= -0.1610	96.78	18500	1579x10 ⁻¹³
720	.0036 .0033 .0028 .0023	145.66 142.13 136.29 130.67	1.366 1.333 1.278 1.226	86.69 87.14 87.72 88.48	r^2 = .9969 b =-1351.0204 k''= -0.1610	91.56	17400	1.89x10 ⁻¹³
840	.0036 .0033 .0028 .0023	144.33 140.90 135.29 129.87	1.354 1.322 1.269 1.218	84.15 84.51 85.09 85.81	r^2 = .9972 b =-1267.3469 k"= -0.161	88.69	16800	2.109x10 ⁻¹³
960	.0036 .0033 .0028 .0023	142.11 138.88 133.65 128.53	1.333 1.303 1.254 1.206	79.84 80.13 80.73 81.30	r^{2} = .9989 b =-1135.7143 k''= -0.1610	83.91	15800	2.35×10 ⁻¹³
	r ² =0.998	3	· • • •			b =2.	536x10	16
	a =5.763	x10 ⁻¹⁵				$k_{40}^{c} = 3$.	593x10	10

т=40⁰С

C(Cellulose)=.0108gm/m1

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Hydrolysis of Cellulose Acid and Ultrasound C(HC1)=3.0 M

T=40[°]C Frequency=17kHz

C(Cellulose)=.0108gm/m1 Power = 200w/cm²

T(min)	C(gm/m1)	ī(s)	nr	ln(n _r)/C	Curve coefficients	[n]	M w	
0							59200	4.820x10 ⁻¹⁵
120	.0036 .0033 .0028 .0023	169.81 163.92 154.23 144.92	1.593 1.538 1.447 1.359	129.31 130.36 131.88 133.48	r ² = .9995 b =-3181.6327 k''= -0.1600	140.80	28000	4.555x10 ⁻¹⁴
240	.0036 .0033 .0028 .0023	157.63 152.90 145.18 137.77	1.479 1.434 1.362 1.292	108.63 109.27 110.28 111.48	r^{2} = .9985 b =-2176.5306 k''= -0.1600	116.44	22700	8.549x10 ⁻¹⁴
360	.0036 .0033 .0028 .0023	151.27 147.16 140.52 133.99	1.419 1.380 1.318 1.257	97.19 97.68 98.63 99.39	r ² = .9979 b =-1715.3061 k''= -0.1610	103.37	19900	1.269x10 ⁻¹³
480	.0036 .0033 .0028 .0023	147.45 143.71 137.67 131.72	1.383 1.348 1.291 1.236	90.09 90.49 91.32 91.96	r ² = .9971 b =-1464.2857 k"= -0.1610	95.36	18200	1.659x10 ⁻¹³
600	.0036 .0033 .0028 .0023	144.53 141.12 135.48 129.99	1.356 1.324 1.271 1.219	84.53 84.98 85.59 86.21	r ² = .9985 b =-1278.5714 k''= -0.1610	89.16	16900	2.072x10 ⁻¹³
720	.0036 .0033 .0028 .0023	142.09 138.89 133.66 128.52	1.333 1.303 1.254 1.206	79.80 80.15 80.76 81.26	r^{2} = .9980 b =-1131.6327 k''= -0.1610	83.89	15800	2.535x10 ⁻¹³
840	.0036 .0033 .0028 .0023	140.55 137.50 132.47 127.60	1.318 1.290 1.243 1.197	76.77 77.11 77.56 78.14	r^2 .9973 b =-1035.7143 k''= -0.1600	80.50	15100	2.904x10 ⁻¹³
960	.0036 .0033 .0028 .0023	139.67 136.68 131.82 127.06	1.310 1.282 1.192 1.192	75.03 75.29 76.30 76.30	r^{2} = .9993 b =- 986.7347 k'' th -0.1600	78.57	14700	3.148x10 ⁻¹³
f	r ² =0.997	9	*****		La companya da parte da	b =3.	320x10	16
	a =6.605	к10 ⁻¹⁵				$k_{40}^{s} = 4.$	705x10 ⁻	10

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Hydrolysis of Cellulose Acid Only C(HCl)=4.0 M

C(Cellulose)=.0108gm/m1

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T(min)	C(gm/m1)	ī(s)	n r	ln(n _r)/C	Curve coefficients	[n]	M _w	<u>M</u> _w ^{−3}
0							59200	4.820×10^{-15}
90	.0036 .0033 .0028 .0023	170.04 164.14 154.41 145.05	1.595 1.540 1.448 1.361	129.68 130.77 132.30 133.87	r ² = .9991 b =-3193.8776 k" -0.1600	141.24	28100	4.507x10 ⁻¹⁴
180	.0036 .0033 .0028 .0023	156.62 152.88 145.23 137.74	1.478 1.434 1.362 1.292	108.61 109.24 110.41 111.39	$r^{2}=$.9987 b =-2160.2041 k''= -0.1590	116.39	22700	8.549x10 ⁻¹⁴
270	.0036 .0033 .0028 .0023	151.69 147.62 140.82 134.27	1.423 1.385 1.321 1.259	97.96 98.63 99.39 100.29	r^2 = .9961 b =-1751.0204 k''= -0.1610	104.32	20100	1.231x10 ⁻¹³
360	.0036 .0033 .0028 .0023	147.65 143.96 137.81 131.86	1.385 1.350 1.293 1.237	90.46 91.02 91.68 92.42	r^2 = .9966 b =-1477.5510 k''= -0.1610	95.83	18300	1.632x10 ⁻¹³
450	.0036 .0033 .0028 .0023	144.56 141.10 135.46 130.00	1.356 1.324 1.271 1.219	84.59 84.94 85.54 86.24	r^2 = .9982 b =-1265.3061 k''= -0.1590	89.12	16900	2.072x10 ⁻¹³
540	.0036 .0033 .0028 .0023	142.31 139.11 133.81 128.66	1.335 1.305 1.255 1.207	80.23 80.63 81.16 81.74	r ² = .9987 b =-1145.9184 k''= -0.1610	84.38	15900	2.488x10 ⁻¹³
630	.0036 .0033 .002- .0023	140.33 137.28 132.33 127.46	1.316 1.288 1.241 1.196	76.34 76.62 77.19 77.66	r^2 = .9983 b =-1030.6122 k''= -0.1610	80.04	15000	2.963x10 ⁻¹³
720	.0036 .0033 .0028 .0023	138.78 135.89 131.15 126.53	1.302 1.275 1.230 1.187	73.25 73.54 73.99 74.48	r^2 .9997 b = 940.8163 k''= -0.1610	76.64	14300	3.420x10 ⁻¹³
	$r^2 = 0.998$	8 ,		an an ann an Anna an A		b =4.	654x10	16
	a =9.002	×10 ⁻¹⁶				$k_{40}^{c} = 6.$	595x10 ⁻¹	10

Hydrolysis of Cellulose Acid and Ultrasound C(HC1)=4.0 M

T=40⁰C Frequency=17kHz

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C(Cellulose)=.0108gm/ml Power = 20.0w/cm²

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T(min)	C(gm/m1)	ī(s)	n _r	$\ln(n_r)/C$	Curve coefficients	[n]	M _w	
0							59200	4.820x10 ⁻¹⁵
90	.0036 .0033 .0028 .0023	166.11 160.55 151.53 142.73	1.558 1.506 1.421 1.339	123.19 124.07 125.57 126.86	r^{2} = .9988 b =-2837.7551 k''= -0.1590	133.44	26400	5.435x10 ⁻¹⁴
180	.0036 .0033 .0028 .0023	154.67 150.23 142.99 136.02	1.451 1.409 1.341 1.276	103.37 103.94 104.86 105.92	r ² = .9989 b =-1951.0204 k"= -0.1600	110.38	21400	1.020x10 ⁻¹³
270	.0036 .0033 .0028 .0023	148.56 144.75 138.46 132.40	1.394 1.358 1.299 1.242	92.19 92.68 93.36 94.20	r ² = .9981 b =-1524.4898 k''= -0.1600	97.68	18700	1.529x10 ⁻¹³
360	.0036 .0033 .0028 .0023	144.97 141.53 135.81 130.26	1.360 1.328 1.274 1.222	85.37 85.86 86.46 87.11	r ² = .9972 b =-1315.3061 k"= -0.1620	90.15	17100	2.000x10 ⁻¹³
450	.0036 .0033 .0028 .0023	142.11 138.87 133.65 128.53	1.333 1.303 1.254 1.206	7984 80.11 80.73 81.30	r^2 = .9978 b =-1141.8367 k''= -0.1620	83.92	15800	2.535x10 ⁻¹³
540	.0036 .0033 .0028 .0023	140.34 137.29 132.30 127.47	1.316 1.288 1.241 1.196	76.36 76.64 77.11 77.70	r^2 = .9964 b =-1024.4898 k" = -0.1600	80.03	15000	2.963x10 ⁻¹³
630	.0036 .0033 .0028 .0023	138.13 135.27 130.66 126.13	1.296 1.269 1.226 1.183	71.95 72.15 72.65 73.10	$r^{2}=$.9967 b =- 903.0612 k''= -0.1600	75.17	14000	3.644x10 ⁻¹³
720	.0036 .0033 .0028 .0023	136.80 134.08 129.66 125.33	1.282 1.258 1.216 1.176	69.26 69.47 69.91 70.34	r^2 = .9986 b =- 839.7959 k''= -0.1610	72.26	13400	4.156x10 ⁻¹³
f	r ² =0.998	4				b =5.	671x10 ⁻	16
	a =7.098	x10 ⁻¹⁶				$k_{40}^{s} = 8.$	037x10 ⁻	10

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Hydrolysis Of Cellulose Acid Only C(HCl)=2.0 M

т=50⁰С

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C(Cellulose)=.0108gm/ml

T(min)	C(gm/m1)	ī(s)	nr	ln(n _r)/C	Curve coefficients	[n]	M. W	
0							59200	4.820x10 ⁻¹⁵
60	.0036 .0033 .0028 .0023	174.52 168.07 157.72 147.63	1.637 1.576 1.479 1.385	136.91 137.94 139.87 141.54	r ² = .9991 b =-3595.9184 k''= -0.1600	149.85	30000	3.704x10 ⁻¹⁴
120	.0036 .0033 .0028 .0023	161.02 156.03 147.73 139.78	1.510 1.464 1.386 1.311	114.54 115.42 116.50 117.78	r^{2} = .9976 b =-2444.8980 k''= -0.1610	123.39	24200	7.056x10 ⁻¹⁴
180	.0036 .0033 .0028 .0028	154.64 150.23 143.05 135.99	1.451 1.409 1.342 1.276	103.31 103.94 105.01 105.83	r^2 = .9961 b =-1954.0816 k''= -0.1600	110.38	21400	1.020x10 ⁻¹³
240	.0036 .0033 .0028 .0023	150.18 1-6.12 139.65 133.34	1.409 1.371 1.310 1.251	95.18 95.53 96.41 97.27	r ² = .9958 b =-1636.7347 k''= -0.1600	101.01	19400	1.370x10 ⁻¹³
300	.0036 .0033 .0028 .0023	147.48 143.70 137.65 131.73	1.383 1.340 1.291 1.236	90.14 90.47 91.26 91.99	r ² = .9972 b =-1448.9796 k''= -0.1600	95.31	18200	1.659x10 ⁻¹³
360	.0036 .0033 .0028 .0023	145.01 141.49 135.82 130.26	1.360 1.327 1.274 1.222	85.45 85.77 86.48 87.11	r^{2} = .9983 b =-1297.9592 k''= -0.1600	90.10	17100	2.000x10 ⁻¹³
420	.0036 .0033 .0028 .0023	143.63 140.32 134.81 129.46	1.347 1.316 1.265 1.214	82.80 83.26 83.82 84.43	r^2 .9971 b =-1231.6327 k''= -0.1620	87.27	16500	2.226x10 ⁻¹³
480	.0036 .0033 .0028 .0023	141.65 138.50 133.31 128.26	1.329 1.299 1.250 1.203	78.94 79.30 79.82 80.38	r^2 = .9995 b =-1097.9592 k" = -0.1600	82.90	15600	2.634x10 ⁻¹³
	r ² =0.998	8		<u></u>	$b = 5.316 \times 10^{-16}$			
	a =6.117:	к10 ⁻¹⁵			$k_{50}^{c} = 7.534 \times 10^{-10}$			10

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Hydrolysis of Cellulose Acid and Ultrasound C(HC1)=2.0 M

T=50[°]C Frequency=17kHz C(Cellulose)=.0108gm/ml Power = 200w/cm²

T(min)	C(gm/m1)	t(s)	nr	$ln(n_r)/C$	Curve coefficients	[n]	M _w	
0							59200	4.820x10 ⁻¹⁴
60	.0036 .0036 .0028 .0023	169.16 163.26 153.69 144.53	1.587 1.531 1.442 1.356	128.24 129.14 130.63 132.31	r^{2} = .9991 b =-3119.3878 k''= -0.1600	139.44	27700	4.705x10 ⁻¹⁴
120	.0036 .0033 .0028 .0023	157.16 152.47 144.90 137.48	1.474 1.430 1.359 1.290	107.80 108.42 109.60 110.57	r^{2} = .9984 b =-2156.1224 k''= -0.1610	115.57	22500	8.779x10 ⁻¹⁴
180	.0036 .0033 .0028 .0023	151.06 146.97 140.30 133.88	1.416 1.379 1.316 1.256	96.81 97.29 98.07 99.03	r^{2} = .9974 b =-1695.9184 k''= -0.1600	102.89	19800	1.288x10 ⁻¹³
240	.0036 .0033 .0028 .0023	147.00 143.31 137.34 131.45	1.379 1.344 1.288 1.233	89.24 89.65 90.46 91.06	r^{2} = .0062 b =-1423.4694 k''= -0.1600	94.37	18000	1.715x10 ⁻¹³
300	.0036 .0033 .0028 .0023	143.64 140.32 134.80 129.46	1.347 1.316 1.264 1.214	82.81 83.26 83.79 84.43	r^{2} = .9969 b =-1219.3878 k''= -0.1610	87.23	16500	2.226x10 ⁻¹³
360	.0036 .0033 .0028 .0023	141.86 138.71 133.48 128.39	1.331 1.301 1.252 1.204	79.35 79.76 80.28 80.82	r ² .9975 b =-1114.2857 k''= -0.1600	83.40	15700	2.584x10 ⁻¹³
420	.0036 .0033 .0028 .0023	140.11 137.08 132.16 127.32	1.314 1.286 1.240 1.194	75.90 76.18 76.73 77.19	r^{2} = .9986 b =-1005.1020 k''= -0.1590	79.52	14900	3.023×10 ⁻¹³
480	.0036 .0033 .0028 .0023	139.01 136.08 131.32 126.66	1.304 1.276 1.232 1.188	73.71 73.96 74.45 74.93	r^2 .9993 b =- 945.9184 k''= -0.1590	77.10	14400	3.349x10 ⁻¹³
	r ² =0.998	9				b =7.	003x10	-16
	a =5.056	×10 ⁻¹⁵				$k_{50}^{s} = 9$.	925x10	-10

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Hydrolysis of Cellulose Acid Only C(HC1)=3.0 M

т=50⁰С

.

C(Cellulose)=.0108gm/ml

T(min)	C(gm/m1)	ī(s)	n r	$\ln(n_r)/C$	Curve coefficients	[n]	м _w	™_w^3
0							59200	4.820×10^{-15}
30	.0036 .0033 .0028 .0023	175.45 168.99 158.37 148.18	1.645 1.585 1.487 1.390	138.33 139.59 141.34 143.15	r ² = .9990 b =-3671.4286 k''= -0.1600	151.62	30400	3.559×10 ⁻¹⁴
60	.0036 .0033 .0028 .0023	162.22 157.02 148.56 140.47	1.522 1.473 1.393 1.318	116.60 117.33 118.50 119.92	r^{2} = .9979 b =-2535.7143 k''= -0.1610	125.69	247700	6.636x10 ⁻¹⁴
90	.0036 .0033 .0028 .0023	155.61 151.00 143.70 136.55	1.460 1.416 1.348 1.281	105.05 105.49 106.63 107.61	r^2 = .9962 b =-2016.3265 k" = -0.1600	112.24	21800	9.652x10 ⁻¹⁴
120	.0036 .0033 .0028 .0023	151.03 146.99 140.32 133.86	1.417 1.379 1.316 1.256	96.75 97.33 98.12 98.96	$r^{2}=$.9989 b =-1680.6122 k"= -0.1590	102.83	19800	1.288x10 ⁻¹³
150	.0036 .0033 .0028 .0023	148.11 144.36 138.14 132.13	1.389 1.354 1.296 1.239	91.33 91.86 92.53 93.31	$r^{2}=9981$ b =-1496.9388 k''= -0.1600	96.75	18500	1.579x10 ⁻¹⁴
180	.0036 .0033 .0028 .0023	145.66 142.12 136.29 130.67	1.366 1.333 1.278 1.226	86.69 87.12 87.72 88.48	r^{2} = .9976 b =-1357.1429 k''= -0.1620	91.57	17400	1.898x10 ⁻¹³
210	.0036 .0033 .0028 .0023	144.09 140.71 135.14 129.72	1.352 1.320 1.268 1.217	83.68 84.10 84.69 85.30	r^2 .9991 b =-1234.6939 k''= -0.1590	88.15	16700	2.147x10 ⁻¹³
240	.0036 .0033 .0028 .0023	142.77 139.49 134.13 128.93	1.339 1.308 1.258 1.209	81.13 81.46 82.01 82.65	r ² = .9985 b =-1164.2857 k''= -0.1600	85.31	16100	2.396x10 ⁻¹³
	$r^2 = 0.998$ a = 7.029	7 ×10 ⁻¹⁵	k	b =9. $k_{50}^{c} = 1.$	915x10 ⁻³ 405x10 ⁻⁹	16		

Hydrolysis of Cellulose Acid and Ultrasound C(HC1)=3.0M

T=50⁰C Frequency=17kHz

C(Cellulose)=.0108gm/ml Power = 200w/cm²

T(min)	C(gm/m1)	īt(s)	n r	ln(n _r)/C	Curve coefficients	[n]	M.w	<u>™</u> _3
0							59200	4.820×10^{-15}
30	.0036 .0033 .0028 .0023	169.82 163.89 154.27 144.90	1.593 1.537 1.447 1.359	129.32 130.31 131.97 133.42	r^{2} = .9989 b =-3166.3265 k''= -0.1600	140.75	28000	4.555x10 ⁻¹⁴
60	.0036 .0033 .0028 .0023	157.83 153.10 145.40 137.88	1.480 1.436 1.364 1.293	108.98 109.67 110.83 111.83	r^{2} = .9987 b =-2202.0408 k''= -0.1610	116.93	22800	8.437x10 ⁻¹⁴
90	.0036 .0033 .0028 .0023	151.27 147.19 140.46 134.01	1.419 1.381 1.318 1.257	97.19 97.74 98.48 99.45	r^2 .9969 b =-1709.1837 k''= -0.1600	103.34	19900	1.269x10 ⁻¹³
120	.0036 .0033 .0028 .0023	147.66 143.95 137.81 131.86	1.385 1.350 1.293 1.237	90.48 91.00 91.68 92.42	$r^{2}=9984$ b =-1471.4286 k''= -0.1600	95.81	18300	1.632x10 ⁻¹³
150	.0036 .0033 .0028 .0023	144.53 141.10 135.50 129.98	1.356 1.324 1.271 1.219	84.53 84.94 85.64 86.18	r ² = .9964 b =-1279.5918 k"= -0.1610	89.16	16900	2.072x10 ⁻¹³
180	.0036 .0033 .0028 .0023	141.87 138.69 133.49 128.39	1.331 1.301 1.252 1.204	79.37 79.72 80.30 80.82	r ² = .9992 b =-1118.3673 k"= -0.1610	83.41	15700	2.584x10 ⁻¹³
210	.0036 .0033 .0028 .0023	140.54 137.50 132.48 127.59	1.318 1.290 1.243 1.197	76.75 77.11 77.59 78.11	$r^{2}=$.9987 b =-1032.6531 k''= -0.1590	8049	15100	2.904x10 ⁻¹³
240	.0036 .0033 .0028 .0023	140.10 137.10 132.15 127.33	1.314 1.286 1.240 1.194	75.88 76.22 76.70 77.22	$r^{2}=$.9993 b =-1020.4082 k''= -0.1610	79.57	14900	3.023x10 ⁻¹³
1 4., 164. W 194. W	r ² =0.992	5	(* 1.)) 6 67-14 - 87 19700 6 47 4 44 44 44 44 44 44 44 44 44 44 44 4	k tantan angangan pertapakan kerangkan kerangkan kerangkan kerangkan kerangkan kerangkan kerangkan kerangkan ke	b =1.	307x10	15
	a =7.938	x10 ⁻¹⁵				$k_{50}^{s} = 1.$	852x10 ⁻⁹	9

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Hydrolysis of Cellulose Acid Only C(HCl)=4.0 M

т=50⁰с

r

C(Cellulose)=.0108gm/ml

T(min)	C(gm/m1)	t(s)	n r	ln(n _r)/C	Curve coefficients	[ŋ]	м w	
0							59200	4.820x10 ⁻¹⁵
30	.0036 .0033 .0028 .0023	164.73 159.29 150.49 141.93	1.545 1.494 1.412 1.331	120.87 121.68 123.11 124.42	r ² = .9997 b =-2744.8980 k"= -0.1610	130.75	25800	5.823x10 ⁻¹⁴
60	.0036 .0033 .0028 .0023	153.32 148.98 142.00 135.21	1.438 1.397 1.332 1.268	100.93 101.40 102.37 103.33	r ² = .9987 b =-1864.2857 k"= -0.1610	107.60	20800	1.111x10 ⁻¹³
90	.0036 .0033 .0028 .0023	147.66 143.93 137.84 131.85	1.385 1.350 1.293 1.237	90.48 90.95 91.76 92.39	r ² = .9967 b =-1481.6327 k"= -0.1610	95.84	18300	1.632×10 ⁻¹³
120	.0036 .0033 .0028 .0023	144.12 140.68 135.14 129.73	1.352 1.320 1.268 1.217	83.74 84.03 84.69 85.34	$r^{2}=9974$ b =-1247.9592 k''= -0.1600	88.19	16700	2.147×10 ⁻¹³
150	.0036 .0033 .0028 .0023	141.45 138.28 133.15 128.13	1.327 1.297 1.249 1.202	78.55 78.82 79.39 79.94	r^2 .9986 b =-1081.6327 k''= -0.1590	82.42	15500	2.685x10 ⁻¹³
180	.0036 .0033 .0028 .0023	139.44 136.49 131.66 126.92	1.308 1.280 1.235 1.191	74.57 74.87 75.37 75.82	$r^{2}=$.9993 b =- 964-2857 k''= -0.1580	78.05	14600	3.213x10 ⁻¹³
210	.0036 .0033 .0028 .0023	138.13 135.27 130.66 126.13	1.296 1.269 1.226 1.183	71.95 72.15 72.65 73.10	r^2 .9967 b =- 903.0612 k''= -0.1600	75.17	1400	3.644x10 ⁻¹³
240	.0036 .0033 .0028 .0023	137.01 134.29 129.84 125.46	1.285 1.260 1:218 1:177	69.69 69.95 70.40 70.79	$r^{2}0.9990$ $b_{n=-}^{2} 851.0204$ $k_{n=-}^{2} -0.1610$	72.76	13500	4.064x10 ⁻¹³
	r ² =0.998	7			$b = 1.695 \times 10^{-15}$			
	a =9.148	×10 ⁻¹⁵				$k_{50}^{c} = 2.6$	402x10 ⁻⁹)

Hydrolysis of Cellulose Acid and Ultrasound C(HC1)=4.0 M

T=50⁰C Frequency=17kHz

C(Cellulose)=.0108gm/ml Power =200w/cm²

T(min)	C(gm/ml)	r(s)	n r	$ln(n_r)/C$	Curve coefficients	[n]	м _w	™_w ⁻³
0					a na pa demonse og a artikulegi skiller fra store en generalegi af blad for fakter af den som en store en store		59200	4.820x10 ⁻¹⁵
30	.0036 .0033 .0028 .0023	161.48 156.43 148.09 140.04	1.515 1.467 1.389 1.314	155.33 116.19 117.37 118.59	r ² = .9988 b =-2481.6327 k''= -0.1610	124.31	24400	6.884x10 ⁻¹⁴
60	.0036 .0033 .0028 .0023	150.37 146.35 139.83 133.46	1.410 1.373 1.312 1.252	95.53 96.01 96.88 97.66	r ² = .9995 b =-1650.0000 k''= -0.1600	101.47	19500	1.349x10 ⁻¹³
90	.0036 .0033 .0028 .0023	145.22 141.72 135.96 130.40	1.362 1.329 1.275 1.223	85.85 86.27 86.85 87.58	r ² = .9978 b =-1311.2245 k''= -0.1600	90.57	17200	1.965x10 ⁻¹³
120	.0036 .0033 .0028 .0023	141.65 138.50 133.31 128.26	1.329 1.299 1.250 1.203	78.94 79.30 79.82 80.38	r ² = .9995 b =-1097.9592 k''= -0.1600	82.90	15600	2.634x10 ⁻¹³
150	.0036 .0033 .0028 .0023	139.23 136.29 131.48 126.80	1.306 1.278 1.233 1.189	74.15 74.43 74.88 75.41	r ² = .9985 b =- 963.2653 k''= -0.1600	77.61	14500	3.280x10 ⁻¹³
180	.0036 .0033 .0028 .0023	136.79 134.10 129.66 125.33	1.283 1.258 1.216 1.176	69.24 69.52 69.91 70.34	r ² = .9992 b =- 836.7347 k''= -0.1600	72.26	13200	4.156x10 ⁻¹³
210	.0036 .0033 .0028 .0023	135.92 133.28 129.00 124.80	1.275 1.250 1.210 1.171	67.47 67.66 68.08 68.49	r ² = .9979 b =- 794.8980 k''= -0.1610	70.31	13000	4.552x10 ⁻¹³
240	.0036 .0033 .0028 .0023	135.03 132.51 128.34 124.26	1.267 1.243 1.204 1.166	65.64 65.90 66.25 66.61	$r^{2}=$.9985 b =- 737.7551 k''= -0.1580	68.31	12600	5.000x10 ⁻¹³
	r ² =0.996	0				b =2.	129x10 ⁻	15
	a =7.516	×10 ⁻¹⁵				$k_{50}^{s} = 3.$	018x10 ⁻	9

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1. In the second se

Hydrolysis of Cellulose Acid Only C(HCl)=2.0 M

т=60⁰с

C(Cellulose)=.0108gm/m1

T(min)	C(gm/ml)	E(s)	n _r	$ln(n_r)/C$	Curve coefficient	[n]	M _w	
0						1	59200	4.820×10^{-15}
30	.0036 .0033 .0028 .0023	162.66 157.42 149.96 140.71	1.526 1.477 1.397 1.320	117.36 118.10 119.46 120.66	r^2 = .9993 b =-2559.1837 k"= -0.1600	126.57	24900	6.477x10 ⁻¹⁴
60	.0036 .0033 .0028 .0023	151.07 146.94 140.33 133.87	1.417 1.378 1.316 1.256	96.82 97.23 98.15 99.00	r^{2} = .9981 b =-1703.0612 k"= -0.1610	102.91	19800	1.288x10 ⁻¹³
90	.0036 .0033 .0028 .0023	145.90 142.29 136.48 130.80	1.369 1.335 1.280 1.227	87.15 87.48 88.21 88.91	r^2 .9981 b =-1372.4490 k''= -0.1620	92.05	17500	1.866x10 ⁻¹³
120	.0036 .0033 .0028 .0023	142.56 139.27 133.98 128.80	1.337 1.306 1.257 1.208	80.72 80.98 81.21 82.21	r^2 = .9968 b =-1166.3265 k''= -0.162	84.88	16000	2.441x10 ⁻¹³
150	.0036 .0033 .0028 .0023	140.10 137.09 132.17 127.32	1.314 1.286 1.240 1.194	75.88 76.20 76.75 77.19	r^2 = .9974 b =-1015.3061 k''= -0.1600	79.55	14900	3.023x10 ⁻¹³
180	.0036 .0033 .0028 .0023	138.12 135.28 130.67 126.12	1.296 1.269 1.226 1.183	71.93 72.17 72.68 73.07	r^2 .9969 b =- 893.8776 k"= -0.1580	75.14	14000	3.644x10 ⁻¹³
210	.0036 .0033 .0028 .0023	137.01 134.29 129.84 125.46	1.285 1.260 1.218 1.177	69.69 69.95 70.40 70.79	r^{r} = .9990 b =- 851.0204 k''= -0.1610	72.76	13500	4.064x10 ⁻¹³
240	.0036 .0033 .0028 .0023	134.59 132.11 128.00 124.00	1.262 1.239 1.201 1.163	64.74 64.99 65.30 65.70	r^2 .9970 b =- 723.4694 k"= -0.1590	67.35	12400	5.245x10 ⁻¹³
	r ² =0.992	4				b =2.	050x10	15
	a =1.376	×10 ⁻¹⁵				$k^{c}_{60} = 2.$	906x10 ⁻⁹	9

-	1	69	-
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Hydrolysis of Cellulose Acid and Ultrasound C(HC1)=2.0 M

т=60⁰С Frequency=17kHz -----

T

C(Cellulose)=.0108gm/ml Power =200w/cm²

T(min)	C(gm/ml)	t(s)	n _r	$\ln(n_r)/C$	Curve coefficients	[n]	M _w	M
0							59200	4.82x10 ⁻¹⁵
30	.0036 .0033 .0028 .0023	158.28 153.44 145.71 138.15	1.485 1.440 1.367 1.296	109.77 110.54 111.59 112.68	r^{2} = .9988 b =-2214.2857 k''= -0.1600	117.79	23000	8.219x10 ⁻¹⁴
60	.0036 .0033 .0028 .0023	148.11 144.36 138.14 132.13	1.389 1.354 1.296 1.239	91.33 91.86 92.53 93.31	r^{2} = .9981 b =-1496.9388 k''= -0.1600	96.75	18500	1.579x10 ⁻¹³
90	.0036 .0033 .0028 .0023	142.77 139.49 134.13 128.93	1.339 1.308 1.258 1.209	81.13 81.46 82.01 82.65	r ² = .9985 b =-1164.2857 k''= -0.1600	85.31	16100	2.396x10 ⁻¹³
120	.0036 .0033 .0028 .0023	139.66 136.69 131.83 127.06	1.310 1.282 1.237 1.192	75.01 75.31 75.83 76.30	r ² = .9995 b =- 996.9388 k"= -0.1610	78.60	14700	3.148x10 ⁻¹³
150	.0036 .0033 .0028 .0023	137.01 134.29 129.84 125.46	1.285 1.260 1.218 1.177	69.69 69.95 70.40 70.79	$r^{2}=$.9990 b =- 851.0204 k''= -0.1610	72.76	13500	4.064x10 ⁻¹³
180	.0036 .0033 .0028 .0023	135,69 133.10 128.82 124.67	1.273 1.248 1.208 1.169	67.00 67.25 67.59 68.04	r ² = .9967 b =- 786.7347 k''= -0.1610	69.83	12900	4.658x10 ⁻¹³
210	.0036 .0033 .0028 .0023	133.93 131.49 127.52 123.59	1.256 1.233 1.196 1.159	63.37 63.56 63.96 64.26	r^2 .9965 b =- 697.9592 k''= -0.1610	65.88	12100	5.645x10 ⁻¹³
240	.0036 .0033 .0028 .0023	132.83 130.52 126.68 122.93	1.246 1.224 1.188 1.153	61.08 61.32 61.60 61.93	r^2 = .9967 b =- 639.7959 k''= -0.1590	63.40	11600	6.407x10 ⁻¹³
	$r^2 = 0.999$	2				b =2.	652×10^{-1}	15

 $a = 1.431 \times 10^{-15}$

 $k_{60}^{s} = 3.758 \times 10^{-9}$
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Hydrolysis of Cellulose Acid Only C(HCl)=3.0 M

T=60⁰C

C(Cellulose)=.0108gm/ml

T(min)	C(gm/m1)	ī(s)	n r	$\ln(n_r)/C$	Curve coefficients	[n] '	м w	<u>™</u> _w ^{−3}
0	na an a				2.1.1.1.1.1.1.1.1.1.1.1.1.1.1.1.1.1.1.1		59200	4.820×10^{-15}
30	.0036 .0033 .0028 .0023	152.64 148.39 141.48 134.81	1.432 1.392 1.327 1.265	99.70 100.20 101.06 102.04	r ² = .9986 b =-1795.9184 k''= -0.1590	106.14	20500	1.161x10 ⁻¹³
60	.0036 .0033 .0028 .0023	143.66 140.31 134.80 129.46	1.348 1.316 1.264 1.214	82.85 83.24 83.79 84.43	r^{2} = .9990 b =-1201.0204 k''= -0.1580	87.18	16500	2.226x10 ⁻¹³
90	.0036 .0033 .0028 .0023	138.77 135.90 131.16 126.53	1.302 1.275 1.230 1.187	73.23 73.56 74.01 74.48	r^2 .9988 b =- 951.0204 k''= -0.1620	76.67	14300	3.420x10 ⁻¹³
120	.0036 .0033 .0028 .0023	135.93 133.28 129.00 124.80	1.275 1.250 1.210 1.171	67.49 67.66 68.08 68,49	$r^{2}=$.9962 b =- 782.6531 k"= -0.1580	70.28	13000	4.552x10 ⁻¹³
150	.0036 .0033 .0028 .0023	133.50 131.10 127.19 123.33	1.252 1.230 1.193 1.157	62.48 62.66 63.04 63.34	r ² = .9975 b =- 673.4694 k"= -0.1600	64.90	11900	5.934x10 ⁻¹³
180	.0036 .0033 .0028 .0023	132.17 129.92 126.18 122.53	1.240 1.219 1.184 1.149	59.70 59.92 60.19 60.51	$r^{2}=$.9976 b =- 611.2245 k"= -0.1590	61.91	11300	6.931x10 ⁻¹³
210	.0036 .0033 .0028 .0023	131.31 129.12 125.52 122.00	1.232 1.211 1.177 1.144	57.88 58.05 58.32 58.63	r ² = .9990 b =- 573.4694 k"= -0.1600	59.94	10900	7.722x10 ⁻¹³
240	.0036 .0033 .0028 .0023	130.21 128.13 124.69 121.33	1.221 1.202 1.170 1.138	55.55 55.72 55.95 56.23	r ² = .9983 b =- 515.3061 k"= -0.1560	57.41	10400	8.890x10 ⁻¹³
	r ² =0.996	6				b =3.	729x10	15
	a =8.450	x10 ⁻¹⁵				$k_{60}^{c} = 5.$	285x10	9

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Hydrolysis of Cellulose Acid and Ultrasound C(HCl)=3.0 M

T=60⁰C Frequency=17kHz

C(Cellulose)=.0108gm/ml Power =200w/cm²

T(min)	C(gm/m1)	īt(s)	n _r	ln(n _r)/C	Curve coefficients	[n]	м _w	
0							59200	4.820x10 ⁻¹⁵
30	.0036 .0033 .0028 .0023	148.56 144.74 138.50 132.39	1.393 1.358 1.299 1.242	92.17 92.66 93.46 94.16	r^2 = .9987 b =-1534.6939 k''= -0.1610	97.72	18700	1.529x10 ⁻¹³
60	.0036 .0033 .0028 .0023	140.11 137.08 132.16 127.32	1.314 1.286 1.240 1.194	75.90 76.18 76.73 77.19	r^{2} = .9986 b =-1005.1020 k''= -0.1590	79.52	14900	3.023x10 ⁻¹³
90	.0036 .0033 .0028. .0023	136.13 133.50 129.16 124.93	1.277 1.252 1.212 1.172	67.90 68.16 68.53 68.95	r ² = .9992 b =- 798.9796 k"= -0.1590	70.78	13100	4.448x10 ⁻¹³
120	.0036 .0033 .0028 .0023	133.51 131.09 127.18 123.33	1.252 1.230 1.193 1.157	62.50 62.64 63.01 63.34	r ² = .9958 b =- 661.2245 k"= -0.1570	64.86	11900	5.934x10 ⁻¹³
150	.0036 .0033 .0028 .0023	131.53 129.32 125.68 122.14	1.234 1.213 1.179 1.146	58.35 58.52 58.77 59.13	r^2 = .9931 b =- 590.8163 k''= -0.1620	60.46	11000	7.513x10 ⁻¹³
180	.0036 .0033 .0028 .0023	130.00 127.92 124.53 121.20	1.219 1.200 1.168 1.137	55.10 55.22 55.49 55.77	$r^{2}=$.9968 b =- 521.4286 k''= -0.1610	56.96	10300	9.151x10 ⁻¹³
210	.0036 .0033 .0028 .0023	129.55 127.53 124.20 120.93	1.215 1.196 1.165 1.134	54.14 54.30 54.54 54.80	r^2 = .9997 b =- 504.0816 k''= -0.1610	55.96	10100	9.706x10 ⁻¹³
240	.0036 .0033 .0028 .0023	128.02 126.14 123.05 119.05	1.201 1.183 1.154 1.126	50.84 50.97 51.22 51.40	r^2 .9954 b =- 437.7551 k''= -0.1590	52.42	9400	1.204x10 ⁻¹²
	r ² =0.995	7			,	ь =4.	884x10	15
	a =6.008	x10 ⁻¹⁵				$k_{60}^{s} = 6.$	922x10 ⁻⁹	9

Hydrolysis of Celluose Acid Only C(HC1)=4.0 M

т=60⁰С

C(Cellulose)=.0108gm/ml

T(min)	C(gm/ml)	ī(s)	n r	$ln(n_r)/C$	Curve coefficients	[n]	M.w	M _w ^{−3}
0							59200	4.820x10 ⁻¹⁵
30	.0036 .0033 .0028 .0023	145.44 141.90 136.16 130.52	1.364 1.331 1.277 1.224	86.27 86.65 87.38 87.98	r ² = .9984 b =-1331.6327 k''= -0.1610	91.06	17300	1.931x10 ⁻¹³
60	.0036 .0033 .0028 .0023	137.67 134.89 130.32 125.86	1.291 1.265 1.222 1.181	71.02 71.30 71.72 72.17	$r^{2}=$.9997 b =- 878.5714 k''= -0.1600	74.19	13800	3.805x10 ⁻¹³
90	.0036 .0033 .0028 .0023	133.70 131.32 127.35 123.46	1.254 1.232 1.195 1.158	62.89 63.17 63.49 63.80	r^{2} = .9929 b =- 686.7347 k''= -0.1610	65.40	12000	5.787x10 ⁻¹³
120	.0036 .0033 .0028 .0023	131.31 129.11 125.52 122.00	1.232 1.211 1.177 1.144	57.88 58.03 58.32 58.63	r ² = .9985 b =- 579.5918 k"= -0.1610	59.95	10900	7.722x10 ⁻¹³
150	.0036 .0033 .0028 .0023	129.78 127.72 124.37 121.06	1.217 1.198 1.167 1.136	54.63 54.75 55.03 55.26	r ² = .9973 b =- 494.8980 k"= -0.1560	56.40	10200	9.423x10 ⁻¹³
180	.0036 .0033 .0028 .0023	128.24 126.34 123.21 120.13	1.203 1.185 1.156 1.127	51.31 51.45 51.68 51.91	$r^2 = 1.0000$ b = -461.2245 k'' = -0.1640	52.97	9500	1.166x10 ⁻¹²
210	.0036 .0033 .0028 .0023	127.15 125.34 122.38 119.45	1.193 1.176 1.148 1.120	48.94 49.05 49.27 49.44	r ² = .9972 b =- 390.8163 k"= -0.1540	50.35	9000	1.372x10 ⁻¹²
240	.0036 .0033 .0028 .0023	126.50 124.75 121.87 119.06	1.187 1.170 1.143 1.117	47.52 47.62 47.78 48.02	r^2 = .9895 b =- 379.5918 k''= -0.1590	48.87	8700	1.519x10 ⁻¹²
	r ² =0.999	3				b =6.	404x10 ⁻	15
	a =1.312	×10 ⁻¹⁵				$k_{60}^{c} = 9.6$	076x10 ⁻	9

Hydrolysis of Cellulose Acid and Ultrasound C(HCl)=4.0 M

T=60⁰C Frequency=17kHz

C(Cellulose)=.0108gm/ml Power =200w/cm²

T(min)	C(gm/ml)	ī(s)	n _r	$\ln(n_r)/C$	Curve coefficients	[n]	М _w	
0							59200	4.820x10 ⁻¹⁵
30	.0036 .0033 .0028 .0023	142.99 139.70 134.30 129.06	1.341 1.310 1.260 1.211	81.55 81.92 82.46 83.09	r^{2} = .9990 b =-1172.4490 k''= -0.1590	85.77	16200	2.352x10 ⁻¹³
60	.0036 .0033 .0028 .0023	135.70 133.09 128.83 124.67	1.273 1.248 1.208 1.169	67.02 67.23 67.61 68.69	r^{2} = .9982 b =- 784.6939 k''= -0.1610	69.83	12900	4.658x10 ⁻¹³
90	.0036 .0033 .0028 .0023	132.19 129.90 126.19 122.53	1.240 1.218 1.184 1.149	59.74 59.88 60.22 60.51	r^2 .9971 b =- 605.1020 k''= -0.1580	61.90	11300	6.931x10 ⁻¹³
120	.0036 .0033 .0028 .0023	129.77 127.72 124.37 121.06	1.217 1.198 1.167 1.136	57.61 54.75 55.03 55.26	r^{2} = .9983 b =- 507.1429 k''= -0.1590	56.43	10200	9.423x10 ⁻¹³
150	.0036 .0033 .0028 .0023	127.37 125.54 122.54 119.59	1.195 1.178 1.149 1.122	49.42 49.53 49.74 49.95	r^{2} = .9994 b =- 410.2041 k''= -0.1580	50,89	9100	1.327x10 ⁻¹²
180	.0036 .0033 .0028 .0023	126.93 125.14 122.22 119.32	1.191 1.174 1.146 1.119	48.46 48.56 48.80 48.97	r^{2} = .9946 b =- 403.0612 k''= -0.1620	49.91	8900	1.419x10 ⁻¹²
210	.0036 .0033 .0028 .0023	126.06 124.35 121.54 118.79	1.182 1.166 1.140 1.114	46.55 46.64 46.81 47.03	r^2 = .9933 b =- 368.3673 k''= -0.1610	47.86	8500	1.628x10 ⁻¹²
240	.0036 .0033 .0028 .0023	125.19 123.55 120.89 118.25	1.174 1.159 1.134 1.109	44.63 44.69 44.89 45.05	r^2 .9917 b =- 334.6939 k''= -0.1590	45.82	8100	1.882x10 ⁻¹²
[r ² =0.993	7			an manan dikata manjakat sadi ayan ng mg	b =7.	904x10	15
	a =6.752	×10 ⁻¹⁵				$k_{60}^{s} = 1$.	120x10	8

CULCULATIONS AND MATHEMATICAL MODELS

The calculations performed involved three major categories, intrinsic viscosity ([n]) calculations, weight average molecular weight (\bar{M}_w) calculations, and rate constant calculations (k). The results of these calculations were used to find the order of the rate equation under the influence of acid only and acid combined with ultrasound. Then, the mathematical model was found that best agreed with the observed experimental data.

In calculating the intrensic viscosity for each sample the Kraemer equation was applied,

$$\frac{\ln(n_r)}{c} = [n] + k''[n]^2 c \qquad (1)$$

The duration required between samples was chosen by trial and error to meet the following criteria for highest precision. The efflux time is kept long, greater than 100 s., to minimize the need for applying corrections to the observed data. The solution concentrations were resticted to the range that gives relative viscosities between 1.1 and 1.5 for accuracy in extrapolating to c=0. Each sample was diluted to four different concentrations, efflux time of each was then used to calculate the curve coefficients, coefficient of detrmination (r²), and regression coefficients a and b which were then tabulated. Intrinsic viscosity was then calculated. Knowing the values of K and a of the Mark-Houwink-Sakurada equation, wich were previously evaluated experimentally, \overline{M}_{w} then can be calculated by means of:

$$\left[n\right] = K \bar{M}_{w}^{a}$$
⁽²⁾

Basedow, Ebert, and Ederer (123) proposed a general rate equation, relating the depolymerization rate to the number of bonds present in the polymer molecule,

$$\frac{dB}{d\tau} = -\frac{1}{\tilde{M}_n} = \frac{d\tilde{M}_n}{d\tau} = k'(\frac{\tilde{M}_n}{M_m})$$
(3)

where the number of bonds in a linear molecular chain is givn by,

$$B = \frac{\bar{M}_{n}(0)}{\bar{M}_{n}(\tau)} - 1,$$

dB is the number of chemical bonds broken per molecule with number average molecular weight (\overline{M}_n) in time interval dt, k' is the rate constant, M_{mon} is the molecular weight of the monomer, and n is the order of the equation of rate. In the case of the acid hydrolysis of a polymer, such as dextran or cellulose, the parameter k is a function of the hydrogen ion in the solution (a_H^+) , polymer concentration, and temperature. Keeping the polymer concentration constant, this equation can be written in the form:

$$-\frac{1}{\frac{M}{m}}\frac{d\overline{M}_{n}}{d\tau} = k \left(a_{H}^{+}\right)^{m} \left(\frac{M}{m}\right)^{n}$$
(4)

where k is function of temperature only.

The procedure used to determine the molecular weight in this study was to measure the intrinsic viscosity, which would lead to the evaluation of the viscosity average molecular weight (\bar{M}_v) . Since \bar{M}_v does not give a good estimate for the number of bonds in the molecule, and since \bar{M}_n can not be evaluated using the viscosity measurement, the weight mo-

lecular weight (\overline{M}_w) was used. The equation which relates intrinsic viscosity to weight average molecular weight (\overline{M}_{L}) is,

$$[n] = K \bar{M}_{w}^{a}$$
(5)

the values of K and a are tabulated by Meyerhoff (1961) and Kurata (1963 and 1966). In some polymers, equation (5) becomes less accurate for molecular weights below about 50,000; in this case Stockmayer (1963) with some theoretical justification proposed the equation,

$$[n] = K' M^{\frac{1}{2}} + K'' M$$
(6)

where the first term is determined by the short-range interactions, and the second term by long-range interactions.

DEXTRAN

As explained before, dextran concentration was kept constant for all the runs. Acid hydrolysis using hydrochloric acid was carried out at 45, 50, 60, and 70°C. At specified durations, a sample withdrawn, and the intrinsic viscosity was determined. Then, \overline{M}_W was calculated for each sample via equations (5) or (6). Another experiment was carried out under the identical conditions plus it was also irradiated with ultrasound waves of different frequencies and power. Ultrasound irradiation was started at the same moment when the acid was mixed with the dextran solution. The sound intensity and frequency were kept constant during the hydrolysis process.

To find the equation of rate, suppose \bar{x}_w is the weight average degree of polymerization. The molecular weight of the monomer (M mon) is 162, therefore

$$\bar{X}_{w} = \frac{\bar{M}_{w}}{162}$$
(7)

and equation of rate for $\bar{X}_{_{\mathbf{W}}}$ is,

$$\frac{d \bar{X}_{w}}{d\tau} = -k (\bar{X}_{w})^{n}.$$
(8)

Differentiating equation (7) with respect to τ yields

$$\frac{d \bar{X}_{w}}{dt} = \frac{1}{162} \frac{d \bar{M}_{w}}{dt} .$$
(9)

Now, substituting equation (8) into equation (9) gives

$$\frac{1}{162} \frac{d \overline{M}_{w}}{d\tau} = -k (\overline{X}_{w})^{n}$$
$$= -k (\frac{\overline{M}_{w}}{162})^{n}$$

with the result that

$$\frac{d \bar{M}_{w}}{d\tau} = -\frac{k}{(162)^{n-1}} \bar{M}_{w}^{n} .$$
(10)

Since dextran concentration is constant, k is a function of a_{H^+} and temperature, therefore equation (10) can be written in the form,

$$\frac{d M_{w}}{dt} = -\frac{k'}{(162)^{n-1}} (a_{H}^{+})^{m} \bar{M}_{w}^{n}$$
(11)

where the value of m has to be evaluated

In a single run, concentration of dextran is constant and both the activity of hydrogen ion and temperature are constants, therefore k also is a constant. The rate equation can be written in the form

$$-\frac{d \bar{M}_{w}}{d\tau} = k_{a11} \bar{M}_{w}^{n}$$
(12)

$$k_{all} = \frac{k}{(162)^{n-1}} \left(a_{H^+}\right)^m$$
(13)

where, k_{a11} is a constant for a single run.

To find the value of n, a differential method of analysis was used to analyse the data. A plot of \overline{M}_w versus t was drawn. The slope of the obtained curve was determined at suitably selected time values. These slopes $(\underline{d\ \overline{M}_w})$ are the rates of reaction at these molecular weights. The natural logarithms of these slopes and of \overline{M}_w were calculated. $\ln(-\frac{d\ \overline{M}_w}{d\tau})$ vs $\ln(\overline{M}_w)$ was plotted, which resulted in a straight line:

$$\ln \left(-\frac{d M_{w}}{dr} \right) = \ln k_{a11} + n \ln (\bar{M}_{w})$$
(14)

The slope of this line was equal to the value of the order of the rate equation, n. This procedure was applied on few runs where an average of the obtained n was calculated. The value obtained for this average is 4/3. A test then was performed on all the available data to verify the value of n. Further verification was also done, using data obtained by Antonini, Bellelli, Bonacci, Bruzzesi, Caputo, Chiancone, and Rossi-Fanelli, Rome, Italy 1960 (118). All the tests verified the value 4/3 for n, therefore the rate equation for the hydrolysis of dextran is

$$-\frac{d\bar{M}_{w}}{d\tau} = k_{all}\bar{M}_{w}^{4/3}$$
(15)

The rate equation under the effect of acid and ultrasound combined is the same as equation 12, except the value of the order n may be different than 4/3. The differential method was also used to analyse the data obtained in case of acid plus ultrasound. The value of n obtained is the same as that of the rate equation under the action of acid only. So that the rate equation of the hydrolysis of dextran under the action of acid only or the combined action of acid and ultrasound is

$$-\frac{\mathrm{d} M_{\mathrm{w}}}{\mathrm{d} \tau} = k_{\mathrm{all}} \bar{M}_{\mathrm{w}}^{4/3} \tag{16}$$

$$= \frac{k}{(162)^{1/3}} \bar{M}_{w}^{4/3}$$
(17)

Analysis of the data obtained under the effect of acid and ultrasonic waves frequencies in the range of 25 to 150 kHz in the power range of 0.4 to 1.93 w/cm^2 showed that n has the same value of 4/3, and the constat k is the same under identical conditions of temperature, dextran concentration, and activity of hydrogen ions. The average deviation of the experimental data for different runs with the same identical conditions is less than 1%, see graph page (185). Equation 17 can be integrated considering k a constant,

 $(\bar{M}_{w})^{-1/3} = (\bar{M}_{wo})^{-1/3} + \frac{k}{3(162)^{1/3}} \tau$

where

thus,

$$k = k' (a_{H}^{+})^{m}$$
 (19)

(18)

Equation 19 was used to calculate the constant k for each of the three frequencies 25, 60, and 150 kHz, then a straigh line was obtained for each frequency. The best straight line in each of these three frequencies are identical within a deviation of 1%. This is shown in the graph page (186).

To evaluate the value of the exponent m in equation 11, $a_{\rm H}^{+}$ was kept constant in each run, $(\bar{\rm M}_{\rm W})^{-1/3}$ was calculated at reaction time τ , plotting $(\bar{\rm M})^{-1/3}$ versus τ should produce a straight line of slope equal to $\frac{k}{3(162)^{1/3}}$. Linear regression analysis was applied to calculate the coefficients of determination (r²), and the regression coefficients a and b. The value of k then was calculated for each run from the value of the slope b using the equation,

$$b = \frac{k}{3(162)^{1/3}}$$
 (20)





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In the case of the hydrolysis under the effect of acid only k in equation 19 is considered as k^{c} , and in case of the hydrolysis under combined effect of acid and sound k is considered as k_{L}^{s} for low power ultrasound (0.4 to 1.93 w/cm²), and k_{H}^{s} for high power ultrasound (200 w/cm²). The mean activity coefficient of hydrochloric acid in water at different acid molarities and temperatures was obtained from data published by Harned and Ehlers, J. Am. Chem. Soc., 55, 2179 (1933),

$$a_{H^+} = No. \text{ of moles of Hcl x } \cancel{Y_+}.$$
 (21)

The value of k'^c was then calculated form equation 19. At the same temperature, it was found that the value of k'^c is constant and independent of $a_{\rm H}^+$ in the range of experimental error. Therefore m=1 and the rate equation for the hydrolysis of dextran under the effect of acid only in the range of the obtained data is

$$-\frac{d \bar{M}_{w}}{dr} = \frac{k'^{c}}{(162)^{1/3}} a_{H} + \bar{M}_{w}^{4/3}$$
(22)

Integrating equation 22, at contant temperature and a_{H}^{+} , gives,

$$(\tilde{M}_{w})^{-1/3} = (\tilde{M}_{wo})^{-1/3} + \frac{k'^{c}}{3(162)^{1/3}} a_{H}^{c} \tau$$
 (23)

Knowing the value of k'^C at different temperatures (45, 50, 60, and 70[°]C), the activation energy (E_a) can be calculated by applying the Arrhenius equation

$$k'^{c} = k'^{c}_{o} \exp(-E_{a}/RT) = \frac{k^{c}}{a_{H}^{+}}$$
 (24)

or

$$\ln (k^{c}/a_{H}^{+}) = \ln (k'_{o}^{c}) - (Ea/R)(\frac{1}{T})$$
(25)

Plotting $\ln(k^{c}/a_{H}^{+})$ versus $\frac{1}{T}$ gives a straight line of slope = E_{a}/R and intersection equal to $\ln(k'_{o}^{c})$. Applying linear regression analysis gives $E_{a}^{c} = E_{a}^{s} = 29986$ cal/mole and $k'_{o}^{c} = 2.001 \times 10^{18}$.

Hydrolysis of dextran under the combined effect of both acid and ultrasound is also a function of $a_{\rm H}^{}+$, the value of $k^{\rm S}/a_{\rm H}^{}+$ is not a constant. To establish a mathematical relation between $a_{\rm H}^{}+$ and $k^{\rm S}$, the relative enhancement ($E_{\rm H}^{}$) for high ultrasound intensity (200 w/cm²), and $E_{\rm L}^{}$ for low ultrasound intensity (.4 to 1.93 w/cm²) were calculated where,

$$E = 100 \ (k^{S} - k^{C})/k^{C}$$
(26)

The value of $E/a_{\rm H}^+$ was calculated, then an empirical relation between $E/a_{\rm H}^+$ and $a_{\rm H}^+$ was established. This relation is

$$E/a_{H}^{} + = \delta Exp (-Ba_{H}^{} +)$$
(27)

where **§** and B are constants.

$$\ln(E/a_{\rm H}^{+}) = \ln(\delta) - Ba_{\rm H}^{+}$$
 (28)

A plot of $\ln(E/a_{H}^{+})$ versus a_{H}^{+} gives a straight line of slope = B, and intersection equal to $\ln(\mathbf{S})$. By applying a linear regression analysis, it was found that,

and

Thus

$$\mathbf{\hat{S}}_{L} = 83.34$$

 $\mathbf{\hat{S}}_{H} = 83.18$
 $\mathbf{B}_{L} = 1.104$
 $\mathbf{B}_{H} = 0.803$

The value of \S_L is equal to $\$_H$ in the range of experimental error, but $B_L \neq B_H$ which shows it is a function of the sound intensity, therefore

$$\frac{E}{a_{H}^{+}} = \frac{k^{S} - k^{C}}{a_{H}^{+} k^{C}} \times 100 = \mathbf{S}_{Exp} (-B a_{H}^{+})$$

$$k^{S} = k^{C} + \frac{\mathbf{S}}{100} a_{H}^{+} k^{C} Exp (-B a_{H}^{+})$$

$$k^{S} = k^{C} \left[1+0.83262 a_{H}^{+} Exp (-B a_{H}^{+}) \right] . \qquad (28)$$

From equation 24

$$k^{c} = k'_{o}^{c} a_{H}^{+} Exp (- E_{a}/RT)$$

$$k^{s} = \left[k'_{o}^{c} a_{H}^{+} Exp (- E_{a}/RT)\right] \left[1+0.8326 a_{H}^{+} Exp (- B a_{H}^{+})\right]$$
(29)

so that

$$= \left[2.001 \times 10^{18} a_{H}^{+} \text{ Exp } (-E_{a}^{}/\text{RT}) \right] \times \left[1 + 0.83262 a_{H}^{+} \text{ Exp } (-B a_{H}^{+}) \right] .$$
(30)

To establish the validity of this empirical relation, the following plots were made:

1. $(k^{s} - k^{c})/a_{H^{+}} vs a_{H^{+}}$ at low and high ultrasound power, graph page(200).

2. E vs a_{H}^{+} at low and high ultrasound power, graph page(199).

- 3. Absolute enhancement $(k^{s} k^{c})$ vs a_{H} + at low and high ultrasound power, graph page (198).
- 4. k^{s} vs a_{H}^{+} at low and high ultrasound intensity, graph page (197).

The following graphs present the empirical curves as calculated via equation (30), and the corresponding data points

Т	1/T	с(н ⁺)	a(H ⁺)	kc	^{к^с/а} (н ⁺)	$k_{\rm L}^{\rm s}$	$E_{\overline{L}}^{k_{\overline{L}}^{S}-k^{C}}x100$	EL/a(H ⁺)	k ^s L-k ^c	$\frac{k_{L}^{s-k^{c}}}{a_{(H}^{+})}$
45 ⁰ C 318.15 ⁰ k	3.143x10 ⁻³	.5 1.0 1.5 2.0 `3.0 4.0	.3694 .7790 1.2776 1.8962 3.6270 6.2680	6.723×10^{-5} 1.249×10^{-4} 2.166×10^{-4} 6.337×10^{-4} 1.102×10^{-3}	1.820x10 ⁻⁴ 1.603x10 ⁻⁴ 1.695x10 ⁻⁴ 					
50 ⁰ C 323.15 ⁰ k	3.095x10 ⁻³	.5 1.0 1.5 2.0 3.0 4.0	.3672 .7697 1.2606 1.8654 3.5430 6.0720	1.298×10^{-4} 2.536×10^{-4} 6.199×10^{-4} 1.233×10^{-3} 2.125×10^{-3}	3.535×10^{-4} 3.295 \text{x10}^{-4} 3.323 \text{x10}^{-4} 3.480 \text{x10}^{-4} 3.500 \text{x10}^{-4} Average= 3.427 \text{x10}^{-4}	3.238×10^{-4} 7.425×10 ⁻⁴ 1.305×10 ⁻³ 2.138×10 ⁻³	27.68 19.78 5.84 0.61	35.96 10.60 1.65 0.10	7.020×10^{-5} 1.226×10^{-4} 7.200×10^{-5} 1.300×10^{-5}	9.1204×10^{-5} 6.5723×10^{-5} 2.0322×10^{-5} 2.1410×10^{-5}
60 [°] C 333.15 [°] k	3.002x10 ⁻³	.5 1.0 1.5 2.0 3.0 4.0	.3619 .7541 1.2267 1.8144 3.3810 5.6840	5.152x10 ⁻⁴ 1.035x10 ⁻³ 1.833x10 ⁻³ 2.595x10 ⁻³ 4.862x10 ⁻³ 8.303x10 ⁻³	1.426x10 ⁻³ 1.372x10 ⁻³ 1.494x10 ⁻³ 1.430x10 ⁻³ 1.438x10 ⁻³ 1.461x10 ⁻³ 1.461x10 ⁻³ Average= 1.437x10 ⁻³	$\begin{array}{r} 6.201 \times 10^{-4} \\ 1.317 \times 10^{-3} \\ 2.294 \times 10^{-3} \\ \hline \\ 5.218 \times 10^{-3} \\ 8.377 \times 10^{-3} \end{array}$	20.36 27.25 25.15 7.32 0.89	56.26 36.14 20.50 2.17 0.157	1.049×10^{-4} 2.820×10^{-4} 4.610×10^{-4} 3.560×10^{-4} 7.400×10^{-5}	2.8986×10^{-4} 3.7396 \times 10^{-4} 3.7581 \times 10^{-4} 1.0529 \times 10^{-4} 1.3019 \times 10^{-5}
70 [°] C 343.15 [°] k	2.914x10 ⁻³	.5 1.0 1.5 2.0	.3582 .7410 1.1958 1.7504	3.907x10 ⁻³ 9.581x10 ⁻³	5.273×10^{-3} 5.474×10^{-3} Average= 5.374 \times 10^{-3}	4.976x10 ⁻³	27.36	36.92	1.069x10 ⁻³ 	1.4426x10 ⁻³

Values of the constants of the equation of rate at low intensity ultrasound for dextran

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Т	1/T	с(н ⁺)	a(H ⁺)	k ^C	^k c ^{/a} (H ⁺)	k_H^S	$E_{H} = \frac{k_{H}^{s} - k^{c}}{k^{c}} \times 100$	^Е н ^{/а} (н ⁺)	k _H ^s −k ^c	$\frac{k_{\rm H}^{\rm s}-k^{\rm c}}{a_{\rm (H}^{\rm +})}$
45 [°] C 318.15 [°] k	3.143x10 ⁻³	.5 1.0 1.5 2.0 3.0 4.0	.3694 .7790 1.2776 1.8962 3.6270 6.2680	$\begin{array}{c} 6.723 \times 10^{-5} \\ 1.249 \times 10^{-4} \\ 2.166 \times 10^{-4} \\ \hline \\ 6.337 \times 10^{-4} \\ 1.102 \times 10^{-3} \end{array}$	1.820x10-4 1.603x10-4 1.695x10-4 1.747x10-4 1.758x10-4 Average= 1.725x10-4	8.276x10 ⁻⁵ 1.669x10 ⁻⁴ 2.937x10 ⁻⁴ 7.347x10 ⁻⁴ 1.138x10 ⁻⁴	23.10 33.63 35.60 15.94 3.27	62.53 43.17 27.44 4.39 0.52	1.553×10^{-5} 4.200×10^{-5} 7.710×10^{-4} 1.010×10^{-4} 3.600×10^{-5}	4.2041x10 ⁻⁵ 5.3915x10 ⁻⁵ 6.0348x10 ⁻⁵ 2.7847x10 ⁻⁵ 5.7435x10 ⁻⁶
50 ⁰ C 323.15 ⁰ k	3.095x10 ⁻³	.5 1.0 1.5 2.0 3.0 4.0	.3672 .7697 1.2606 1.8654 3.5430 6.0720	1.298×10^{-4} 2.536×10^{-4} 6.199×10^{-3} 1.233×10^{-3} 2.125×10^{-3}	3.535x10-4 3.295x10-4 3.323x10-4 3.480x10-4 3.500x10-4 Average= 3.427x10-4	1.640×10^{-4} $$	26.64 	72.55 17.53 4.69 0.59	3.420×10^{-5} $$ 2.027 \times 10^{-4} 2.050 \times 10^{-4} 7.600 \times 10^{-5}	9.3137×10^{-5} $$ 1.0866×10^{-4} 5.7861×10^{-5} 1.2516×10^{-5}
60 ⁰ C 333.15 ⁰ k	3.002x10 ⁻³	.5 1.0 1.5 2.0 3.0 4.0	.3619 .7541 1.2267 1.8144 3.3810 5.6840	5.152x10 ⁻⁴ 1.035x10 ⁻³ 1.833x10 ⁻³ 2.595x10 ⁻³ 4.862x10 ⁻³ 8.303x10 ⁻³	1.426x10 ⁻³ 1.372x10 ⁻³ 1.494x10 ⁻³ 1.430x10 ⁻³ 1.438x10 ⁻³ 1.461x10 ⁻³ Average= 1.437x10 ⁻³	6.271×10^{-4} $$	21.72 33.53 18.24 4.77	60.02 18.48 5.40 0.84	1.119×10^{-4} 4 8.700×10^{-4} 8.880×10^{-4} 3.960×10^{-4}	3.0920×10^{-4} -4 4.7950×10^{-4} 2.6264×10^{-4} 6.969×10^{-5}
70 [°] C 343.15 [°] k	2.914x10 ⁻³	.5 1.0 1.5 2.0	.3582 .7410 1.1958 1.7504	3.907×10^{-3} 9.581×10^{-3}	5.273×10^{-3} 5.574×10^{-3} Average= 5.374 \times 10^{-3}	 1.285x10 ⁻²	34.12	 19.49	 3.269x10 ⁻³	 1.8676x10 ⁻³

Values of the constants of the equation of rate at high intensity ulrtasound for dextran

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CELLULOSE

Hydrolysis of cellulose was carried out in a heterogeneous system; therefore, evaluating the order of the rate eqution required a tremendous number of trial and error calculations. To overcome this diffeculty, the calculations were processed on a high speed computer. A Digital corporation minicomputer PDP-11, VT 100 video terminal, and RT-120 printer were used.

Integrating equation 10 yields

$$(\bar{M}_{W})^{1-n} = (\bar{M}_{WO})^{1-n} + \frac{(n-1)k}{(162)^{n-1}}\tau.$$
 (31)

At a specified value of n, knowing \bar{M}_{wo} and \bar{M}_{w} at time τ , k can be calculated by applying equation 31. Letting k_{o} equal the calculated value of k at $\tau = \tau_{o}$, the time of the first sample withdrawn; k_{1} equal the value of k at time τ_{1} , and k_{2} the value of k at time τ_{2} , the time of the sample withdrawn relative to that withrawn at time τ_{1} ; the values of k, $k_{2} - k_{1}$, k/k_{o} , k_{2}/k_{1} and k/a_{H} + were calculated. At the correct value of n, $k_{2}-k_{1} = 0$, $k/k_{o} = 1$, and $k_{2}/k_{1} = 1$. Also, plotting $(\bar{M}_{w})^{1-n}$ versus τ should give a straight line. Therefore, the linear regression method was applied and the coefficient of determination (r^{2}) was calculated, using the equation

$$r^{2} = \frac{\left[\left(\bar{M}_{w}\right)^{1-n}\tau - \frac{\sum \tau \left(\bar{M}_{w}\right)^{1-n}}{N}\right]^{2}}{\left[\sum \tau^{2} - \frac{(\epsilon\tau)^{2}}{N}\right]\left[\sum \left(\bar{M}_{w}\right)^{2(1-n)} - \frac{\left(\sum (\bar{M}_{w}\right)^{1-n}\right)^{2}}{N}\right]}$$

where N is the number of samples. The Coefficient of Determination

should be equal to unity at the correct value of n. The values of n which give the closest value of r^2 to 1 for all runs are listed below. Control 4, 4, 3.8, 4.1, 4.2, 4.2, 3.7, 4.1, 4 Ultrasound 3.9, 4.1, 3.8, 4, 4.2, 4.1, 3.9, 4, 4.1 The average value of n was found equal to 4, for each hydrolysis under the influence of acid only and hydrolysis under the influence of both acid and ultrasound.

The procedure used to evaluate the value of m in equation (11) in the case of the cellulose was exactly the same as that used for dextran. The rate equation of the hydrolysis of cellulose either under the influence of acid only or under the action of both acid and sound is

$$\frac{d M_{w}}{d t} = -\frac{k'}{(162)} a_{H}^{a} + \bar{M}_{w}^{4}$$
(33)

The value of k'=k^C/a_H+ was calculated at 40, 50, and 70^oC. In the range of experimental error, it was found that k' is constant at each temperature. The average at each temperature was obtained and then the Arrhenius equation was applied to calculate E_a^c and E_a^s . This calculation showed that $E_a^c = E_2^s = 28623$ cal/mole and k' $_o^c = 9.389 \times 10^9$.

To create the mathematical relation between a_H^+ and k^s , E/a_H^+ was calculated where E is the relative enhancement percentage. Equation 27 was then applied; using linear regression analysis showed that,

$$\delta = 29.660$$

B = 0.336
r²= 0.9936

Therefore, the empirical relation, which relates k^{s} , k^{c} , and a_{H}^{+} is

$$k^{s} = k^{c} + \frac{S}{100} k^{c} a_{H}^{+} Exp(-B a_{H}^{+})$$
 (34)

But,

$$k^{c} = k'_{o}^{c} a_{H}^{+} Exp (-E_{A}^{/}RT)$$

$$= 9.389 \times 10^{9} (a_{H}^{+}) Exp (-28623/RT) \qquad (35)$$
therefore,

$$k^{s} = [9.389 \times 10^{9} (a_{H}^{+}) Exp (-28623/RT)] \times [1 + 0.2966 (a_{u}^{+}) Exp (-B a_{u}^{+})]. \qquad (36)$$

$$k^{s} = [9.389 \times 10^{9} (a_{H}^{+}) Exp (-28623/RT)] \times [1 + 0.2966 (a_{H}^{+}) Exp (-B a_{H}^{+})].$$
(36)

To show the validity of this empirical relation, the following

1. E vs
$$a_{H}^{+}$$
, graph page (207).

graphs were plotted,

- 2. $(k^{s} k^{c})/a_{H}^{+} vs a_{H}^{+}$, graph page(208).
- 3. $k^{s} k^{c} vs a_{H}^{+}$, graph page(206).
- 4. k^{s} vs a_{H}^{+} , graph page(205).

The continuous curve in each graph represents the empirical equation, the points placed in position on each curve represent the experimental data.

Т	1/T	C(H+)	a(H+)	k ^C	k ^C /a _(H+)	k ^S	$E = \frac{k^{s} - k^{c}}{k^{c}} \times 100$	E/a _(H+)	k ^s -k ^c	$\frac{k^{s}-k^{c}}{a_{(H+)}}$	
40 [°] C 313.15 [°] K	3.193x10 ⁻³	2.00 3.00 4.00	1.9204 3.7080 6.4640	1.955x10 ⁻¹⁰ 3.593x10 ⁻¹⁰ 6.595x10 ⁻¹⁰	1.018×10 ⁻¹⁰ 9.690×10 ⁻¹¹ 1.020×10 ⁻¹⁰ Average= 1.002×10 ⁻¹⁰	2.525x10 ⁻¹⁰ 4.705x10 ⁻¹⁰ 8.037x10 ⁻¹⁰	29.16 30.95 21.87	15.18 8.35 3.38	5.700x10 ⁻¹⁰ 1.112x10 ⁻¹⁰ 1.442x10 ⁻¹⁰	2.968x10 ⁻¹⁰ 2.999x10 ⁻¹¹ 2.231x10 ⁻¹¹	
50°C 323.15°K	3.095x10 ⁻³	2.00 3.00 4.00	1.8654 3.5430 6.0720	7.534x10 ⁻¹⁰ 1.405x10 ⁻⁹ 2.402x10 ⁻⁹	4.039x10 ⁻¹⁰ 3.966x10-10 3.956x10-10 Average= 3.987x10-10	9.925x10 ⁻¹⁰ 1.852x10 ⁻⁹ 3.018x10 ⁻⁹	31.74 31.81 25.65	17.01 8.98 4.22	2.391x10 ⁻¹⁰ 4.470x10 ⁻¹⁰ 6.160x10 ⁻¹⁰	1.282x10 ⁻¹⁰ 1.262x10 ⁻¹⁰ 1.014x10 ⁻¹⁰	-204-
60 [°] C 333.15 [°] K	3.002x10 ⁻³	2.00 3.00 4.00	1.8144 3.3810 5.6840	2.906x10 ⁻⁹ 5.285x10 ⁻⁹ 9.076x10 ⁻⁹	1.602x10 ⁻¹⁰ 1.563x10 ⁻⁹ 1.597x10 ⁻⁹ Average= 1.587x10 ⁻⁹	3.758x10 ⁻⁹ 6.922x10 ⁻⁹ 1.120x10 ⁻⁸	29.32 30.97 23.40	16.16 9.16 4.12	8.520x10 ⁻¹⁰ 1.637x10 ⁻⁹ 2.124x10 ⁻⁹	4.696x10 ⁻¹⁰ 4.842x10 ⁻¹⁰ 3.737x10 ⁻¹⁰	

Constants	of	the	equation	of	rate
	foi	cel	Llulose		

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CONCLUSION AND DISCUSSION

The hydrolysis of dextran in acidic medium was found to be a first order reaction with respect to the hydrogen acid activity (a_H^++) , and of the order of 4/3 with respect to the weight average molecular weight (\bar{M}_W) of dextran. Hydrolysis under the effect of ultrasonic waves did not change these orders, only the hydrolysis rate was increased, in other words, the rate constant was increased. Therefore, the rate equation of the hydrolysis of dextran in an acidic medium with or without irradiation with ultrasound can be represented in the form,

$$-\frac{d\bar{M}_{w}}{d\tau} = \frac{k'^{c \text{ or s}}}{(162)^{1/3}} a_{H}^{+} \bar{M}_{w}^{4/3}$$
(37)

integrating this equation gives

$$(\bar{M}_{w})^{-1/3} = (\bar{M}_{wo})^{-1/3} + \frac{k'^{c \text{ or s}}}{3(162)^{1/3}} a_{H}^{+} \tau.$$
 (38)

The activation energy (E_a) of this reaction was found to be equal to 30,000cal/mole for both cases. These results indicate that irradiating with ultrasonic waves does not affect the mechanism of the reaction; it only increases the reaction rate, by increasing the rate constant of the rate equation. Therefore, ultrasonic action appears to be a mechanical energy, similar to that produced from an agitation process.

The enhancement of the reaction rate under the effect of ultrasonic waves of the frequencies ranging from 17to150kHz was independent of fr-equency. Increasing the intensity of the ultrasound caused an increase in the reaction rate.

To relate the rate constant, k^{c} , under the effect of acid only (control), and that under both effects of acid and ultrasound combined,

 k^{s} , to the ultrasonic power (intensity) and the activity of hydrogen ions (a_{H}^{+}) , the relative enhancement $E = 100 (k^{s} - k^{c})/k^{c}$, and the absolute inhancement $(k^{s} - k^{c})$ were calculated, then related to the activity of hydrogen ions (a_{H}^{+}) . The empirical relation,

$$\frac{E}{a_{H}^{+}} = \mathbf{\delta} Exp(-B a_{H}^{+})$$
(27)

was established, then tested at the hydrogen ion activity $(a_{\rm H}^{+})$ which predicted the maximum enhancement. The experimental data was in a very good agreement with the predicted value using this equation.

It was found that $\mathbf{\hat{s}}$ is a constant independent of the ultrasound intensity and related to the polymer type. The constant B was found to be a function of ultrasound intensity and polymer type. The relationships of E vs a_H^+ , $(k^S - k^C)/a_H^+$ vs a_H^+ , $(k^S - k^C)$ vs a_H^+ , and k^S vs a_H^+ show that these empirical relation is valid in the range of the available experimental data.

Basedow and Ebert (123) showed that the hydrolysis of dextran in acidic medium (phosphoric acid) is a reaction of the order of 5/3 with respect to number average molecular weight \overline{M}_n . They also showed that the reaction order of a combined action of acid and ultrasound ranging between 4/3 to 5/3 with respect to \overline{M}_n depending on a limiting value of molecular weight. The method they used to measure \overline{M}_n was based on the separation of the polymer from the solution by precipitating with cold methanol at -30° C, then \overline{M}_n was determined by GPC. The margin of experimental error of this method is quite large because dextran molecules with degree of polymerization less than 5 stay in solution. Since the favorable position for polymer fractionation is close to the terminals (122), any factionation producing a molecule with degree of polmerization of 5 or less would not be detected. Nevertheless this results are in a good agreement with that obtained in this work. The hydrolysis of cellulose under the effect of an acid (HCl) was also shown to be a first order reaction with respect to hydrogen ion activity (a_{H}^{+}) , and forth order reaction with respect to \overline{M}_{w}^{-} . The rate equation for the hydrolysis of cellulose in acidic medium with or without the irradiation with ultrasonic waves in heterogeneous system is,

$$-\frac{d\bar{M}_{w}}{dr} = \frac{k'^{c \text{ or } s}}{(162)^{3}} a_{H}^{+} \bar{M}_{w}^{4}$$
(39)

integrating this equation,

So,

$$(\bar{M}_{w})^{-3} = (\bar{M}_{wo})^{-3} + \frac{3k' c^{ors}}{(162)^{3}} a_{H}^{+} \tau$$
 (40)

The relation between ultrasound enhancement and activity of hydrogen ions was found to be similar to that for dextran equation 27. Therefore,

$$\frac{k^{S}-k^{C}}{a_{H}^{H}+k^{C}} \times 100 = \mathbf{S} \exp(-B a_{H}^{H}+)$$
(41)

$$k^{s} = k^{c} + \frac{8}{100} k^{c} a_{H}^{+} Exp(-Ba_{H}^{+})$$
 (42)

$$= k^{c} \left[1 + \frac{\delta}{100} a_{H}^{+} Exp \left(-B a_{H}^{+} \right) \right]$$
(43)

This shows that the rate constant has been increased by the enhancement factor (F), where

$$F = \frac{\$}{100} a_{H}^{+} Exp (-B a_{H}^{+})$$
(44)

Equation 44 shows that the enhancement factor is a function of the activity of hydrogen ions in the reaction medium. This equation has a maximum which can be obtained by differenting with respect to $a_{\rm H}^+$ and

then equating to zero, therefore,

$$\frac{\mathbf{\delta}}{100} \left[-B a_{H}^{+} Exp \left(-B a_{H}^{+} \right) + Exp \left(-B a_{H}^{+} \right) \right] = 0$$
(45)

So,
$$B a_{H}^{+} = 1$$

Or $(a_{H}^{+})_{Max.} = \frac{1}{B}$ (46)

The maximum enhancements predicted by this relationship are at $a_H^{+=2.98}$ M for cellulose, and at $a_H^{+} = 1.25$ M for dextran at high intensity ultrasound, and at $a_H^{+} = 0.91$ M for dextran at low intensity ultrasound. These results agreed with the obtained experimental data.

The activation energy of cellulose hydrolysis is the same with or without irradiating with ultrasonic waves, which was found to be 28600 cal/mole. The rate constant of the control reaction k^{c} is a function of temperature and activation energy E_{a} ,

$$k^{c} = k_{o}^{c} a_{H}^{+} Exp (- E_{a}^{/RT})$$
 (47)

subistituting into equation 43 with equation 47,

$$k^{s} = k_{o}^{c} a_{H}^{+} Exp (-E_{a}^{/RT}) \left[1 + \frac{\delta}{100} a_{H}^{+} Exp (-B a_{H}^{+})\right]$$
 (48)

This equation relates \textbf{k}^{S} with $\textbf{E}_{a}^{},$ T, and $\textbf{a}_{H}^{}+$

RECOMMENDATIONS

Further work is recommended to invistigate the following:

- 1. The kinetics of dextran and cellulose under the effect of different acids such as sulfuric, and phosphoric acids.
- 2. The effect of ultrasound of higher wavelength than 150 kHz.
- 3. The effect of ultrasound power and its relation to the obtained constant B.
- 4. Studying the hydrolysis of other carbohydrates such as those present in body tissues and food.

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APPENDIX

COMPUTER PROGRAM TO CALCULATE

THE RATE CONSTANTS

```
10 OPEN "HYDRLS" FOR INPUT AS FILE #1
20 OPEN "LP:" FOR OUTPUT AS FILE #2
30 PRINT
40 FRINT "FROM (VALUE OF N)";
50 INPUT X
60 FRINT
70 FRINT "TO (VALUE OF N)";
80 INPUT Z
90 FRINT
100 FRINT "INCREMENT OF N";
110 INPUT D
120 N=X
130 IF END #1 THEN 890
140 PRINT #2,
150 FRINT #2,
160 INPUT #1,A$
170 FRINT #2, TAB(29)A$
180 INFUT #1,A$
190 FRINT #2,TAB(2?)A$
200 INPUT #1,A$,A2
210 PRINT #2, TAB(31)A$;A2
220 FRINT #2,
230 INPUT #1,A$
240 PRINT #2, TAB(34)A$
250 INPUT #1,A$
260 PRINT #2,
270 PRINT #2,A$;TAB(29) N=";N
280 PRINT #2,
290 PRINT #2, "R. TIME"; TAB(10) "M.W. "; TAB(22) "K"; TAB(33) "K2-K1";
300 PRINT #2, TAB(46) *K/K0*; TAB(57) *K2/K1*; TAB(69) *K/aH+*
310 FRINT #2,
320 INPUT #1,T0,M0
                           +.+++^^^^
330 F$=* ###
                 *****
                                                       #.###*^^^^
340 PRINT #2,USING F$,TO,MO
350 FRINT #2,
360 INPUT #1,T1,M1
370 IF N=1 THEN 920
3B0 K1=((M1^(1-N))-(M0^(1-N)))*((162)^(N-1))/((N-1)*T1)
390 F1$=*
                                                                     #.####^^^^
                                          #.###^^^^
400 K0=K1
410 Y=K1/K0
420 K3=K1/A2
430 PRINT #2, USING F$, T1, M1, K1, Y, K3
440 F=T0+T1
450 H=T0^2+T1^2
460 IF N=1 THEN 520
470 G=(M0/162)^(1-N)+(M1/162)^(1-N)
```

480 L=((M0/162)^(1-N))^2+((M1/162)^(1-N))^2 490 E=T0*(M0/162)^(1-N)+T1*((M1/162)^(1-N)) 500 IF N=1 THEN 520 510 GO TO 550 520 G=LOG(M0/162)+LOG(M1/162) 530 L=(LOG(M0/162))^2+(LOG(M1/162))^2 540 E=T0*LOG(M0/162)+T1*LOG(M1/162) 550 FOR I=1 TO 7 560 INPUT #1,T2,M2 570 IF N=1 THEN 940 580 K2=((H2^(1-N))-(H0^(1-N)))*((162)^(N-1))/((N-1)*T2) 590 K3=K2/A2 600 S=K2-K1 610 Y=K2/K1 620 Y1=K2/K0 630 FRINT #2,USING F1\$,5,Y 640 FRINT #2, USING F\$, T2, M2, K2, Y1, K3 650 K1=K2 660 H=H+T2^2 670 F = F + T2680 IF N=1 THEN 740 690 G=G+((M2/162)^(1-N)) 700 L=L+((M2/162)^(1-N))^2 710 E=E+T2*((M2/162)^(1-N)) 720 IF N=1 THEN 740 730 GO TO 770 740 G=G+LOG(M2/162) 750 L=L+(LOG(M2/162))^2 760 E=E+T2*LOG(M2/162) 770 NEXT I 780 P1=(F*G)/9 790 P2=(E-P1)^2 800 P3=F^2 810 F4=6^2 820 P1=(H-P3/9)*(L-P4/9) 830 P=P2/P1 840 PRINT #2, 850 FRINT #2, 860 P=INT(P*1074+.5)/1074 870 PRINT #2, TAB(64) * r2=*;P 880 GO TO 130 890 RESTORE #1 900 N=N+D 910 GO TO 960 920 K1=-LOG(M1/M0)/T1 930 GO TO 390 940 K2=-LOG(M2/M0)/T2 950 GO TO 590 960 IF (N-D)>Z THEN 980 970 GO TO 130 980 CLOSE #1,#2

990 END

A SAMPLE OF COMPUTER CALCULATIONS Acid conc.= 2 Mole Temp.= 40 Celcius a(H+)= 1.9204

Control

Conc.= 3.61000E-03 sm/ml				N= 4			
R.	TIME	M • W •	к	K2-K1	K/KO	К2/К1	K∕aH+
	0	59200					
12	20	36400	1.880E-10	2.2005-12	1.000E+00	1 0175100	9.787E-11
24	\$0	30000	1,902E-10	5418-13	1.012E+00	9.9975-01	9.906E-11
36	50	26600	1.902E-10	117E-11	1.012E+00	9.9385-01	9.903E-11
48	30	24400	1.890E-10	-•111E-11	1.006E+00	9.941E-01	9.842E-11
60	0	22800	1.879E-10	6.659E-13	9,997E-01	1.004E+00	9.784E-11
72	20	21500	1.886E-10	864E-12	1.003E+00	9.954E-01	9.819E-11
84	10	20500	1.877E-10	4.274E-12	9,987E-01	1.023E+00	9.774E-11
96	, O	19500	1.920E-10		1.021E+00		9.997E-11

r2= .9997

Acid conc.= 2 Mole Temp.= 40 Celcius a(H+)= 1.9204

			Sound			
Conc.= 3	.61000E	-03 sm/ml	N= 4			
R. TIME	M.W.	к	K2-K1	К/КО	K2/K1	K∕aH+
0	59200					
120	33900	2.462E-10		1.000E+00		1,282E-10
240	27700	2.494E-10	3+14/E-12	1.013E+00	1.013E+00	1.299E-10
360	24600	2.455E-10	4905-17	9.969E-01	9+843E-01	1.278E-10
480	22500	2.450E-10	6.118E-12	9.949E-01	1.0255+00	1.276E-10
600	20800	2.511E-10	-,312E-11	1.020E+00	9.876E-01	1.307E-10
720	19700	2.480E-10	1.905E-12	1,007E+00	1,008E+00	1.291E-10
840	18700	2.499E-10	4.770E-12	1.015E+00	1,019E+00	1.301E-10
960	17800	2.546E-10		1.034E+00		1.326E-10

COMPUTER PROGRAM TO FILE EXPERIMENTAL DATA

```
10 OPEN "HYDRLS" FOR INPUT AS FILE #1
20 OPEN "CHRLS" FOR OUTPUT AS FILE #2
30 IF END #1 THEN 70
40 LINPUT $1,A$
50 FRINT #2,A$
60 GO TO 30
70 FRINT
80 PRINT "Acid conc.";
90 INPUT D
100 IF D=0 THEN 430
110 PRINT #2, "Acid conc.=";D;"Mole"
120 PRINT
130 PRINT "Temperature(Celcius)";
140 INPUT T
150 FRINT #2, "Temp.=";T;"Celcius"
160 PRINT
170 PRINT "a(H+)"; .
180 INFUT A2
190 PRINT #2, *a(H+)=*;**,*;A2
200 PRINT
210 FRINT *Control or Sound(C or S)*;
220 INPUT L$
230 IF L$="C" THEN 270
240 IF L$<>"S" THEN 200
250 PRINT #2, "Sound"
260 GO TO 280
270 PRINT #2, "Control"
280 PRINT
290 FRINT *Concentration*;
300 INPUT C
310 IF C=0 THEN 420
320 PRINT #2, "Conc. = ";C; "sm/ml"
330 FOR I=1 TO 9
340 PRINT
350 PRINT "Reaction time(min.)";
360 INPUT T1
370 FRINT
380 FRINT "Molecular wt.";
390 INPUT M
400 PRINT #2, T1; *, *; M
410 NEXT I
420 GO TO 70
430 CLOSE #1,#2
440 NAME "CHRLS" TO "HYDRLS"
450 OPEN "HYDRLS" FOR INPUT AS FILE #1
460 OPEN "LP:" FOR OUTPUT AS FILE #2
470 IF END #1 THEN 700
480 FRINT #2,
490 PRINT #2,
500 INPUT #1,A$
510 PRINT #2, TAB(7)A$
520 INPUT #1,A$
```

530 PRINT #2, TAB(7)A\$ 540 INPUT #1,A\$,M 550 PRINT #2, TAB(10)A\$;M 560 INPUT #1,A\$ 570 PRINT #2, TAB(12)A\$ 580 PRINT #2, 590 INPUT #1,A\$ 600 FRINT #2,A\$ 620 FRINT #2, "Reaction time"; TAB(20) "Molecular wt." 630 FRINT #2, 640 FOR I=1 TD 9 650 F\$=* ***** ******* 660 INPUT #1,M1,M2 670 FRINT #2,USING F\$,M1,M2 680 NEXT I 690 GO TO 470 700 CLOSE #1,#2 710 END

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A SAMPLE OF COMPUTER FILING OF EXPERIMENTAL DATA							
Acid conc.= 2 Mole Temp.= 40 Celcius a(H+)= 1.9204 Control							
Conc.= 3.61000E-03	⊴m∕ml						
Reaction time	Molecular wt.						
0	59200						
120	36400						
240	30000						
360	26600						
480	24400						
600	22800						
720	21500						
840	20500						
960	19500						
Acid conc.= 2 Mole Temp.= 40 Celcius a(H+)= 1.9204 Sound							
Conc.= 3.61000E-03 gm/ml Reaction time Molecular wt.							
0	59200						
120	33900						
240	27700						
360	24600						
480	22500						
600	20800						
720	19700						
840	18700						
960	17800						
Acid conc.= 3 Mole Temp.= 40 Celcius a(H+)= 3.708 Control							
Conc.= 3.61000E-03	sm∕ml						
Reaction time	Molecular wt.						
0	59200						
120	30100						
240	24700						
360	21800						
480	19700						
600	18500						
720	17400						
840	16800						
960	15800						

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REFERENCES

- 1. Weissler, A., J. Acous. Soc. Am., 25, 651 (1953)
- Bitz, J., "Fundamentals of Ultrasonics" 2nd ed. Plenum press. New York, N.Y. (1966)
- Resnick, R. and Halliday, D., "Physics: Part II," Wiley, New York, N.Y. (1966)
- 4. Brown, B. and Goodman, J.E., "High Intensity Ultrasonic Industrial Application" Iliffe, London, (1965)
- 5. Weissler, A., J. accoust. Soc. Amer. 25, 651 (1953)
- Lindstrom, O. and Lamm, O., J. phys. and colloid. Chem. 55, 1138 (1951)
- 7. Rozenberg, L. D. "High Intensity Ultrasonic Fields" Plenum press N.Y. (1971)
- 8. Vigoureux, P. "Ultrasonics" John Wiley N.Y. (1951)
- 9. Herzfeld, K. F. and Litovitz, T. A. "Absorption and Dispersion of Ultrasonic Waves" Academic Press N.Y. (1959)
- 10. El'piner, I. E. "Ultrasound" Consultants Bureau N.Y. (1964)
- 11. Hueter, T. F. and Bolt, R. H. "Sonics" Wiley N.Y. (1955)
- 12. Jarman, P., J. acoust. Soc. Amer., 32, 1459 (1960)
- 13. Kornfeld, M. and Suvorov, L. J. appl. Phys., 15, 494 (1944)
- 14. Briggs, H. B., Johnson, J.B. and Mason, W. P. J. acoust. Soc. Amer., 19, 664 (1947)
- 15. Willard, G. W., J. acoust. Soc. Amer., 25, 669 (1953)
- 16. Pielemeier, W. H., J. acoust. Soc. Amer., 23,224 (1951)
- 17. Von Angerer, E. and Landenburg, R. Ann. Phys., Lpz. 66,293 (1921)
- Bergmann, L., Der Ultraschall, p353. S. Herzel Verlag, Zurich (1949)
- 19. Szent-Gyorgyi, "Chemical and biological effects of Ultrasonic radiation", Nature 131,378 (1933)

- 20. Gihr, H., and Wedekind, T., Der Ultraschall in der Medizin, Klin. Wschr. 19:25, (1940)
- 21. Khenokh, M. A., Effect of Ultrasound on Carbohydrate Solutions, Zhur. Obshchei Khim. 25:928 (1955)
- 22. El'piner, I. E., and Sokol'skaya, A. V., Effect of Ultrasound waves on carbohydrates, Biofiz. 2(2):225 (1957)
- 23. Thomas, Rene C. R., Acad. Sci., Ser. 270(7), 635-8(Fr) (1970)
- 24. Buchnea, D. Z., Zuckerind 11, 197-203 (1961)
- 25. Velikodnyi, P. L., and Chernogorenko, B.V. Sakharn Prom 38(12) 9-10 (1964)
- 26. Roikh, I. L., and Starkermann, A.S. Compt. rend. Sci U.R.S.S. 39,10-12 (1943)
- 27. El'piner, I. E., and Surova, M. D. Doklady Akad. Nauk S.S.S.R. 90,1083-6 (1953)
- 28. Woodcock, J. P., and Connolly, C. C., Acustica 21(1), 45-50 (1969)
- 29. Gaberyelski, W. N., and Marschlewski, z., Zur Kenntnis reduzierender Zucker, Z. Biockem. 265:50 (1933)
- 30. Mohern, M., Uber den Einfluss des Ultraschalles auf Ascorbinsaure, Dissertation, Koln (1938)
- 31. Kasahara, M., and Kawashima, K., Uber den Einfluss der Ultraakustischen Wellen auf das Vitamin C, Klin, Wochschr 16:1191 (1937)
- 32. El'gort, V. M., Markman, A. L., and El'piner, I. E., Effect of proteins on polarographic oxidation of acetaldenyde in fermenting media, Uzbekskit Khim. Zhur. 5:79 (1960)
- 33. El'piner, I. E., and Sokol, A. V., Action of Ultrasonic waves on aliphatic amino acids, Biofiz 3(2):190 (1958)
- 34. Robert, B. Prudhomme, R. O., and Grabar, P., Contribution a' l'etude du mecanisme d'action des Ultrasons. I. Oxydation des noyaux aromatique, Bull. Soc. Chim. Biol. 37:897, (1955)

- 35. Stein, G., and Weiss, J., Chemical actions of ionizing radiation on aqueous solutions. Part 4, The action of X rays on some amino acids, J. Chem. Soc. 3256, (1949)
- 36. Robert, B., Contribution a l'etude du meeanisme d'action des ultasons. 2. Sur la fixation de l'azote de l'air sur les noyaux aromatiques sous l'action des ultrasons, Bull. Soc. Chem. Biol. 37:911, (1955)
- 37. Iliboutry, L., The effect of ultrasound waves on some chemical reactions, J. chim. phys. 41:173 (1944)
- 38. Prudhomme, R. O., and Grabar, P., Etude de la denaturation des proteides. I. Action des ultrasons sur les proteides du serum de cheval normal et sur les acides amines cycliques, Bull. Soc. Chim. Biol. 29:122 (1947)
- 39. Khenokn, M. A., and Lapinskaya, E. M., Action of ultrasonic vibrations on solutions of gelatin and amino acids in presence of air, Doklady Akad. Nauk SSSR 80:921 (1951)
- 40. Khenokh, M. A., and Lapinskaya, E. M., Effect of ultrasound on aqueuos solutions of aromatic hydrocarbons, Zhur. Obshchei Khim. 26:2439 (1956)
- 41. Zechmeister, L., and Wallcave, L. On the cleavage of benzene, thiophene, and furan rings by means of ultrasonic waves, J. Am. Chem. Soc. 77:2853 (1955)
- 42. Zechmeister, L., and Magoon, E. F., On the ultrasonic cleavage of the pyridine ring, J. Am. Chem. Soc. 78:2149 (1956)
- Garay, K., and Berenski, G., The effect of ultrasonic Waves on benzopyrene, Experientia 4:272 (1948)
- 44. Werkman, C., and Wilson, R., Bacterial Physiology IL, (1954)
- 45. El'piner, I. E. Kats, Ts. B., Effect of ultrasonic waves on purine and pyrimidine bases, Doklady Akad. Nauk SSSR 82(4):611 (1952)

46. El'piner, I. E., and Sikol'skaya, A. V., Oxidation of biologically active substances in an ultrasonic field, Biofiz. 5:21 (1960) 47. Demann, W. and Asbach, H. R. Tech. Mitt. Krupp A3, 12 (1940) 48. Technical note. Electronics 23, 206 (1950) 49. Lindstrom, O. and Lamm, O., J. phys. Colloid Chem. 55,1139 (1951) 50. Freundlich, H. and Gillings, D. W., Trans. Faraday Soc. 34,649 (1938)51. Schmid, G., Z. phys. Chem. A186,113 (1940) 52. Weissler, A., J. appl. Phys. 21,171 (1950) 53. Klink, A., Midler, M. and Allegretti, J. Chem. Eng. Prog. Sym. Series 109,67 (1967) 54. Fogler, S. and Barnes, D. I&EC Fundamentals 7,2 (1968) 55. Doulah, M. S., J. applied Poly. Sci. 22,1735-1743 (1978) 56. Okkuama, M., J. applied Poly. Sci. 7,591-602 (1963) 57. Heymach, G. and Jost, D., J. poly. Sci 25,145-153 (1968) 58. Rassing, J. and Lassen, H., Acta Chem. Scand. 23 (1969) 59. Boucher, R. M., Brit. Chem. Eng. 15,3 (1970) 60. Aerstin, F., Timmerhaus, K. and Fogler, H., AIChE 13,3 (1967) 61. Couppis, E. and Klnging, G., AIChE 20,3 (1974) 62. Springer, E. L. and Harris, J. F. "Prehydrolysis of Aspen Wood with water and with Dilute Aqueous Sulphuric Acid", "USDA Forest Service Publication" Oct. (1981) 63. Converse, A. O. and Grethlein, H. E. "Acid Hydrolysis of Cellulosic Biomass", SERI Third Annual Biomass Energy Systems Conference, Golden, Colorado June (1979) 64. Lieser, T. and Ebert, R., Ann. 528, 276-95 (1937) 65. Lieser, T., Kolloid Z. 81, 234-41 (1937) 66. Lieser, T., Spinner u. Weber 55, No. 48,6 (1937) 67. Straus, P. and Levy, R., Ibid 735-6 (1942)

- 68. Staudinger, H. and Jurisch, I. Papier-Fabr. 37,181-4 (1939)
- 69. McParland, J., Grethlein, H. and Converse, A. "Sulfuric Acid Hydrolysis of Cellulosic Materials", Biomass Conversion, SERI, Denver, Colorado Dec. 18-20 (1978)
- 70. Millett, M. effand, M. and Caulfield, D., Am. Ch. Soc. (1979)
- 71. Jellinek, H. H. G., and White, G., "The degradation of longchain molecules by ultrasonic waves" J. Polymer Sci 7(1) :21 (1951)
- 72. Mark, H., Application of ultrasonics in high polymer research, J. Acoust. Soc. Am. 16:183 (1945)
- 73. Bresler, S. E., and Frenkel, Ya. I., On the shape and character of thermal motion of long-chain organic molecules and the elasticity of rubber-like substances, Acta Physicochim. USSR 11:485 (1939)
- 74. Kargin, V. A., and Sogolova, T. I., Flow of polyvinyl chloride unde the action of great forcrs, Doklady Akad. Nauk SSSR 108:662 (1956)
- 75. Mostafa, M. A., "Degradation of addition polymers by ultrasonics waves"J. Polymer Sci 33:295 (1958)
- 76. Mostafa, M. A., "Degradation of addition polymers by ultrasonic waves"J. Polymer Sci. 33(126):311 (1958)
- 77. Schmid, G. and Rommel, O., Zerreissen von Makromolekulen mit Ultraschall, Z. Elektrockem. 45(9):659 (1939)
- Okuyama, H., Der Ultraschallabbau langkettiger Molekule und der Mechanismus der Kavitation, II Z. Elektrochem 59(6):565 (1951)
- 79. Henglein, A. Die Auslosung und der Verlauf der polymerisation des Acrylamids unter dem Einflussvon Ultraschallwellen, Makromol. Chem 14(1):15 (1954)
- 80. Weissler, A., Depolymerization by ultrasonic irradiation: the role of cavitation, J. Appl. Phys. 21(2):171 (1950)

- 81. Weissler, A., Cavitation in ultrasonic depolymerization, J. Acoust. Soc. Am. 23(3):370 (1951)
- Prudhomme, R. O., and Grabar, P., Depolymerisations sous l'action des ultrasons, J. chim. phys. 46:667 (1949)
- Brett, H. and Jellinek, H., Degradation of long chain molecules by ultrasonic waves, J. Polymer sci 13(71):441 (1954)
- 84 Zapior, B. and Litynska, A., Dalsze badania nad wplywem pola udzwiekowego na sacharoze, Z. Naukowe Uniwersytetu Jagiellonskiego, Z. 11 (1966)
- 85. Zapior, B. and Litynska, A., Wplyw pola ultradzwiekowego na przebieg hydrolizy roztworow wodnych sachatrozy i dekstryny, Z. Naukowe Uniwersytetu Jagiellonskiego Z. 10 (1965)
- 86. Moon, S., Duchin, L. and cooney, J., Application of ultrasound to organic reactions, Tetrahedron letters No. 41 Pergamon Press 1td, England 3917-3920 (1979)
- 87. de Boer, J., The influence of van der Waals forces and primary bonds of binding energy, strength, and orientation, with special references to some artificial resins, Tran. Faraday Soc. 32(1):10 (1936)
- Allen, C. H., Frings, H. and Rudnick, I., J. acoust. Soc. Amer. 20,62 (1948)
- 89. Krusen, F. Sth. med., J. Nashville 45,55 (1952)
- 90. Freundlich, H, Sollner, K. and Rogowski F., Klin. Wschr. 11,1512 (1932)
- 91. Harvey, E. Biol. Bull. Wood's Hole 59,306 (1930)
- 92. Chambers, L. and Gaines, N., J. cell. comp. Physiol. 1,451 (1932)
- 93. Richard, W., J. appl. Physiol. 9,298 (1938)
- 94. Boyle, R., Froman, D. and Field, G. Canad., J. Res. 6,102 (1932)
- 95. Herrick, J. and Krusen, F., J. acoust. Soc. Amer. 26,236 (1954)
- 96. De Forest, R., Janes, J., Herrick, J. and Krusen, H., ibid. 34,21 (1953)
- 97. Rosenberger, H., Chirug 21,404 (1950)
- 98. Lehmann, J., J. acoust. Soc. Amer. 25,17 (1953)

- 99. Lehmann, J. and Vorschutz, R., Strahlentherapie 82,278 (1950)
- 100. Lehmann, J. and Vrschutz, R., ibid 81,639 (1950)
- 101. Hehre, E. J. and Hamilton, D.M., J. Biol. Chem. 192,161-174 (1951)
- 102. Neely, W. B. "Dextran: Structure and Synthesis" in Wolform, M. L. and Tipson, R. S., eds., "Advances in Carbohydrate Chemistry", Vol. xv, Academic Press, Inc. N.Y. 341-369 (1960)
- 103. F. M. Mazzolai, M. Nuovo Consiglio Nazionale Delle Ricerche, "La Ricerca Sci." Vol. 36,1307 (1966)
- 104. N. Tuchel "Studiu comparativ al procesului de hidroliza sub actiunea ultrasunetelor si a caldurii" Farmacia XXI, nr.4 (1973)
- 105. Neely, W. B. "Adu. Carbohydrate Chem." 15,341 (1960)
- 106. Abott, D. and Weigel, H., J. Chem. Soc. 816 (1966)
- 107. Goldstein, I. J. and Shelan, W. J., J. Chem. Soc. 816 (1962)
- 108. Abott, D., Bourne, E. J. and Weigel, H., J. Chem. Soc. (C),827 (1966)
- 109. Lindberg, B. and Svensson, S., Acta Chem. Scand. 22, 1907 (1968)
- 110. Tarr, H. L. A., and Hibbert, H. Can., J. Research 5,414 (1931)
- 111. Hassid, W. Z. and Barker, H. A., J. Biol. Chem 134,163 (1940)
- 112. Hehre, E. J. and Sugg, J.Y., J. Exptl. Med., 75,339 (1942)
- 113. Fairhead, E. C., Hunter, M. J. and Hibbert, H., Can. J. Research, B 16,151 (1938)
- 114. Daker, W. D. and Stacey, M., J. chem. Soc. 585 (1939)
- 115. Levi, I. Hawkins, W. L. and Hibbert, H., J. Am. Chem. Soc. 64,1959 (1942)
- 116. Ingelman, B. and Siegbahn, K., Nature, 154,237 (1944)
- 117. Scott, T. A., Hellman, N. N., and Senti, F. R., J. Am. Chem. Soc. 79,1178-1182 (1957)
- 118. Antonini, E., Bellelli, L., Bonacci, M. L., Bruzzesi, M. R., Caputo, A., Chiancone, E. and Rossi-Fanelli, A., Biopolymers 2,35-42 (1964)

- 119. Barker, P. J., "Dextrans" in Whister, R. L. and BeMiller, J. N., eds, Industrial Gums, Academic press, Inc. N.Y. (1959)
- 120. Wolff, A., Mellies, R. L., Lohmar, R. L., Hellman, N.N., Rogovin, S. P., Watson, P.R., Soloan, J.W., Hofreiter, B. T., Fisher, B. E., and Rist, C. E., Indst. Eng. Chem. 46,12 (1954)
- 121. Wolff, I. A., Mehltretter, C. L., Mellies, R. L., Watson, P. R., Hofreiter, B. T., Patrick, P. L. and Rist, C. E., Indst. Eng. Chem. 46,2 (1954)
- 122. Basedow, A. M., Ebert, K. H. and Ederer, H., J. Macromolecules, 11,4 (1978)
- 123. Basedow, A. M. and Ebert, K. H., Polymer Bulletin 1,299-306 (1979)
- 124. Basedow, A. M., Polymer Bulletin 2,337-342 (1980)
- 125. Basedow, A. M. and Ebert, K. H. "Zum Mechanisms des Abbaus von Polymeren in Losung durch ultraschall", Die Makromolekulare Chemie 176.745-767 (1975)
- 126.Kato, S., Suzuki, T., Nomura, H., and Miyahara, Y., Macromolecules 13,889-892 (1980)
- 127. Wise, L. E., Tappi 41,9, 14A (1958)
- 128. Irvine, J. C. and Hirst, E. L., J. Chem. Soc. 121,1585 (1922)
- 129. Hearon, W. M., Hiatt, G. D. and Fordyce, C. R., J. Am. Chem. Soc., 65,2449 (1943)
- 130. Spencer, C., Cellulosechemi, 10,61 (1929)
- 131. Hibbert, H. and Percival, E. V., J. Am. Chem. Soc., 52,3995 (1930)
- 132. Meyer, K. H. and Misch, L., Helv. Chim. Acta 20,232 (1937)
- 133. Hermans, P. H., "Physics and chemistry of cellulose fibers", Elsevier, N.Y. (1949)
- 134. Liang, C. Y. and Marchessault, R. H., J. Polymer Sci., 37,385 (1959)
- 135. Keller, A., Makromol. Chem., 34,1 (1959)
- 136. Lieser, T., Ann., 528,276 (1937)
- 137. Staudinger, H. and Ritzenthaler, B., Ber., 68,1225 (1935)
- 138. Hatch, R. S., Ind. Eng. Cgem., 16,104 (1944)

- 139. Heddle, W. J. and Percival, G.V., J. Chem. Soc. 249 (1939)
- 140. Lieser, T., Henrich, L. and Fichtner, F., Ann., 538,99 (1939)
- 141. Elias, H. G. "Polymer Handbook" Interscience Div., John Wiley and Sons, N.Y. (1966)