DIFFUSION STUDIES WITH NOVEL PLASTICS

BY

MARION TOOHEY CONWAY

A THESIS

PRESENTED IN PARTIAL FULFILLMENT OF

THE REQUIREMENTS FOR THE DEGREE

OF

MASTER OF SCIENCE IN CHEMICAL ENGINEERING

AT

NEWARK COLLEGE OF ENGINEERING

Newark, New Jersey

1973

ABSTRACT

The rates of diffusion through two fluorinated groups and two non-fluorinated groups of laboratory prepared membranes were compared with each other and with commercially available cellulose membranes. The membranes were evaluated, in particular, for possible use with the artificial kidney. Diffusion experiments were conducted with sodium chloride, urea and uric acid. Experimental results were compared to diffusion coefficients calculated in the literature for cellulose membranes. The results show that the rates of diffusion of all of the solutes tested for the laboratory prepared membranes are comparable to that of the cellulose membranes. The fluorinated group had a slightly higher diffusion coefficient with urea than the non-fluorinated group. However, the non-fluorinated membranes had a higher diffusion coefficient by an order of magnitude over the fluorinated membranes for sodium chloride and uric acid.

APPROVAL OF THESIS

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MARION TOOHEY CONWAY

FOR

DEPARTMENT OF CHEMICAL ENGINEERING

NEWARK COLLEGE OF ENGINEERING

BY

FACULTY COMMITTEE

APPROVED:

NEWARK, NEW JERSEY

MAY, 1973

ACKNOWLEDGEMENTS

I would like to thank Dr. D. S. Kristol for his advise and assistance; without his work on the novel plastics used in this work this thesis would not have been possible. I am also grateful to Paul Wynne for preparing the polymers used. I am most deeply appreciative of my husband, Hugh, whose patience and encouragement made this work possible. I am also grateful to Margaret Keaveny who typed the manuscript.

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I. INTRODUCTION

A. Object

The object of this thesis was to evaluate laboratory prepared plastics for possible use with the artificial kidney. Four groups of plastics were studied. Two groups were fluorine substituted and were compared to the non-fluorinated membranes. Since the fluorinated membranes should have higher mechanical properties, it would be desirable for them to have a higher diffusion coefficient.

B. Scope

Available data on diffusion coefficients for cellulose membranes from the literature were used for comparison with the calculated diffusion coefficients of the laboratory prepared membranes. Diffusion experiments with sodium chloride,urea and uric acid were conducted. Diffusion coefficients of the laboratory prepared membranes, especially the fluorinated ones, comparable to that of the cellulose membranes were sought. The work reported herein was conducted over the period from June 1971 to May 1973.

THEORY

Diffusion is a process in which molecules of a liquid or solute disperse or intermingle by virtue of their thermal energy. It is a spontaneous process which leads a system ultimately to thermodynamic equilibrium. Diffusion is accompanied by an increase in total entropy, or when it is conducted isothermally, by a decrease in total free energy. (14)

Fick's Laws

Fick's first law of diffusion states that species A diffuses more rapidly in the direction of decreasing mole fraction of A and that this process is dependent upon the temperature and solution composition. The Concentration gradient dC/dx at a certain point is the driving force for diffusion. The mathematical expression of this law is

$$Cv = -RTU(dC/dx) = -D(dC/dx) \qquad (1)$$

where R is the Gas Law constant, T is the absolute temperature and U is the molecular mobility. The negative sign indicates that the flux is in a down-gradient direction. The coefficient, D, is the Diffusivity. The concentration, C, times the velocity, v, can be expressed as the molecular flux, J, in units of moles per square centimeter of traverse area per second

$$J_x = -D(dC/dx) \qquad (2)$$

Fick's second law is similar to the first but it is expressed in terms of concentration which is experimentally measurable instead of molecular flux which must be determined indirectly.

The rate of change of flux with distance (dJ_x/dx) represents the rate of change of concentration with time (dC/dt). Therefore,

$$\frac{dC}{dt} = -D\left(\frac{d^2C}{dx^2}\right) \qquad (3)$$

The Diffusivity, which has the units of cm^2/sec is defined by equation 3. (2,14)

Theories of Diffusion in Liquids

Rigorous theories on the mechanisms of diffusion are not available. Two theories are covered in this dicussion: (a) Eyring's theory of absolute rates and (b) the hydrodynamic theory. Although these theories offer far from perfect models, they explain the relationships between diffusion and the structure of matter.

1. Eyring's Theory of Absolute Rates (5) assumes a simple model for the liquid state as its basis. It is assumed that molecules do not undergo any change in position unless they are first transformed to an intermediate and unstable configuration. Once they are transformed, they react according to a independent of the nature of the reactants and type of reaction. (14) The assumptions made by Eyring to fit the above model are as follows:

(1) A liquid is regarded as made up of "holes" moving about in matter. In a liquid at rest the individual molecules are constantly in motion. However, because of close packing the motion is largely confined to vibrations of each molecule with its nearest neighbors. A liquid at rest continually undergoes rearrangements in which one molecule at a time escapes from this interaction with its nearest neighbors into an adjoining hole. The molecules thus move in each of the cartesian coordinate

directions in jumps of λ length at a frequency of k per molecule. (2) (See Figure 1). Therefore, considering this model of a liquid, in order to diffuse in solution a molecule of solute and one of solvent are required to slip past each other.

(2) The standard free energy is the same in all the equilibrium positions the molecule occupies in the course of diffusion.

(3) The second assumption can hold only if the solution is ideal. Therefore, it is assumed that the solution is ideal.

(4) If the standard free energy is the same in the initial and final states and the energy barrier is assumed to be symmetrical, the free energy of activation will be the same in the forward and backward directions and therefore the rate constant, k, is the same in both directions

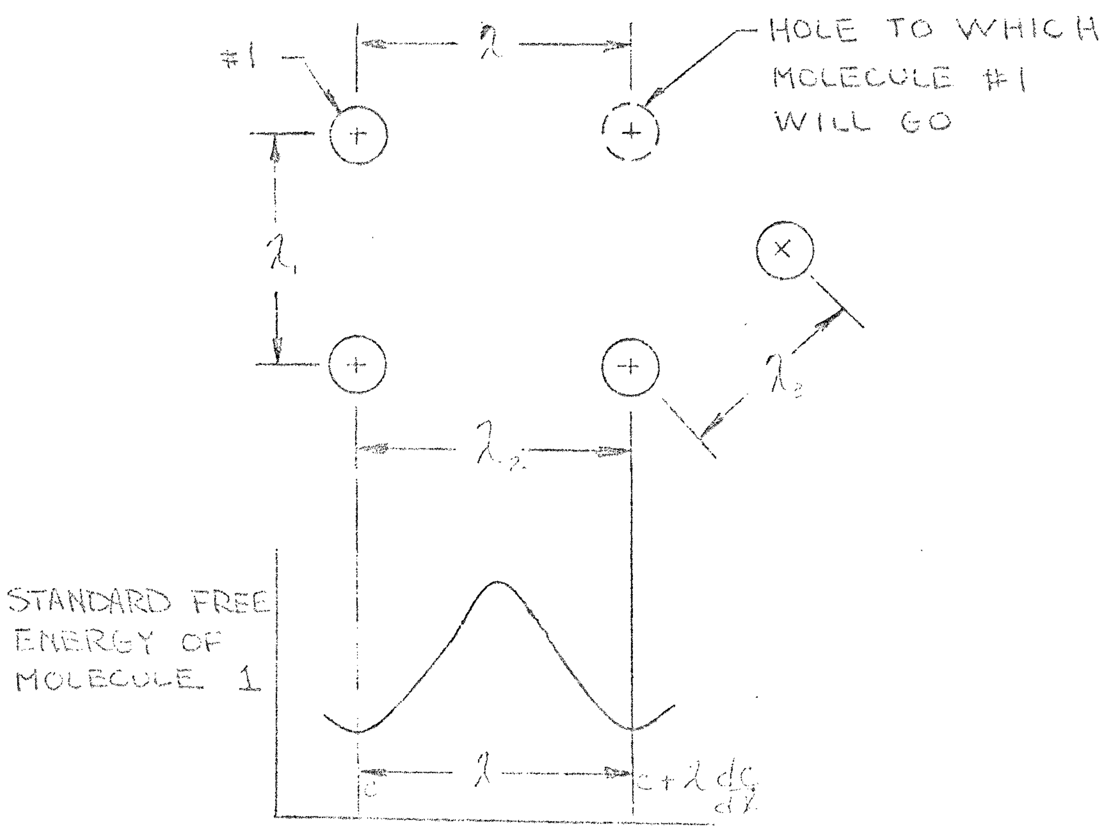


FIGURE 1

The rate equation is developed as follows:

The number of molecules moving in the forward direction through a cross section of one square centimeter is described as

$$v_f = NC\lambda k \qquad (4)$$

where N is Avagadro's Number, v_f is the flow in the forward direction and λ is the jump distance between two equilibrium positions.

The rate of movement in the backward direction is

$$v_b = N(C + \lambda \frac{dC}{dx})\lambda k \qquad (5)$$

The resultant flow is

$$v_f - v_b = -N\lambda^2 k\frac{dC}{dx} = v \qquad (6)$$

where the diffusion coefficient is $\lambda^2 k$. (5)

According to Eyring, if the mechanism of activation diffusion can be assumed identical with that of viscous flow, the relation between the self-diffusion coefficient and viscosity in liquids is

$$\frac{D\mu}{kT} = \frac{\lambda_1}{\lambda_2\lambda_3} \qquad (7)$$

where λ_1 is the distance between two adjacent layers and λ_2 and λ_3 are the distances between two neighboring molecules in the moving layer perpendicular to, and in the direction of motion, respectively. If it is assumed that the λ's are equal to the intermolecular distances, and that the molecules form a cubic lattice configuration, Equation 7 can be reduced to

$$\frac{D_{AA}\mu_A}{kT} = \left(\frac{N}{V_A}\right)^{1/3} \qquad (8)$$

for self-diffusion. D_{AA} is the self-diffusion coefficient and V_A is the molar volume of the solute, A. (11) This theory is important for its usefulness in correlating diffusion coefficients and measurable parameters such as viscosity, and thermodynamic activities.

Unfortunately, the difficulties of correlation are greatest in the systems which are of most practical interest, i.e., aqueous solutions at moderate temperatures. (14)

The relationship for self-diffusion derived from Eyring's Theory (Equation 8) differs by a factor of 2π from the expression for the self-diffusion coefficient according to the hydrodynamic theory. The hydrodynamic theory has been shown to fit experimental data better than Equation 8. However, a modification of Eyring's theory by Li and Chang (11) accounts for the discrepancy in the two theories. The modification of Eyring's theory uses the same model of liquid and assumption that in order to diffuse in solution a molecule of solute must slip past a molecule of solvent. However, it is assumed that the neighboring molecules are moving instead of fixed, and an equation is developed for relative velocity on this new basis:

$$v = \frac{2\sigma k' \Gamma \lambda}{\sigma - \gamma N k T} \tag{9}$$

where Γ is a uniform potential field applied to the diffusing molecules only, σ is the number of all the closest neighbors in all directions, and γ is the number in one layer. In terms of the Diffusion coefficient this becomes

$$\frac{D\mu}{KT} = \frac{\sigma - \gamma}{2\sigma}\left(\frac{N}{V_A}\right)^{1/3} \tag{10}$$

Equation 10 agrees with Eyring's relationship when the molecules form a cubic lattic configuration. In this case $\sigma = 6$ and $\gamma = 4$. (11)

2. The hydrodynamic theory states that the diffusivity of a single particle or solute molecule (A) through a stationary medium (B) is

$$D_{AB} = kT\, u_A / F_A = KTU \tag{11}$$

where u_A/F_A is the steady state velocity attained by the particle under the action of a unit force and this is defined as the mobility. Equation 11 is the Nernst-Einstein equation. Hydrodynamics offers a relationship between force and velocity for a rigid sphere moving in "creeping flow" (Reynolds Number $<<1$). If the possibility of slip at the sphere-fluid interface is taken into account then

$$F_A = 6\pi \mu_B \mu_A R_A \left(\frac{2\mu_B + R_A \beta_{AB}}{3\mu_B + R_A \beta_{AB}}\right) \tag{12}$$

where R_A is the radius of the diffusing particle and β_{AB} is the coefficient of sliding friction. There are two limiting cases of this theory:

A. No tendency for the fluid to slip at the surface of the diffusing particle: In this case β_{AB} is infinity and Equation 12 becomes Stokes' Law:

$$F_A = 6\pi \mu_B \mu_A R_A \tag{13}$$

and substitution into Equation 11 gives

$$\frac{D_{AB}\mu_B}{k\,T} = \frac{1}{6\pi R} \tag{14}$$

which is usually called the Stokes-Einstein equation. (2) This equation has been shown to be fairly good for describing the diffusion of large spherical molecules. Experimentally it has been shown by Friedman and Carpenter that the Stokes-Einstein equation is valid in dilute solutions for molecules weights down to 180 for various polyols and polysaccharides. This equation is adapted to the case of systems containing small and medium sized solutes and becomes

$$\frac{D_{AB}\mu_B}{k\,T} = \frac{1}{2AR_A} \tag{15}$$

The Stokes-Einstein equation is developed according to hydrodynamic theory for large spherical molecules. The factor, A, accounts for molecules of small and medium sizes and of shapes other than spherical. In the Stokes-Einstein equation, A corresponds to 3π, but in the above equation A may very from 3π to almost unity, as in the case of self-diffusion of the solvent. (14)

B. No tendency for the fluid to stick at the surface of the diffusing particle: In this case $\beta_{AB}=0$ and Equation 12 becomes

$$F_A = 4\pi \mu_B \mu_A R_A \tag{16}$$

and substitution in Equation 11 gives

$$\frac{D_{AB}\mu_B}{K\ T} = \frac{1}{4\pi R_A} \tag{17}$$

If the molecules are all alike (self-diffusion) and if they can be assumed to be arranged in a cubic lattice with all molecules just touching then $2R_A$ may be set equal to $(V_A/N_A)^{1/3}$ where V_A is the molar volume and N_A is Avagadro's Number and then equation 17 becomes

$$\frac{D_{AA}\mu_A}{K\ T} = \frac{1}{2\pi}\left(\frac{N_A}{V_A}\right)^{1/3} \tag{18}$$

It has been shown that Equation 18 predicts the self diffusion data for a number of liquids within 12 percent. (11)

Membranes

A membrane can be defined in simple terms as a phase acting as a barrier to the flow of molecular and ionic species present in the liquids contacting the two surfaces. When a membrane separates two solutions, the forces that normally cause a molecular or ionic flux in the absence of external magnetic and gravitational forces are: (a) difference of a chemical potential, $\Delta\mu$, (b) difference of electric potential, ΔE, (c) difference of pressure, ΔP, and (d) difference of temperature, ΔT (10). The specific force which was examined in detail in this work was that of $\Delta\mu$. The driving force, $d\mu/dx$, is proportional to the concentration gradient, dC/dx , when the activities can be assumed equal to the concentration as in dilute or perfect solutions. Since the driving force examined in this work is the concentration gradient, this aspect is covered in detail in the following theory.

The suitability of a given membrane for any particular operation is determined by a number of factors. Some basic requirements for an acceptable membrane are: a membrane should have chemical stability, mechanical strength, and low electrical resistance. (10) Other desirable properties which a membrane may have to become of practical importance are: (a) high ionic selectivity, (b) low salt diffusion in a membrane concentration cell, (c) low electroosmotic water transport, and (d) flexibility. The above ideal characteristics cannot be met by any single membrane material.

The membranes studied in this work have been developed in our laboratory with the intent of biological suitability.(9)There are three main factors which characterize the acceptability of a biocompatible membrane. It must be a regulator of concentration- and pressure-induced transport, a mechanical barrier, and a surface which is compatible with the biological environment (15).

Characterization of Membranes

A particular membrane may be characterized by its permeance, which is defined as the ratio of the rate of transport of a substance across the membrane to the difference in concentration of the substance on the two sides of the membrane. The permeance of a membrane depends on its surface area, thickness, chemical composition and morphology.

The permeability is often defined as the permeance per unit area. However, if permeability is to be considered a specific property of a material the following definition is more precise: Permeability is the ratio of the rate of transport of a substance across a unit area of a membrane to the driving force for the transport. This is the definition of permeability considered in the following theory, where the driving force is the chemical potential gradient but is estimated to be proportional to the concentration gradient. (6)

One of the possible uses for membranes studied in this work is hemodialysis. For this application the permeability to small molecules should be as large as possible and the permeability to macromolecules such as albumin, hemoglobin and virus particles should be essentially zero. (15)

Three factors can be used to evaluate membrane permeability and describe the permeation mechanism: (a) the effect of boundary layers, (b) the relationship between permeability and thickness, and (c) the solubility of the permeant in the membrane phase.

A. Instead of the permeability of a material, the permeance per unit area of material plus boundary layers of fluid is measurable. The effect of the boundary layers differs depending on the solute and membrane involved. For combinations giving high permeance per unit area, the boundary layer resistances can mask the differences between membranes. This seems to occur particularly in the case of low molecular weight solutes. For combinations which give low permeance per unit area, the boundary layer resistance may be only a small effect of negligible importance.

B. To evaluate the usefulness of potential membrane materials, consideration must be given to the permeability and the range of thickness in which a membrane may be fabricated for practical applications. A material which can be cast in the form of a thin but strong film may have a permeance per unit area equal to or better than a material with a higher permeability which must be prepared as a thicker film in order to be strong enough for use.

C. The solubility of the permeant in the membrane phase does affect the diffusion process. In the case of a single component permeating a membrane, the transport may occur as flow through existing pores or as molecular diffusion of the permeant through an homogeneous membrane phase. In the latter mechanism, the solubility of the permeant in the phase is of great importance. However, when there are two permeating components, a solvent and a solute, the solubility of the solute in the membrane may be relatively unimportant, if the amount of solvent contained in the membrane is great enough. In this case the solute may be considered to diffuse down a concentration gradient through the solvent with the membrane phase playing an indirect role. The membrane will complicate the diffusion path by creating barriers to diffusion, and it may effect the diffusion of the solute by changing the water structure.

This theory leads to the conclusions made by L.D. Ikenberry, H.K. Yasuda, and H.G. Clark (6) that for water soluble solutes permeating nonionic membranes:

(1) The membrane water content is the controlling factor in

permeation of solutes through such membranes.

(2) The permeability approaches a maximum at the diffusion coefficient of the solute in water.

(3) Membrane material must have at least a certain degree of equilibrium hydration (probably about 20%) to insure sufficiently fast transport of water soluble molecules.

(4) In general, the higher the hydration of a material, the poorer its strength.

Another factor that affects solute transport is the chemical composition of the membrane. Cellulose membranes, which are currently popular for use in hemodialyses, permit transport on the basis of a pore sieving mechanism whereby small solutes permeate quickly and larger ones more slowly. Recently, membranes of copolymers containing methylacrylate, which is similar to the polymers used in this work, have been prepared (12). These copolymer systems seem to allow solute diffusion through the membrane materials as well as through the pores. The suggested mechanism to describe this phenomenon is that dissolution of a permeant whose chemical structure is similar to the liquid-like structure of the membrane is facilitated by that similarity and moves under the influence of a concentration gradient.

Basic Concepts of Irreversible Thermodynamics Applied to Permeation of Membranes

Irreversible thermodynamics provides rigorous equations relating measurable properties of systems in which transport processes are taking place. The theory states:

(1) The thermodynamic variables for a non-equilibrium system are the same functions of the local state as the corresponding equilibrium quantities.

(2) The rate of entropy production inside such a system can be expressed as

$$\Upsilon = \sum_i J_i X_i \quad (i = 1, 2, \ldots n) \tag{19}$$

where X_i are the generalized thermodynamic forces.

(3) The flows J_i of Equation 19 are related linearly to the forces X_i by a general relation:

$$J_i = \sum_j L_{ij} X_j (i,j = 1,2,\ldots n) \tag{20}$$

where L_{ij} are the phenomenological coefficients.

(4) If the Ji's and the Xl's are mutually independent then the matrix of phenomenological coefficients is symmetric and $L_{ij} = L_{ji}$.(7)

These basic thermodynamic principles can be applied to describe membrane permeability.

For the permeation of a single solute in aqueous solution, the irreversible thermodynamic description of membrane transport is

$$J_v = L_p(\Delta P - \sigma_x)\Delta \pi_s \tag{21}$$

$$J_s = \bar{C}_s(1-\sigma_x) J_v + \omega \Delta \pi_s \tag{22}$$

where J_v and J_s are the net volume flux and solute flux. L_p, x and ω are the hydraulic conductivity, Staverman reflection coefficient and permeability coefficient respectively. $\bar{C}_s$ is the mean solute concentration in the membrane and ΔP and π_s are the hydrostatic and osmotic pressure differences between the solutions on either side of the membrane.

For the case of zero volume flow,

$$\omega = \frac{J_s}{\Delta \pi_s}\Big/_{J_v=0} = \frac{J_s}{RT\Delta \bar{C}_s}\Big/_{J_v=0} \qquad (23)$$

or

$$J_s = P_m \Delta \bar{C}_s \qquad (24)$$

where P_m is the membrane permeability. Fick's first law of diffusion across a membrane with a linear concentration gradient is

$$J_s = \frac{D_{eff} \Delta \bar{C}_s}{t} \qquad (25)$$

where D_{eff} is the effective Diffusion coefficient when the driving force is based upon concentrations in the external solution (at the membrane-solution interface) and t_m is the membrane thickness. (3) Therefore,

$$P_m = \frac{D_{eff}}{t_m} \qquad (26)$$

Effect of Boundary Layer Resistance

This analysis does not account for the boundary layer resistance. It has already been established that this can be an important factor in comparing membranes. Therefore, it is necessary, that the mass transfer resistance in the liquid phase and the measurement of true membrane permeability be discussed.

The experimental system which is the simplest and most popular configuration is the most often studied. It consists of two stirred chambers separated by an unsupported membrane. Initially, chamber 1 is charged with a solution of the solute and chamber 2 with the pure solvent. The overall permeability or mass transfer coefficient is obtained by monitoring the change in concentration with time. There are basically three approaches that have been suggested in order to account for the liquid phase mass transfer resistance in such a system: (1) estimates of a hypothetical stagnant diffusion film thickness, (2) operation above an empirically determined critical impeller speed where it is assumed that that the liquid mass transfer resistances are eliminated, and (3) use of a Wilson plot.

The modified Wilson plot method is the most rational and is therefore discussed in detail here. The diffusion coefficient is defined by the equation

$$-\frac{d(C/V)_2}{dt} = \frac{d(C/V)_1}{dt} = KA(C_2 - C_1) \tag{27}$$

Excluding the effect of volume transport Equation 27 integrates to

$$\ln\left[\frac{(C_1 - C_2)_t}{(C_1 - C_2)_0}\right] = -KAt\left[\frac{1}{V_1} + \frac{1}{V_2}\right] \tag{28}$$

where A is the area of the membrane, K is the overall mass transfer coefficient and V_1 and V_2 are the volumes of chambers 1 and 2, respectively. A plot of $\ln\left[\frac{(C_1 - C_2)_t}{(C_1 - C_2)_0}\right]$ versus time yields a straight line and K can be determined from the slope of the line. K^{-1} is plotted against a stirrer speed, n , reused to a power, a , as suggested by Wilson for separating wall and fouling coefficients from film coefficients in heat exchangers. The power, a , is varied until the best least squares line is fit. The data is extrapolated to infinite stirrer speed where the true membrane resistance is estimated. Values of a vary between -.5 and -.8. Leonard and Kaufman (8) have suggested -.68 as the best statistical fit. In keeping with Wilson's theory the fluid resistances may be broken down in series as

$$R_o = R_m + R_{f1} + R_{f2} \tag{29}$$

where Rm is the true membrane mass transfer resistance, and Rf_1 and Rf_2 are the liquid phase resistances. Or in terms of mass transfer coefficients:

$$\frac{1}{K} = \frac{1}{P_m} + \frac{1}{k_{f1}} + \frac{1}{k_{f2}} \qquad (30)$$

If the two liquid phase resistances are assumed identical, then

$$\frac{1}{P_m} = \frac{1}{K} - \frac{2}{k_f} \qquad (31)$$

This method is tedious but will yield a reasonably good estimation of the permeability with the boundary layer resistance accounted for (3,8).

All of these approaches have drawbacks, and a better approach by which the true membrane permeability may be determined has been suggested by Smith, Colton, Merrill and Evans (10). The theory is based on sound physical postulates and its development leads to a better understanding of the transport process involved in diffusion, particularly laminar, to turbulent transition and membrane flutter. Basically, the resultant method of determining boundary layer resistances is as follows: the overall measured mass transfer coefficient, K, is first assumed equal to the permeability, Pm, from which the Sherwood Number is calculated $\left(N_{Shw} = \frac{2P_m\sqrt{\frac{\nu}{\omega}}}{D}\right.$ where ν is the kinematic viscosity, and ω is the impeller rotational velocity). A correction factor $\phi(N_{Shw})$ is then estimated from a plot of $\phi(N_{Shw})$ versus N_{Shw} and the liquid phase resistances are calculated from the corrected correlation and subtracted from the overall resistance to yield the true membrane resistance. The Ø (Nshw) has been developed for the laminar boundary layer only. (13)

Existing Correlations Used to Estimate Diffusion Coefficients and Membrane Permeability

Some correlations used for estimating diffusion coefficients and membrane permeability have already been discussed. These, plus a few others will be summarized here with a statement of their applicability.

1. Eyring's theory leads to a correlation for self-diffusion when it can be assumed that the molecules form a cubic lattice configuration:

$$\frac{D_{AA}\,\mu_A}{\kappa T} = \left(\frac{N}{V_A}\right)^{1/3} \tag{8}$$

Li and Chang have suggested a modification of Eyring's theory by which the diffusion coefficient can be estimated when the molecules do not form a cubic lattice configuration:

$$\frac{D_{AA}\,\mu_A}{\kappa T} = \frac{\xi}{2\pi}\left(\frac{N}{V_A}\right)^{1/3} \tag{10}$$

The Hydrodynamic theory leads to the Stokes-Einstein equation in the case of the coefficient of sliding friction being infinity:

$$\frac{D_{AB}\,\mu_A}{\kappa T} = \frac{1}{6\pi R} \tag{14}$$

This equation is fairly good for describing diffusion of spherical molecules with molecular weights down to 180. Or it can be adapted to small and medium sized solutes as:

$$\frac{D_{AB}\,\mu_B}{\kappa T} = \frac{1}{2AR} \tag{15}$$

In the case of the coefficient of sliding friction equal to zero, the hydrodynamic theory leads to

$$\frac{D_{AB}\,\mu_B}{\kappa T} = \frac{1}{4\pi R_A}$$

and if a cubic lattice configuration is assumed for self diffusion, equation 17 becomes:

$$\frac{D_{AA}\,\mu_A}{\kappa T} = \frac{1}{2\pi}\left(\frac{N_A}{V_A}\right)^{1/3} \tag{18}$$

Wilke and Chang (15) have developed an empirical correlation on the basis of the Stokes-Einstein equation which is valid for small concentrations of A in B:

$$D_{AB} = 7.4 \times 10^{-8} \frac{(\psi_B M_B)^{1/2} T}{\mu V_A^{.6}} \qquad (32)$$

where M_B is the molecular weight of the solvent and ψ_B is an "association parameter" for the solvent. Recommended values of ψ_B are 2.6 for water, 1.9 for methanol, 1.5 for ethanol and 1.0 for benzene and other unassociated solvents. (2)

Recently two simple relationships have been suggested which can be used to predict self-diffusion coefficients of liquids with an average error of $\pm$ 4%. This is much better accuracy than any of the above correlations claim. Both relations were derived by using a general relation between transport coefficients of pure fluids and a molecular-kinetic-model of liquids. The first equation assumes that the molecular diameter can be expected to be proportional to the cube root of the critical volume of the solute. It should be good for most solvents except methanol, ethonal and others in which the group $\mu V D_{AA}/RT$ is strongly temperature dependent. The resultant relationship as:

$$\frac{\mu V D_{AA}}{RT} = .124 \times 10^{-16} V_c^{2/3} \qquad (33)$$

where Vc is the critical volume. The second equation suggests the possibility of a correlation for critical volume is terms of Tc and Lennard-Jones parameters:

$$\frac{\mu V D_{AA}}{RT} = .129 \times 10^{-16} \sigma^2 (\Omega_D / \Omega_V) T_c^{1/2} \qquad (34)$$

where σ is the Lennard-Jones distance parameter and Ω_D and Ω_V are generalized collision integrals for diffusion and viscosity. (4)

A relationship has been suggested by Smith (13) et. al. which is valid in the laminar flow region and it accounts for the correction of the liquid phase resistances:

$$N_{St} N_{Sc}^{2/3} = \phi(N_{Shw}) \psi\left(\frac{b}{a}\right)\theta\left(\frac{s}{a}\right) \eta\left(N_{Sc}\right) A N_{RE}^{C} \tag{35}$$

where the correction factor $\eta(N_{Sc})$ is defined as

$$\eta\left(N_{Sc}\right) = 1.009\left[1 - .00255\left(5 - \log N_{Sc}\right)^2\right] \tag{36}$$

and A and C are defined as follows:

$8000 < Nre < 32000$

$A = .285 \pm .027$ $\quad$ $c = -.433 \pm .010$

$32000 < Nre < 82000$

$A = .0443 \pm .012$ $\quad$ $c = .254 \pm .023$

where N_{SH}, N_{ST} and N_{Re} refer to the Sherwood, Stanton and Reynolds Number respectively; b is the membrane radius, a is the impeller radius and s is the axial gap distance. $\psi(b/a)$ and $\theta(S/a)$ are correction factors for which there are plots vs. b/a and s/a respectively. (13)

Kaufman and Leonard (8) developed a relationship which is valid for stirrer speeds from 46 to 500 rev./min. corresponding to Reynolds Numbers of about 10000 to 109000. This correlation is

$$\frac{k_{el} d}{D} = .105\left(\frac{\mu}{\rho D}\right)^{.32}\left(\frac{d^2 \Omega \rho}{\mu}\right)^{.62}$$

where d is the impeller diameter and Ω is the angular velocity.

The correlation developed by Wilke and Chang is used for comparison with experimental results of this work. This correlation is used because it does not specify solute size and it is valid for dilute solutions.

EXPERIMENTAL

Membranes

All membranes tested were laboratory cast non-commercially available polymers. All were 56-58.5% hydroxyethyl methylacrylate (HEMA) by weight percent. One of the following monomers was also a component of the membranes in the amount of 0.2-2.9 weight percent:

Heptyl acrylate (HA)	$C_{10}H_{18}O_2$
Trifluoroethyl acrylate (TFEA)	$C_5H_5O_2F_3$
Isopropyl acrylate (IPA)	$C_6H_{10}O_2$
Hexafluoroisopropyl acrylate (XFIPA)	$C_6H_4O_2F_6$

The HEMA based polymer was chosen because it is inert with blood. However, HEMA membranes have a low tensile strength which limits their applications. Fluorine substituted acrylates were introduced in order to improve the tensile strength of the membranes. The diffusion experiments provide comparative data for fluorinated and non-fluorinated HEMA based membranes.

One experiment on a commercially available membrane material HYDRON was performed. Sodium Chloride was the solute. The results agreed well with published data.

Solutes

Sodium Chloride was selected for initial studies with all membranes because of its ease of measurement and common usage for comparative evaluations. Two organic solutes, urea and uric acid were selected for their revelence to the artificial kidney.

Solvents

Distilled water of conductivity grade (Resistance is above

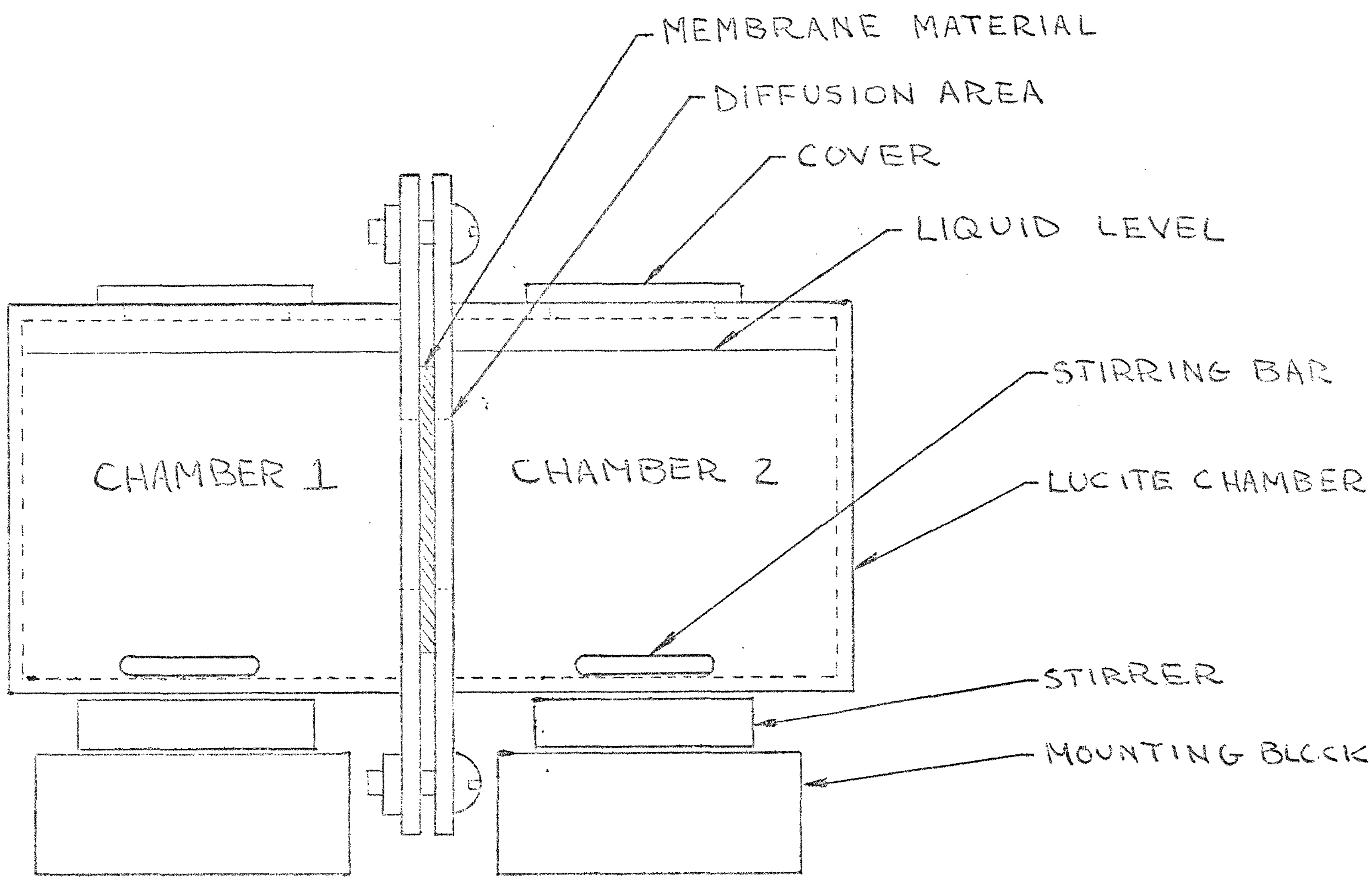
150000 ohms) was used in all experiments. Urea and uric acid solutions were prepared in buffered distilled water at $_pH$ = 7.4. A $_pH$ of 7.4 was chosen since this is the $_pH$ of blood.

Diffusion Studies

Membrane permeability was measured using a diffusion apparatus consisting of two identical, stirred lucite chambers between which the membrane was securely clamped. (See Figures 2,3). Four sets of apparatus, each with a different set of dimensions were used. All sets would hold between 500 ml and 1500 ml of solution in each chamber. Dimensions for one set of apparatus were 7cm X 6cm X 15cm. The diffusion opening had a 3.8 cm diameter. Water driven magnetic stirrers were placed in each chamber to keep the solutions well stirred. In the sodium chloride experiments one chamber (1) was initially filled with .1 molar sodium chloride and the other chamber (2) with distilled water. In subsequent experiments chamber 1 was filled with 1M urea or 0.0019M(2 grams/liter) uric acid at $_pH$ = 7.4. The uric acid solution was saturated.

Analysis

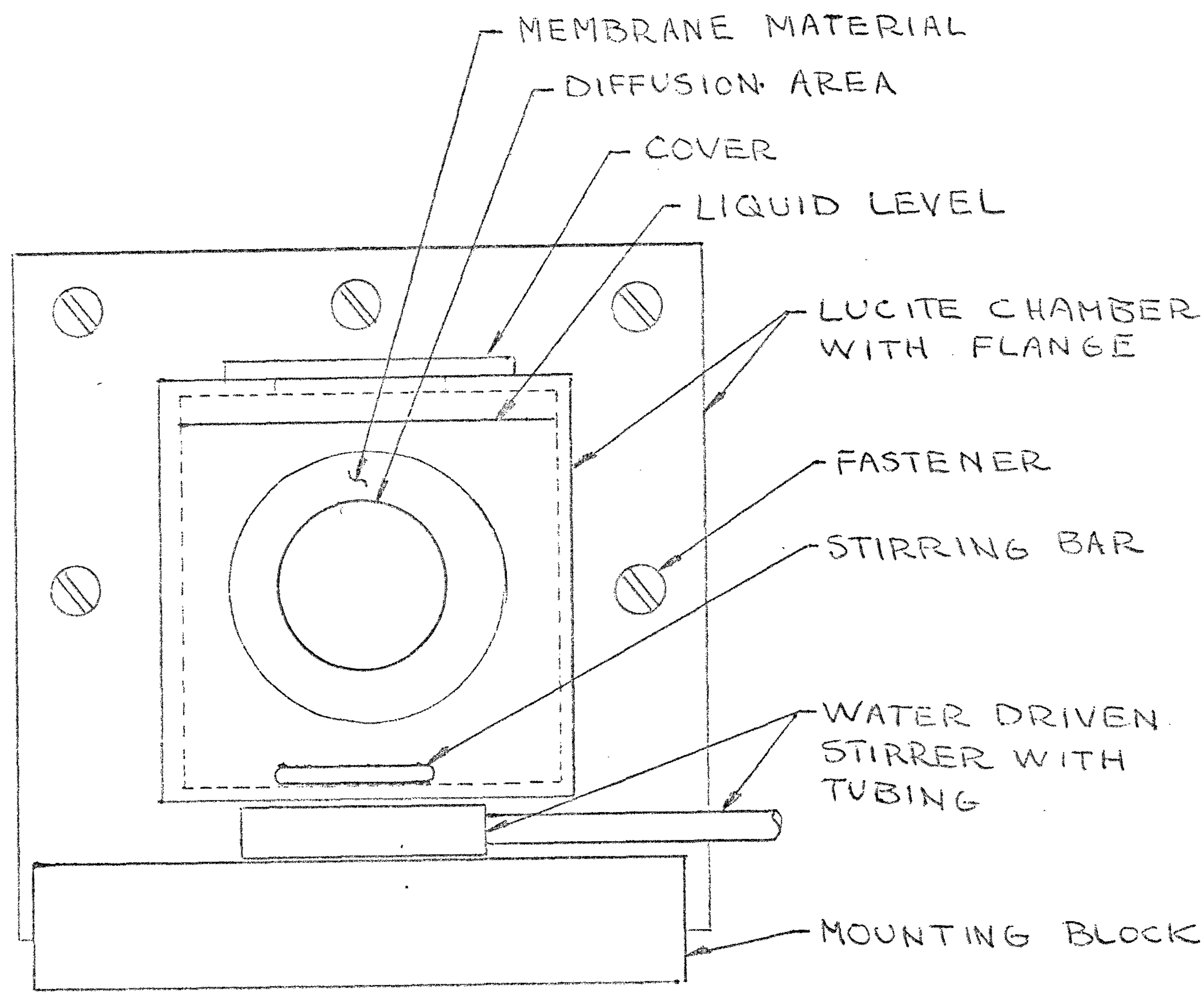
Sodium Chloride - Concentration in chamber 2 was monitored with time by means of conductivity measurements using a conductivity cell and bridge. The conductivity bridge used was a Model RC-16B2 of Industrial Instruments, Cedar Grove, New Jersey. The sodium chloride experiment usually lasted 3-4 days. When a resistance reading of 10000-15000 was reached the experiment was terminated. A calibration curve of log resistance versus log concentration was prepared for solutions of known concentration that were prepared from the same batch of



FRONT VIEW

DIFFUSION APPARATUS

FIGURE 2



SIDE VIEW

DIFFUSION APPARATUS

FIGURE 3

distilled water as the sodium chloride used in the experiment.

Uric Acid - Concentration in chamber 2 was estimated by means of spectrophotometric measurement of optical density at 292 mu. A Beckman Model DB-G Grating Spectrophotometer was used for all measurements of the optical density. The uric acid experiment lasted for 3-7 days and a sample of 3-5 ml was taken periodically. A calibration curve of optical density versus log concentration was prepared for solutions of known concentration. The calibration curve was used to estimate the concentration of uric acid in the sample.

Urea - Concentration in chamber 2 was determined spectrophotometrically following the method of Watt and Crisp. The urea diffusion experiment lasted for 5-7 days and a sample of 3-5 ml. was taken periodically. A yellow-green color is produced when p-dimethylaminobenzaldehyde is added to urea in dilute hydrochloric acid solution. This complex exhibits an absorption peak at 420 mu. The color reagent consists of p-dimethylaminobenzaldehyde (2.00 grams), 95% ethyl alcohol (100.00 ml.) and concentrated hydrochloric acid (10.00 ml.). Two milliliter aliquots of urea solution taken from chamber 2 were placed in 25 ml. flasks. Ten milliliters of color reagent were added to each flasks and diluted to a total volume of 25 ml. with distilled water. The optical density was measured at 420 mu. A calibration curve of optical density versus log concentration was prepared for solutions of known concentration and this curve was used to estimate the concentration of urea in the sample.

TABLE I

DIFFUSION COEFFICIENTS

Sample No.	NaCL $cm^2/sec \times 10^5$	Urea $cm^2/sec \times 10^5$	Uric Acid $cm^2/sec \times 10^5$
IPA			
95	61.67		28.50
101	27.98	9.63	10.23
HA			
94	28.04	11.20	4.48
100	71.73	3.04	17.16
XFIPA			
92	18.39	10.49	-
98	17.09	-	-
103	19.61	-	2.33
109	15.12	6.05	4.18
TFEA			
93	19.13	18.30	10.00
99	19.69	5.47	-
104	11.11	-	-
110	16.30	6.12	5.17

TABLE II

AVERAGE VALUE OF DIFFUSION COEFFICIENTS

	NaCL $cm^2/sec \times 10^5$	Urea $cm^2/sec \times 10^5$	Uric Acid $cm^2/sec \times 10^5$
Estimated Value[a]	1.92	1.29	.79
Literature Value[b]	2.16	1.81	1.16
Values estimated in this study			
IPA	45.0	9.6	19.0
HA	50.0	7.1	17.2
XFIPA	18.0	8.3	3.3
TFEA	16.6	9.96	7.6

a. Wilke-Chang (16) correlation

$$D = 7.4 \times 10^{-8} \frac{(\psi_B M_B)^{1/2} T}{\mu \tilde{V}_A^{.6}}$$

where ψ is an "association parameter" which is 1.0 for water M_B is the molecular weight of the solvent, T is the absolute temperature, μ is the viscosity of the solution and $\tilde{V}_A$ is the molar volue of the solute as liquid at its normal boiling point.

b. Results of Colton et.al. (10) on cellulose membranes.

TABLE III

DIFFUSION COEFFICIENTS OF MEMBRANES CONTAINING IPA AND XFIPA

Weight Percent of Variable Polymer	Diffusion Coefficients $cm^2/sec \times 10^5$					
	NaCL		Urea		Uric Acid	
	IPA	XFIPA	IPA	XFIPA	IPA	XFIPA
3	61.67				28.50	
.6	27.98	18.39	9.63	10.49	10.23	
1.2		17.09				
2.2		15.72		6.05		4.18
2.8		19.61				2.33

METHOD OF CALCULATION OF DIFFUSION COEFFICIENTS FOR MEMBRANES

The quantity of material Q which diffuses through a membrane of area A in unit time t is proportional to the concentration difference ΔC between the two boundaries and inversely proportional to the thickness x of the membrane. Under steady-state conditions this relationship is

$$\frac{dQ}{Adt} = \left(\frac{D}{x}\right)\Delta C \qquad (1)$$

where D is the proportionality constant or diffusion coefficient. When the material diffuses into a large volume,V, where the concentration of the diffusing species is considered to be zero, equation 1 takes the form

$$\frac{dQ}{dt} = \frac{DCA}{x} \qquad (2)$$

The quantity of material,or solute, at any time can be expressed as

$$Q = (C_0 - C)V \qquad (3)$$

where C_0 is the initial concentration of the diffusing solute in chamber 2 (chamber 2 is initially filled with distilled water) and C is the concentration in chamber 2 at time, t. In these experiments C is the final concentration.
Differentiation of equation 3 gives

$$dQ = -VdC + (C_0 - C)dV \qquad (4)$$

If the change involume is negligible and can be assumed equal to zero,

$$-VdC = \frac{DCAdt}{x} \qquad (5)$$

Integration of equation 5 gives

$$D = \frac{Vx}{At} \ln\left(\frac{C}{C_0}\right) \qquad (6)$$

Equation 6 has been used to calculate the diffusion coefficients for the experiments of this work.

SAMPLE CALCULATION

The relationship used to estimate the diffusion coefficient is:

$$D = \frac{Vx}{At} \ln\left(\frac{C}{C_c}\right)$$

The development of this relationship is on page 29. The sample calculation is for the diffusion coefficient of sodium chloride through membrane number 92.

Volume = 1100 cm^3

Thickness of membrane = .27 cm

Surface Area = $(\pi)(2.54)^2 = 20.27 cm^2$

Length of time of experiment = 74.33 hours

Initial Sodium Chloride concentration = $.016 \times 10^{-3}$

Final Sodium Chloride concentration = $.460 \times 10^{-3}$

$$D = \frac{(1100\ cm^3)(27\ cm\ )(hours\ )\ \ 2.3}{(20.27\ cm^2)(74.33 hours)3600\ sec)} \log\left(\frac{.460 \times 10^{-3}}{.016 \times 10^{-3}}\right)$$

$$D = 18.39 \ \frac{cm^2}{sec}$$

DISCUSSION OF RESULTS

In this work two fluorinated and two non-fluorinated groups of membranes were studied. The hope was that the fluorine substituted membranes would have a higher tensile strength while maintaining a diffusion rate which would make the membrane acceptable for hemodialysis. The membranes were evaluated in two ways:

(1) The fluorinated membranes were compared to the non-fluorinated membranes all of which were prepared in our laboratory.

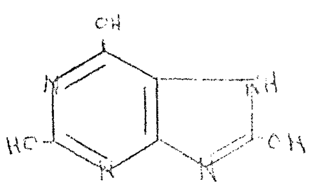
(2) The diffusion coefficients of the membranes were compared to the literature values of commercially available cellulose membranes.

Sodium Chloride - the nonfluorinated membranes had a higher diffusion coefficient than the fluorinated membranes. In particular the membranes containing isopropyl acrylate and heptyl acrylate had a diffusion coefficient almost three times as great as the membranes containing hexafluoroisoprapyl acrylate and trifluoroethyl acrylate. All of the laboratory prepared membranes had a higher diffusion coefficient than cellulose.

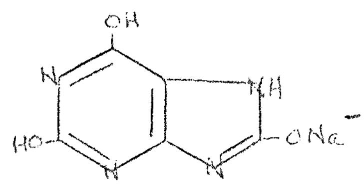
Urea - There was a small difference in diffusion coefficient between the fluorinated and non-fluorinated membranes; the fluorinated membranes had a slightly higher rate of diffusion. The rates of diffusion in membranes containing isopropyl acrylate and membranes containing hexafluoroisopropyl acrylate were almost identical. This would indicate that for diffusion of urea a fluorine group could be added to the polymers of the membrane in order to alter its mechanical properties, without changing its efficiency in hemodialysis.

Uric Acid - as in the case of sodium chloride, the non-fluorinated membranes had a higher diffusion coefficient than the fluorinated membranes by an order of magnitude. However, the rate of diffusion of uric acid through the membranes was better than through cellulose in all cases.

There is a possible explanation why the rates of diffusion of uric acid and sodium chloride are slower through the fluorinated polymers, but the rate of diffusion of urea is not. It could be that the electronegative fluorines in the membranes retard the rates of diffusion of uric acid and sodium chloride but not of urea. Urea is a neutral molecule. Sodium chloride exists in the ionic state of positively charged sodium ion and negatively charged chloride ions. Uric acid is also ionized in these experiments. Uric acid was in a buffered solution of $_pH$ = 7.40. The $_pK_a$ of uric acid is 3.89. At $_pH$ = 7.4 the diffusion coefficient of negatively charged sodium urate, and not uric acid was being measured.

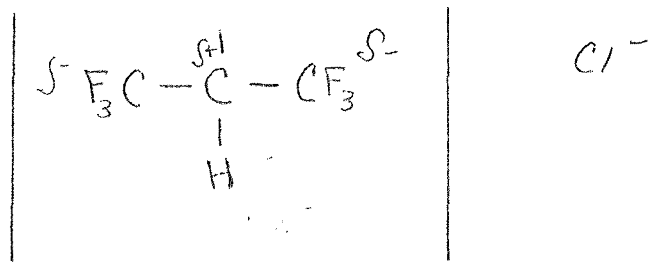


URIC ACID



SODIUM URATE

For example, membranes containing trifluoroethyl acrylate have a negative fluorine sphere and a position carbon at the core.



Trifluoro Arrangement

This arrangement may present a barrier to diffusion of ionic solutes. Muir, et. al (12) concluded that permeants with charge characteristics similar to the membrane show reduced diffusion rates. The reduced rate of diffusion through the fluorinated membranes for uric acid and sodium chloride but not urea indicates that the diffusion mechanism may include solute diffusion through the membrane materials as well as through the pores.

Colton et. al. (3) suggests that if the mechanism of diffusion is solely transport through pores, the percent water content will be the controlling factor in the rate of diffusion. Water content was measured by surface drying the wet membrane and immediately weighing the polymer. The membranes were then dried in an oven to constant weight and reweighed. The wet weight minus the dry weight divided by the wet weight of the membrane was the calculation used to determine the weight percent of water in the membrane. A direct relationship between the percent water in the membrane and the rate of diffusion does not exist. Also if transport through pores was the sole diffusion mechanism, then there should be a relationship between molecular weight and diffusion coefficient. There is the anticipated trend of high molecular weight, low diffusion coefficient for the fluorinated membranes, but a similar relationship does not result for the non-fluorinated membranes.

This result suggests that although the diffusion mechanism of the non-fluorinated membranes also involves more than a pore - sieve mechanism, the mechanism is probably different than that of the fluorinated membranes.

CONCLUSIONS

The data obtained from this introductory work of the laboratory prepared membranes enable certain conclusions to be drawn:

1. The diffusion rate per area for urea, uric acid, and sodium chloride is as great as, or greater than, that through the present commercial cellulose membranes. This is the most important result. A polymer would have to be at least as permeable to the toxic solutes removed by the kidneys as the cellulose membranes to be considered acceptable for hemodialysis. If the diffusion rate of these toxics through the membranes is low, a potential can be set up due to a large concentration gradient on either side of the membrane. This condition could cause hemolysis which is the breaking down of red blood cells. It is clearly necessary for a hemodialysis membrane to be antithrombogenic. Also, not only will the toxics usually removed by the kidney build up, but their precursors which also may be toxic will also dangerously build up.
2. The weight percent of the variable monomer (HA,IPA,XFIPA, TFEA) did affect the rate of diffusion of the sodium chloride and uric acid. This indicates that although a high percent fluorine group may be desirable for increased tensile strength, it will decrease the hemodialytic efficiency of the membrane an optimization point between the two should be determined.

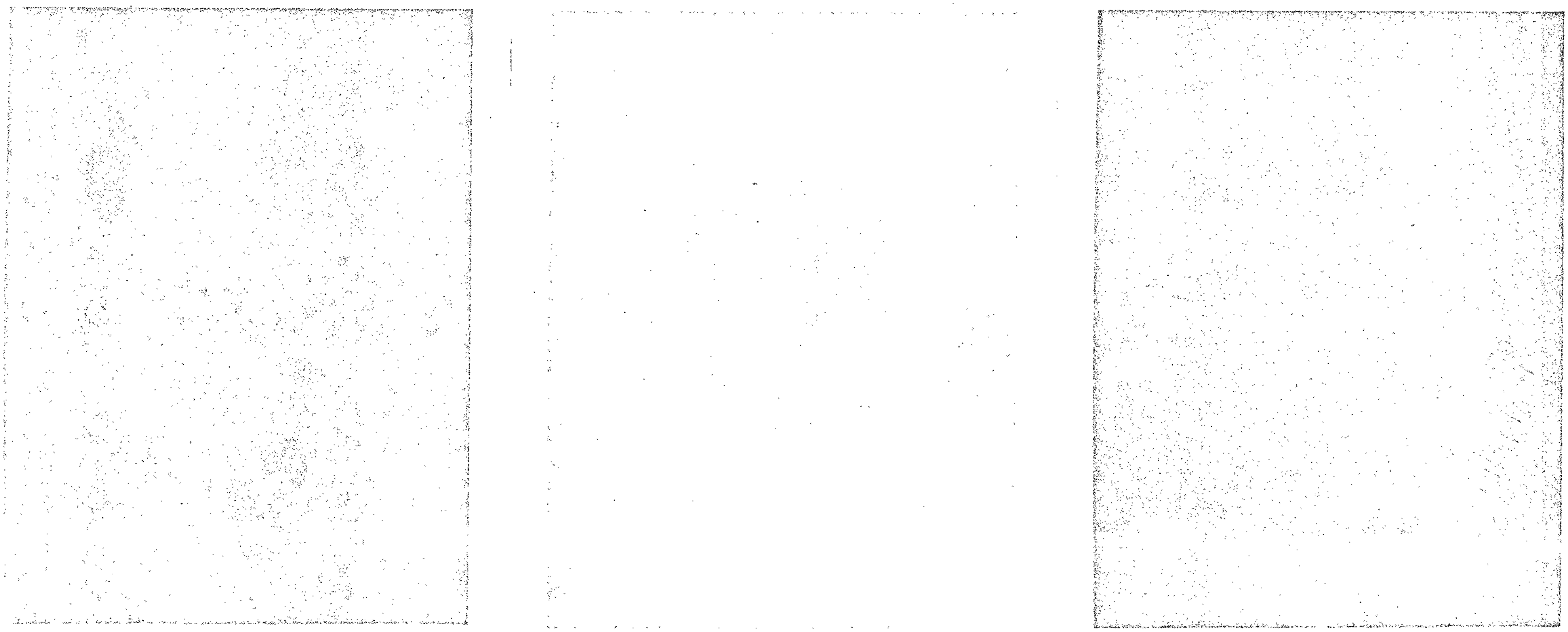
3. Solute transport through the membranes does involve diffusion through the membrane materials. This differs from the cellulose membranes which show no solute selectivity whatever, and permit transport solely on the basis of a pore sieving meehanism whereby small solutes permeate quickly and larger ones more slowly.

RECOMMENDATIONS

Considering that preliminary results indicate the laboratory prepared membranes, in particular the fluorine substituted ones, will be acceptable for hemodialysis, the following recommendations are made for further study:

1. Diffusion studies should be run using creatinine as a solute since this is a known toxic and product of protein metabolism that must be removed by the kidney.
2. The membrane split during eight experiments. In six of those experiments, uric acid was the solute. Uric acid was a saturated solution is these studies. A saturated solution of uric acid was chosen for two reasons: (A) to determine the maximum rate of diffusion with uric acid and (B) to maintain a constant concentration of uric acid in chamber. The concentration of uric acid that is of physiological interest is .05 grams per liter. It is suggested that future diffusion experiments of uric acid through the laboratory prepared membranes be at this concentration.
3. The specific nature of all toxics which are removed by the kidney are not known. Therefore, diffusion experiments involving a variety of molecular weights sizes and shapes is advisable. By this means, membrane permeabilities could be evaluated for solutes of various characteristics.
4. The laboratory prepared membranes should be tested for tensile strength. This is the main remaining condition to be satisfied for the membrane to be considered acceptable.

5. No pore size data is available on the membranes at this time. Since transport through pores is one mechanism of diffusion, there should be some correlation data on pore size and rate of diffusion.



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MEMBRANE SAMPLE SURFACE
VIEWS UNDER MAGNIFICATION

Sodium Chloride - H_2O Diffusion Data

Membrane - HA Series

Membrane Sample No. 94 - HEMA = 58.26 Wt %

H_2O = 41.30

HA = .44

Resistance ohms	Log R	Log C	Concentration moles/liter X 10^4	Time hours
610000	5.7853	-6.1853	.007	0.00
542000	5.7340	-6.1132	.008	1.33
400000	5.6021	-5.9278	.012	3.42
98000	4.9912	-5.0692	.085	14.50
84000	4.9243	-4.9752	.106	21.00
45000	4.6532	-4.5941	.225	28.50
34300	4.5353	-4.4284	.373	38.50
29500	4.4698	-4.3363	.461	43.50
24000	4.3802	-4.2104	.616	47.50
20000	4.3010	-4.0991	.796	58.00
19000	4.2788	-4.0679	.855	60.75
14200	4.1523	-3.8901	1.292	84.25

Sodium Chloride - H_2O Diffusion Data

Membrane - HA Series

Membrane Sample No. 100 - HEMA = 58.08 Wt %

H_2O = 41.00

HA = .92

Resistance ohms	Log R	Log C	Concentration moles/liter X 10^4	Time hours
580000	5.7634	-6.1543	.007	0.00
197000	5.2945	-5.4955	.032	8.92
100000	5.0000	-5.0816	.083	18.08
77000	4.8865	-4.9220	.120	27.00
54000	4.7324	-4.7054	.197	39.92
42500	4.6284	-4.5592	.276	49.67
33600	4.5263	-4.4158	.384	64.00
26500	4.4232	-4.2708	.536	80.00
23800	4.3766	-4.2053	.623	88.00
20500	4.3118	-4.1143	.769	89.58

Sodium Chloride - H_2O Diffusion Data

Membrane - IPA Series

Membrane Sample No. 95 - HEMA = 58.36 Wt %

H_2O = 41.36

IPA = .28

Resistance ohms	Log R	Log C	Concentration moles/liter x 10^4	Time hours
650000	5.8129	-5.0944	.081	0.00
580000	5.7634	-5.0412	.091	.5
568000	5.7543	-5.0314	.093	1.0
365000	5.5623	-4.8247	.150	1.5
400000	5.6021	-4.8675	.136	2.25
81500	4.9112	-4.1236	.752	15.75
7800	4.8921	-4.1031	.789	16.83
74500	4.8722	-4.0816	.829	17.75
69500	4.8420	-4.0491	.893	18.83
67500	4.8293	-4.0354	.922	19.92
32000	4.5051	-3.6863	2.059	38.17
31200	4.4942	-3.6746	2.115	39.5
24900	4.3962	-3.5691	2.698	46.0
24100	4.3820	-3.5538	2.794	46.5
18000	4.2553	-3.4174	3.824	66.17

Sodium Chloride - H_2O Diffusion Data

Membrane - IPA Series

Membrane Sample No. 101 - Hema = 58.24 Wt %

H_2O = 41.14

IPA = .62

Resistance ohms	Log R	Log C	Concentration moles/liter X 10^4	Time hours
890000	5.9494	-6.4159	.004	0.00
275000	5.4393	-5.6990	.020	4.83
110000	5.0414	-5.1397	.073	10.75
66000	4.8195	-4.8278	.149	18.58
41000	4.6128	-4.5373	.290	29.50
36100	4.5575	-4.4596	.347	34.08
27800	4.4440	-4.3001	.501	43.00
23100	4.3636	-4.1871	.650	52.08
17900	4.2529	-4.0315	.930	66.67
15600	4.1931	-3.9474	1.130	83.08
12100	4.0828	-3.7924	1.610	97.08

Sodium Chloride - H_2O Diffusion Data

Membrane - XFIPA Series

Membrane Sample No. 92 - HEMA = 58.23 Wt %

H_2O = 41.14

XFIPA = .63

Resistance ohms	Log R	Log C	Concentration moles/liter X 10^3	Time hours
356000	5.5514	-4.7844	.016	0.00
225000	5.3522	-4.5688	.027	1.08
59000	4.7709	-3.9395	.115	18.75
47200	4.6739	-3.8344	.146	26.42
27000	4.4314	-3.5720	.268	44.25
27000	4.4314	-3.5720	.268	47.25
24200	4.3838	-3.5204	.302	50.75
17000	4.2384	-3.3543	.442	70.25
16400	4.2148	-3.3375	.460	74.33

Sodium Chloride - H_2O Diffusion Data

Membrane - XFIPA Series

Membrane Sample No. 98 - HEMA = 57.82 Wt %

H_2O = 41.01

XFIPA = 1.17

Resistance ohms	Log R	Log C	Concentration moles/liter X 10^3	Time hours
410000	5.6128	-4.8510	.014	0.00
52500	4.7202	-3.8846	.130	24.00
31000	4.4914	-3.6369	.231	42.83
29000	4.4624	-3.6055	.248	43.08
26000	4.4150	-3.5542	.279	43.33
25000	4.3979	-3.5357	.291	47.50
11900	4.0755	-3.1867	.650	91.58
10600	4.0253	-3.1323	.737	94.33

Sodium Chloride - H_2O Diffusion Data

Membrane - XFIPA Series

Membrane Sample No. 103 - HEMA = 56.83 Wt %

H_2O = 40.34

XFIPA = 2.83

Resistance ohms	Log R	Log C	Concentration moles/liter X 10^3	Time hours
500000	5.6990	-4.9443	.011	0.00
460000	5.6628	-4.9051	.012	1.25
85500	4.9320	-4.1139	.077	16.08
58500	4.7672	-3.9355	.116	22.42
57200	4.7574	-3.9249	.119	24.42
49000	4.6902	-3.8521	.140	27.17
31000	4.4914	-3.6369	.231	42.75
30800	4.4886	-3.6339	.232	47.67
19000	4.2788	-3.4067	.392	69.92
21200	4.3263	-3.4582	.348	71.67

Sodium Chloride - H_2O Diffusion Data

Membrane - XFIPA Series

Membrane Sample No. 109 - HEMA = 55.44 Wt %

H_2O = 42.32

XFIPA = 2.24

Resistance ohms	Log R	Log C	Concentration moles/liter X 10^3	Time hours
335000	5.5250	-4.7559	.018	0.00
51000	4.7076	-3.8710	.134	23.50
26700	4.4265	-3.5667	.271	45.50
23200	4.3655	-3.5006	.316	49.33
12200	4.0864	-3.1984	.633	93.50
11500	4.0607	-3.1706	.675	97.50

Sodium Chloride - H_2O Diffusion Data

Membrane - TFEA Series

Membrane Sample No. 99 - HEMA = 58.00 Wt %

H_2O = 41.12

TFEA = .88

Resistance ohms	Log R	Log C	Concentration moles/liter X 10^3	Time hours
390000	5.5911	-4.8321	.015	0.00
310000	5.4914	-4.7247	.019	.75
26000	4.4150	-3.5648	.272	50.50
13500	4.1303	-3.2581	.552	74.50

Sodium Chloride - H_2O Diffusion Data

Membrane - TFEA Series

Membrane Sample No. 110 - HEMA = 56.59 Wt %

H_2O = 41.75

TFEA = 1.66

Resistance ohms	Log R	Log C	Concentration moles/liter X 10^3	Time hours
490000	5.6902	-4.9389	.012	0.00
30000	4.4771	-3.6318	.233	46.00
30000	4.4771	-3.6318	.233	48.00
19800	4.2967	-3.4374	.365	72.50
15800	4.1987	-3.3318	.466	91.83
15500	4.1903	-3.3227	.476	94.00

Sodium Chloride - H_2O Diffusion Data

Membrane - TFEA Series

Membrane Sample No. 104 - HEMA = 57.38 Wt %

H_2O = 40.65

TFEA 1.97

Resistance ohms	Log R	Log C	Concentration moles/liter X 10^3	Time hours
550000	5.7404	-4.9930	.012	0.00
66200	4.8209	-4.0022	.100	23.50
13000	4.1139	-3.2404	.575	119.50
12400	4.0934	-3.2183	.605	143.50

Sodium Chloride - H_2O Diffusion Data

Membrane - TFEA Series

Membrane Sample No. 93 - HEMA = 58.34 Wt %

H_2O = 41.26

TFEA .40

Resistance ohms	Log R	Log C	Concentration moles/liter X 10^3	Time hours
450000	5.6532	-4.8990	.013	0.00
55000	4.7404	-3.9155	.121	19.67
23600	4.3729	-3.5195	.302	35.58
16600	4.2201	-3.3548	.441	59.75
13100	4.1173	-3.2441	.570	78.25
13000	4.1139	-3.2404	.575	80.58

Urea - H_2O Diffusion Data

Membrane - HA Series

Membrane Sample No. 94 - HEMA - 58.26 Wt %

H_2O - 41.30

HA - 0.44

Optical Density	Concentration moles/liter X 10^3	Time hours
.089	0.5	0.00
.250	1.4	25.25
.440	10.0	48.83
.440	10.0	72.50
.635	24.3	97.67
.760	33.5	122.42
.850	47.0	148.83

Urea - H_2O Diffusion Data

Membrane - HA Series

Membrane Sample No. 100 - HEMA - 58.08 Wt %

H_2O - 41.00

HA - 0.92

Optical Density	Concentration moles/liter X 10^3	Time hours
.025	0.4	0.00
.150	0.7	26.00
.335	3.3	49.50
.450	7.1	73.00
.720	32.0	97.00
.880	45.0	125.25
1.050	52.0	137.00

Urea - H_2O Diffusion Data

Membrane - IPA Series

Membrane Sample No. 101 - HEMA - 58.24 Wt %

H_2O - 41.14

IPA - 0.62

Optical Density	Concentration moles/liter X 10^3	Time hours
.084	0.5	0.00
.157	0.7	23.92
.250	1.4	49.67
.400	7.0	76.08
.600	25.0	94.92
.735	32.5	120.75
.805	36.0	124.25
.960	46.0	174.00

Urea - H_2O Diffusion Data

Membrane - XFIPA Series

Membrane Sample No. 92 - HEMA - 58.23 Wt %

H_2O - 41.14

XFIPA - .63

Optical Density	Concentration moles/liter X 10^3	Time hours
.04	0.4	0.00
.35	4.2	23.33
.19	1.1	26.17
.21	1.2	46.00
.49	10.4	48.42
.44	10.0	59.17
.50	10.5	152.42

Urea - H_2O Diffusion Data

Membrane - XFIPA Series

Membrane Sample No. 109 - HEMA - 55.44 Wt %
H_2O - 42.32
XFIPA - 2.24

Optical Density	Concentration moles/liter X 10^3	Time hours
.05	0.4	0.00
.15	0.8	49.50
.25	2.8	72.00
.28	3.2	145.33

Urea - H_2O Diffusion Data

Membrane - TFEA Series

Membrane Sample No. 93 - HEMA - 58.34 Wt %

H_2O - 41.26

TFEA - 1.40

Optical Density	Concentration moles/liter X 10^3	Time hours
.14	0.6	0.00
.15	0.7	21.50
.36	5.0	118.17
.45	10.6	165.67

Urea - H_2O Diffusion Data

Membrane - TFEA Series

Membrane Sample No. 99 - HEMA - 58.00 Wt %

H_2O - 41.12

TFEA - .88

Optical Density	Concentration moles/liter X 10^3	Time hours
.19	0.9	0.00
.33	3.7	48.17
.35	4.3	121.50
.40	7.0	168.00

Urea - H_2O Diffusion Data

Membrane - TFEA Series

Membrane Sample No. 110 - HEMA - 56.59 Wt %

H_2O - 41.75

TEFA - 1.66

Optical Density	Concentration moles/liter X 10^3	Time hours
.22	1.0	0.00
.26	1.5	45.50
.40	7.0	141.58

Uric Acid - H_2O Diffusion Data

Membrane - HA Series

Membrane Sample No. 94 - HEMA - 58.26 Wt %

H_2O - 41.30

HA - .44

Optical Density	Concentration grams/liter	Time hours
.012	.015	0.00
.069	.148	26.75
.031	.042	27.75
.035	.050	29.00
.070	.150	50.25
.094	.269	74.75

Uric Acid - H_2O Diffusion Data

Membrane - HA Series

Membrane Sample No. 100 - HEMA - 58.08 Wt %

H_2O - 41.00

HA - .92

Optical Density	Concentration grams/liter	Time hours
.035	.050	0.00
.045	.074	1.17
.040	.063	2.25
.080	.178	22.34
.078	.174	46.34

Uric Acid - H_2O Diffusion Data

Membrane - IPA Series

Membrane Sample No. 95 - HEMA - 58.36 Wt %

H_2O - 41.36

IPA - .28

Optical Density	Concentration grams/liter	Time hours
.015	.017	0.00
.035	.050	0.75
.076	.170	1.92
.052	.091	13.75
.075	.170	21.92
.078	.174	22.17
.080	.178	37.75

Uric Acid - H_2O Diffusion Data

Membrane - IPA Series

Membrane Sample No. 101 - HEMA - 58.24 Wt %

H_2O - 41.14

IPA - .62

Optical Density	Concentration grams/liter	Time hours
.030	.040	25.33
.044	.071	26.42
.045	.074	27.92
.078	.200	45.50
.056	.105	51.00
.067	.150	73.00
.050	.085	75.75
.080	.178	96.67

Uric Acid - H_2O Diffusion Data

Membrane - XFIPA Series

Membrane Sample No. 103 - HEMA - 56.83 Wt %

H_2O - 40.34

XFIPA - 2.83

Optical Density	Concentration grams/liter	Time hours
.032	.043	0.00
.040	.063	23.33
.050	.085	47.25
.055	.100	167.58
.062	.120	192.75

Uric Acid - H_2O Diffusion Data

Membrane - XFIPA Series

Membrane Sample No. 109 - HEMA - 55.44 Wt %

H_2O - 42.32

XFIPA - 2.24

Optical Density	Concentration grams/liter	Time hours
.01	.013	2.17
.016	.020	51.83
.035	.050	75.75
.045	.074	100.83
.050	.085	167.67
.052	.091	219.92
.065	.132	243.75

Uric Acid - H_2O Diffusion Data

Membrane - TFEA Series

Membrane Sample No. 93 - HEMA - 58.34 Wt %

H_2O - 41.26

IPA - .40

Optical Density	Concentration grams/liter	Time hours
.040	.063	0.00
.050	.085	23.83
.085	.209	51.08
.190	.708	63.33
.210	.832	99.08

Uric Acid - H_2O Diffusion Data

Membrane - TFEA Series

Membrane Sample No. 110 - HEMA - 56.59 Wt %

H_2O - 41.75

TFEA - 1.66

Optical Density	Concentration grams/liter X 10^{-2}	Time hours
.015	1.26	0.00
.023	3.16	31.00
.036	5.62	56.75
.060	1.00	80.75
.035	5.62	105.00
.030	4.79	246.00

Calibration Curve Data

Sodium Chloride Concentration Vs. Resistance

Distilled H_2O Used - Batch I

Concentration moles/liter X 10^3	Resistance ohms	Log Concentration	Log Resistance
100.00	104	-1.000	2.017
50.00	196	-1.301	2.293
25.00	370	-1.602	2.568
2.50	3000	-2.602	3.477
0.25	27800	-3.602	4.444

Membranes used with Batch I distilled water: 95

Calibration Curve Data

Sodium Chloride Concentration Vs. Resistance

Distilled H_2O Used - Batch II

Concentration moles/liter X 10^3	Resistance ohms	Log Concentration	Log Resistance
100.00	108	-1.000	2.037
50.00	199	-1.301	2.299
25.00	380	-1.602	2.580
10.00	921	-2.000	2.964
1.00	7800	-3.000	3.892
0.10	52000	-4.000	4.716

Membranes used with Batch II of distilled water: 94, 101, 100

Calibration Curve Data

Sodium Chloride Concentration Vs. Resistance

Distilled H_2O Used - Batch III

Concentration moles/liter X 10^3	Resistance ohms	Log Concentration	Log Resistance
50.00	220	-1.301	2.3424
25.00	399	-1.602	2.6010
12.50	765	-1.903	2.8837
10.00	970	-2.000	2.9868
2.50	3520	-2.602	3.5465
.25	26500	-3.602	4.4232
.13	58000	-3.903	4.7634

Membranes used with Batch III of distilled water: 92, 98, 103, 109

Calibration Curve Data

Sodium Chloride Concentration Vs. Resistance

Distilled H_2O Used - Batch IV

Concentration moles/liter X 10^3	Resistance ohms	Log Concentration	Log Concentration
100.00	110	-1.000	2.0414
50.00	208	-1.301	2.3181
25.00	375	-1.602	2.5740
10.00	935	-2.000	2.9708
0.10	66000	-4.000	4.8195

Membranes used with Batch IV of distilled water: 93,99,104,110

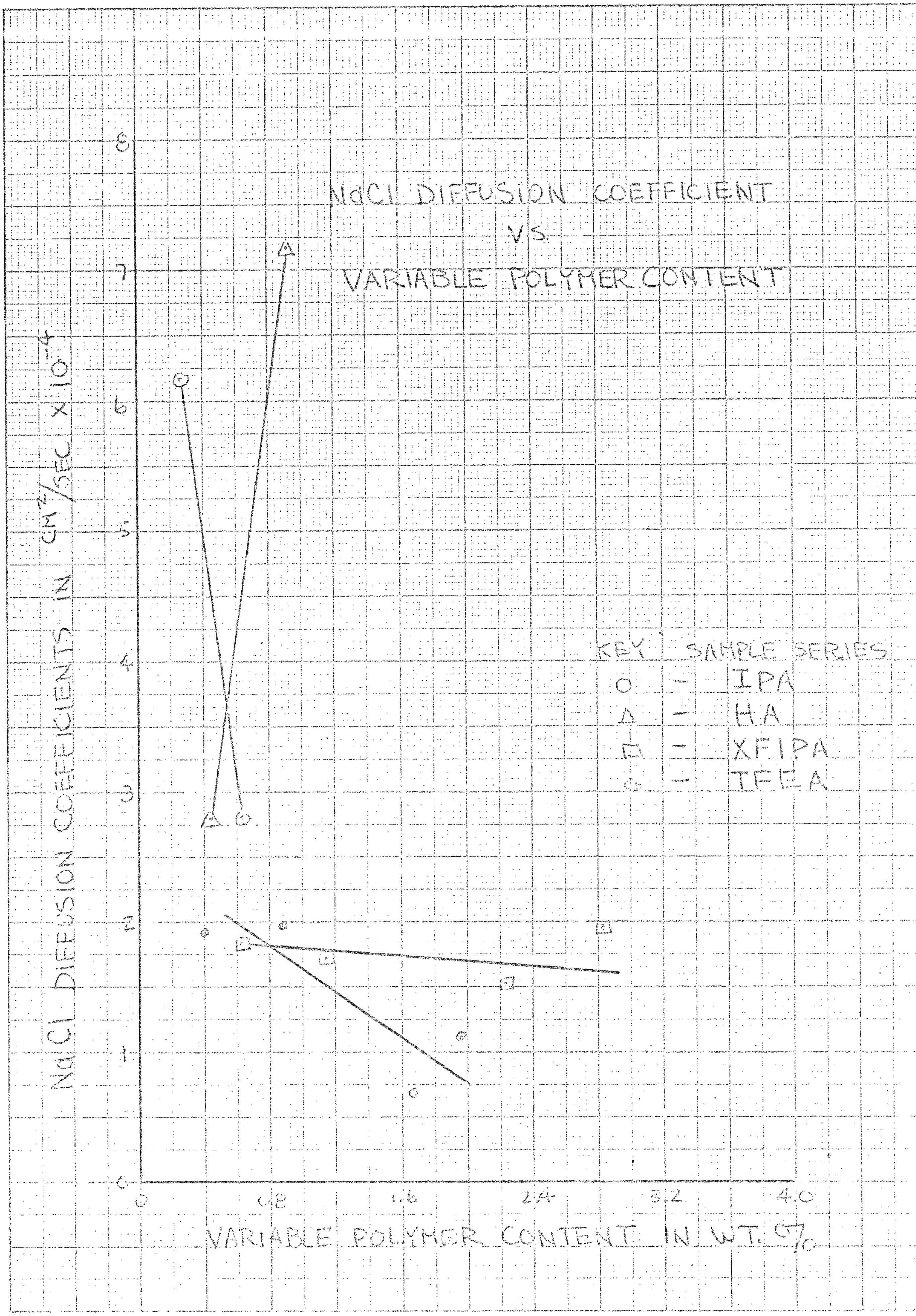
Calibration Curve Data

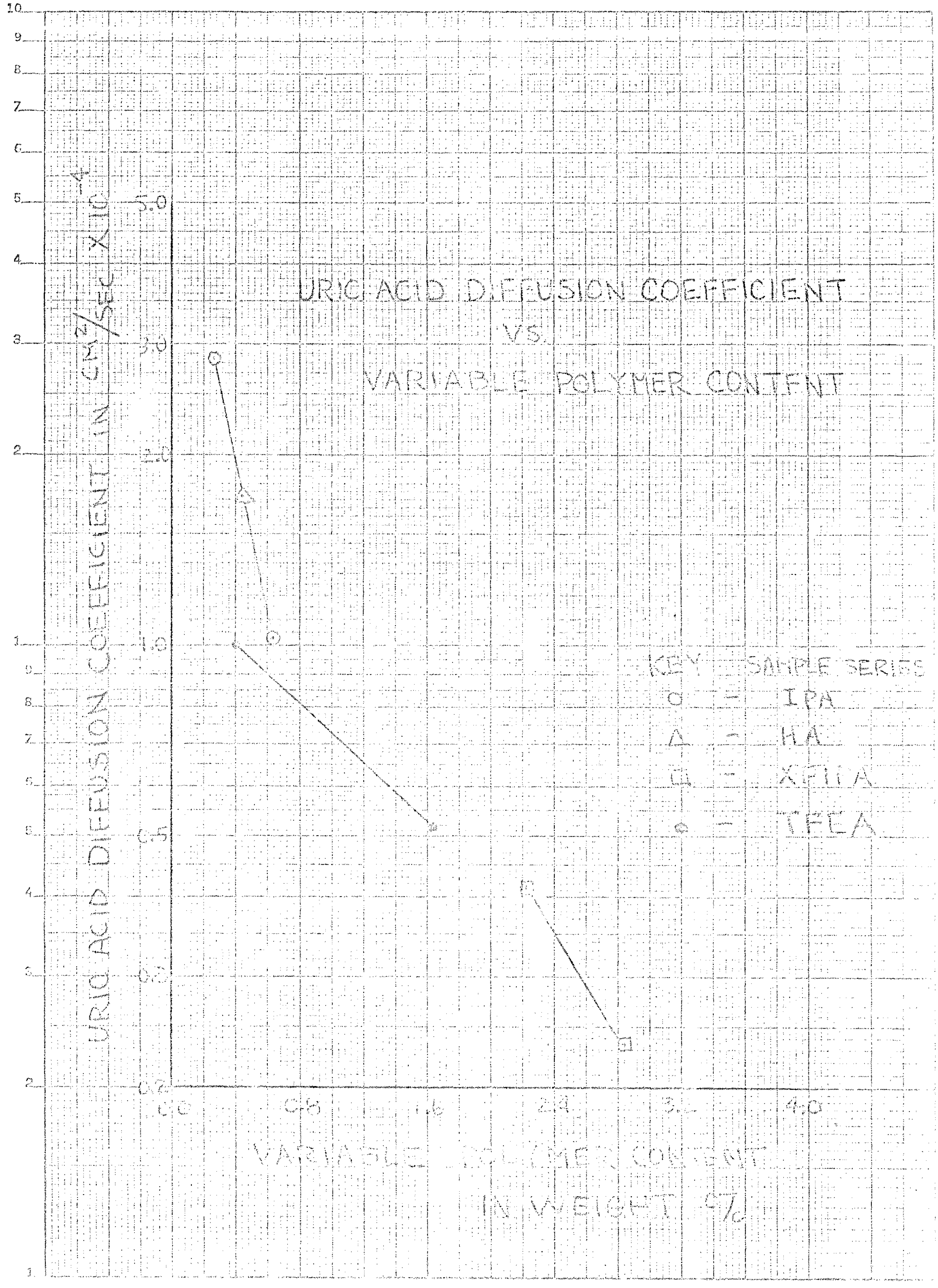
Uric Acid Concentration Vs. Optical Density

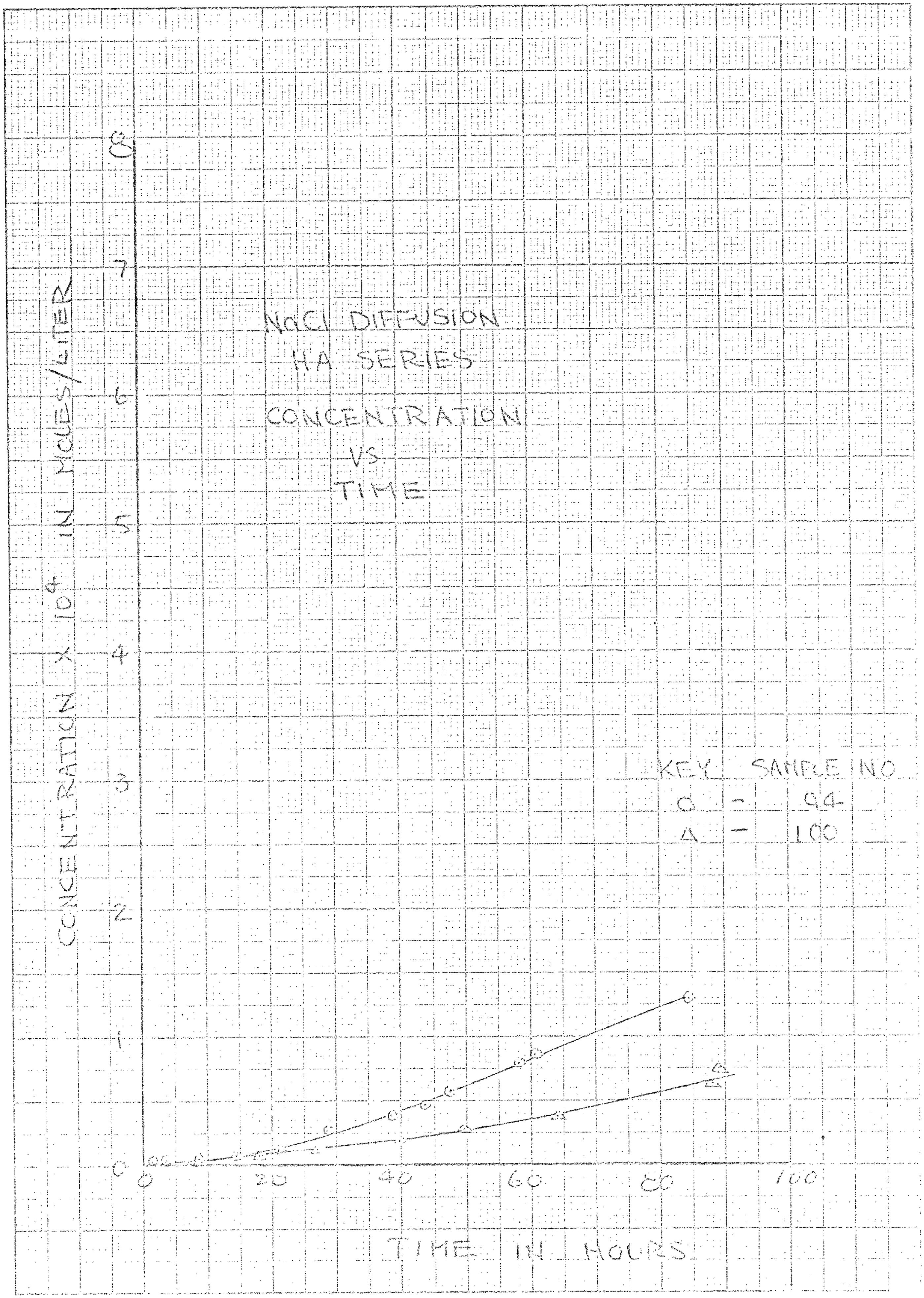
Concentration grams/liter	Optical Density
2.00	.360
1.00	.250
0.10	.035
0.02	.045
0.01	.020

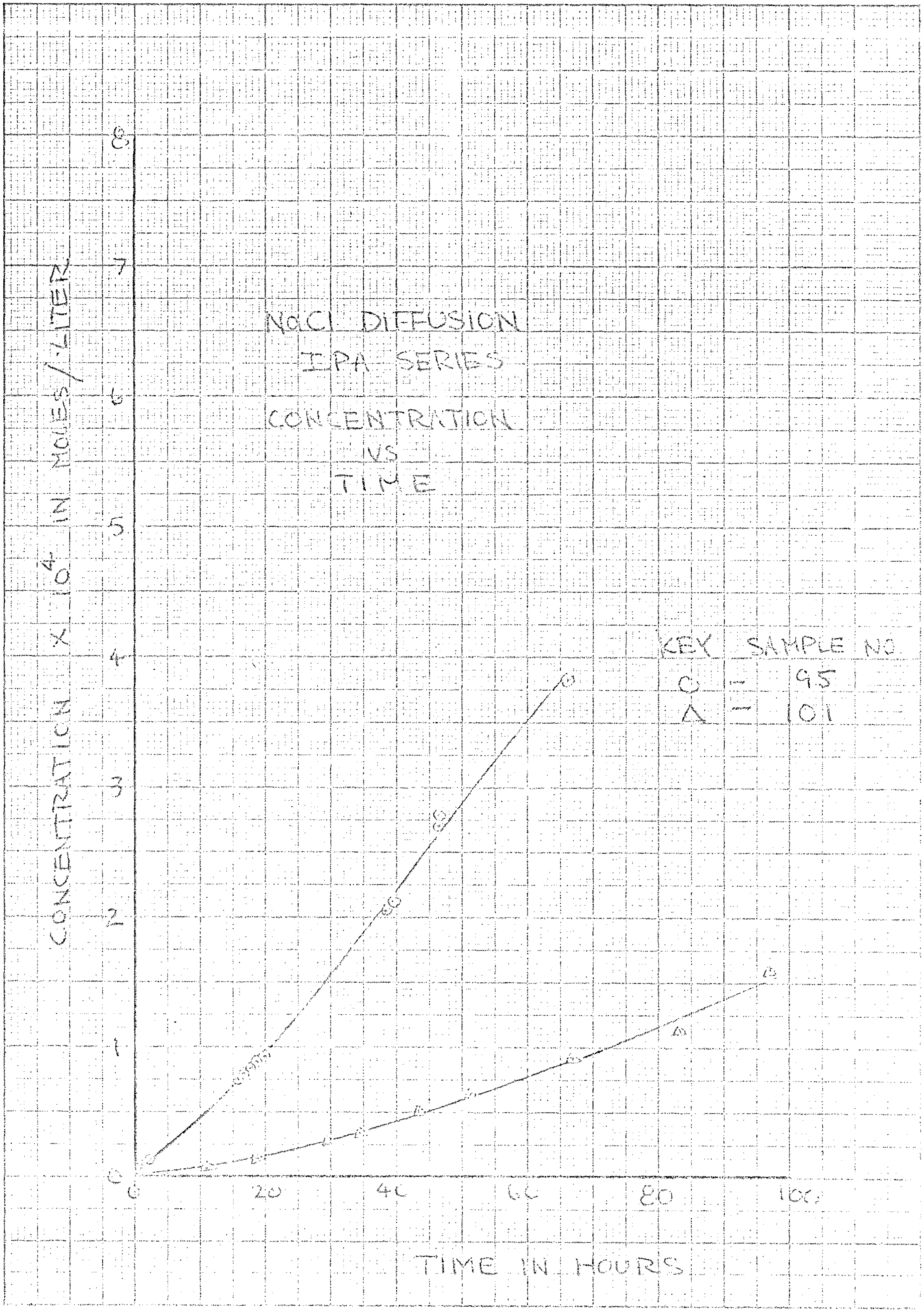
Urea Concentration vs. Optical Density

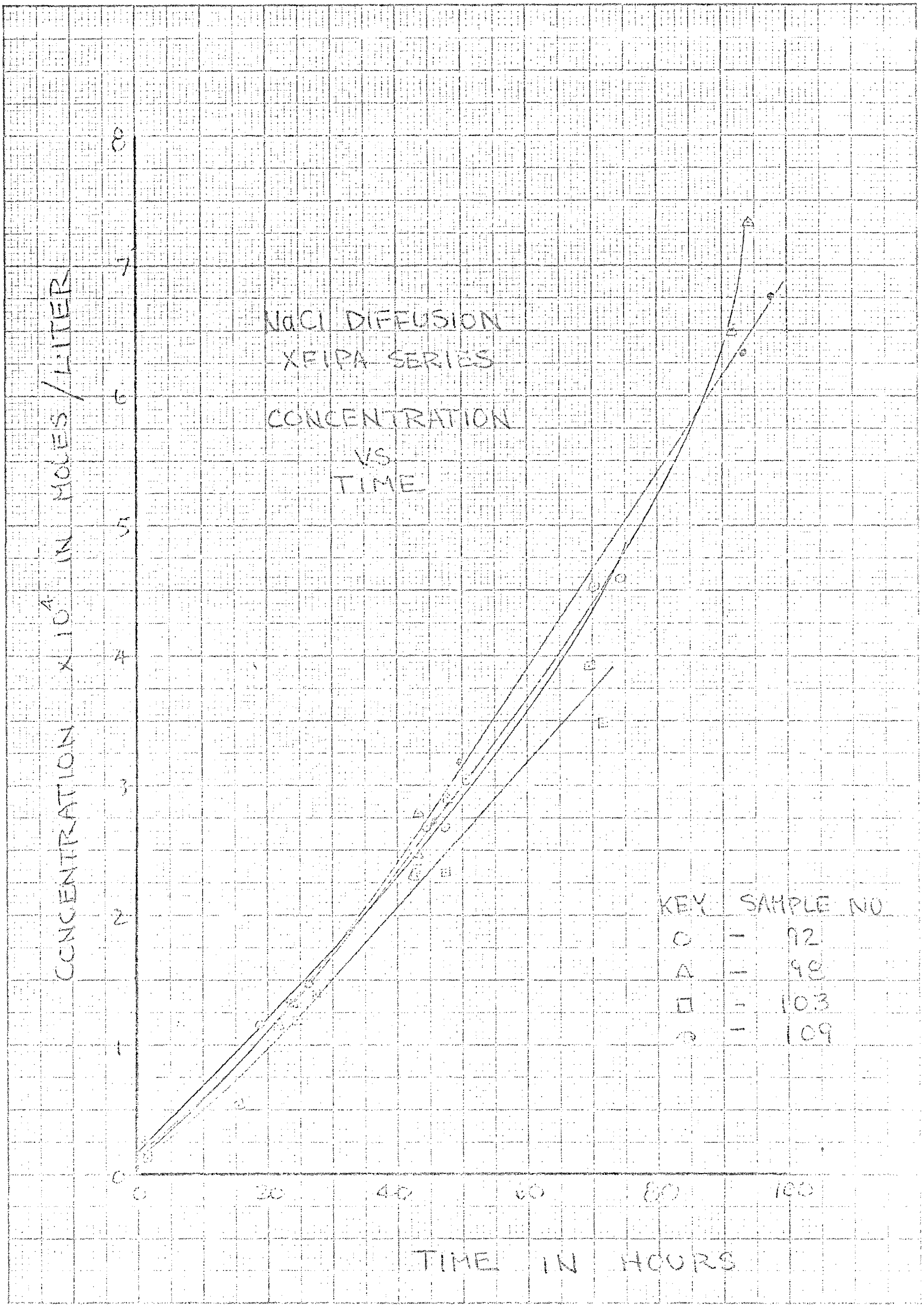
Concentration grams/liter	Optical Density
.1000	1.600
.0500	1.100
.0400	.950
.0300	.700
.0100	.450
.0010	.155
.0005	.085

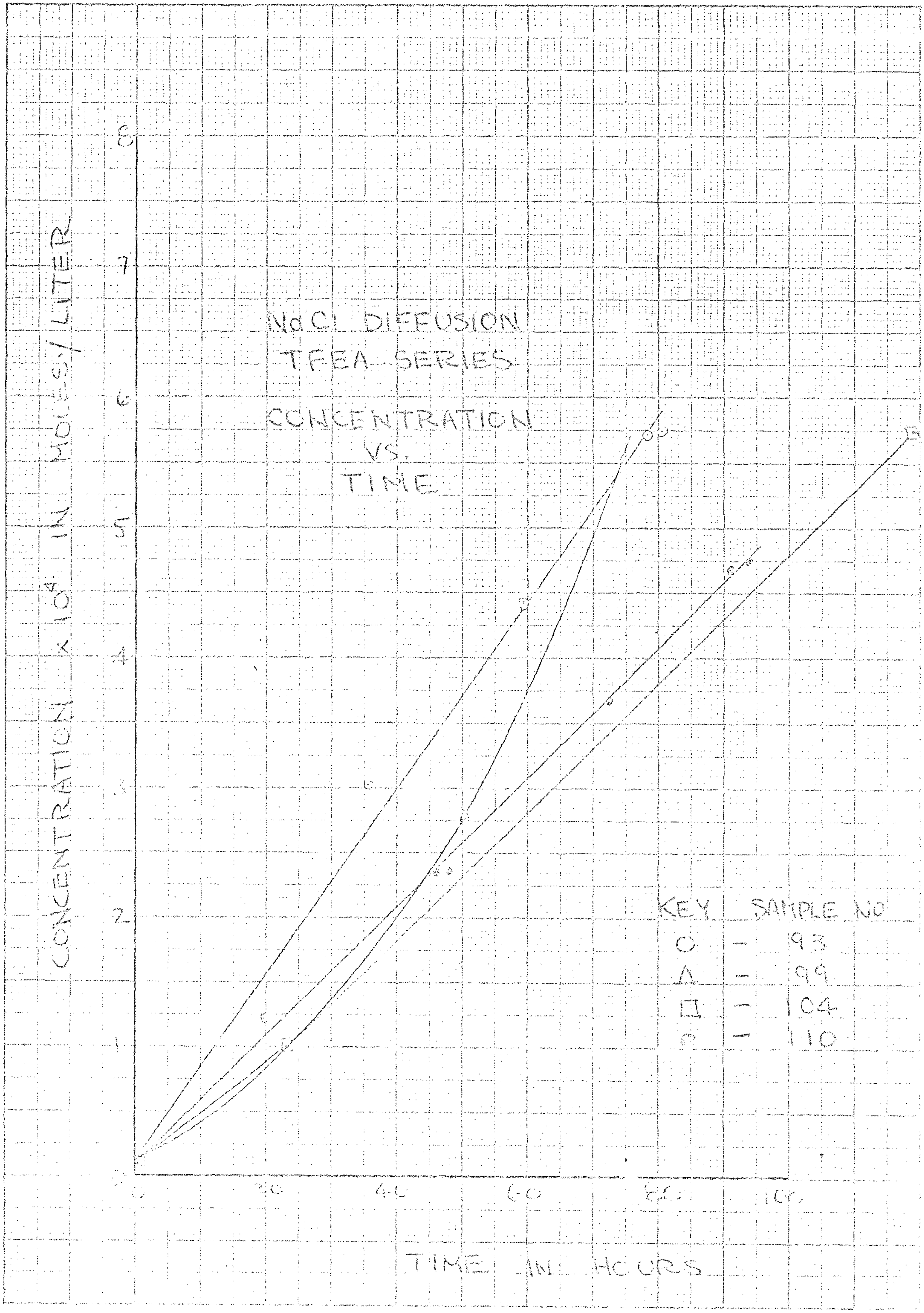

NaCl DIFFUSION COEFFICIENT
VS
VARIABLE POLYMER CONTENT
NaCl DIFFUSION COEFFICIENTS IN CM²/SEC X 10⁻⁴
0
1
2
3
4
5
6
7
8
0
0.8
1.6
2.4
3.2
4.0
VARIABLE POLYMER CONTENT IN WT. %
KEY SAMPLE SERIES
○ – IPA
△ – HA
□ – XFIPA
⊙ – TFEA

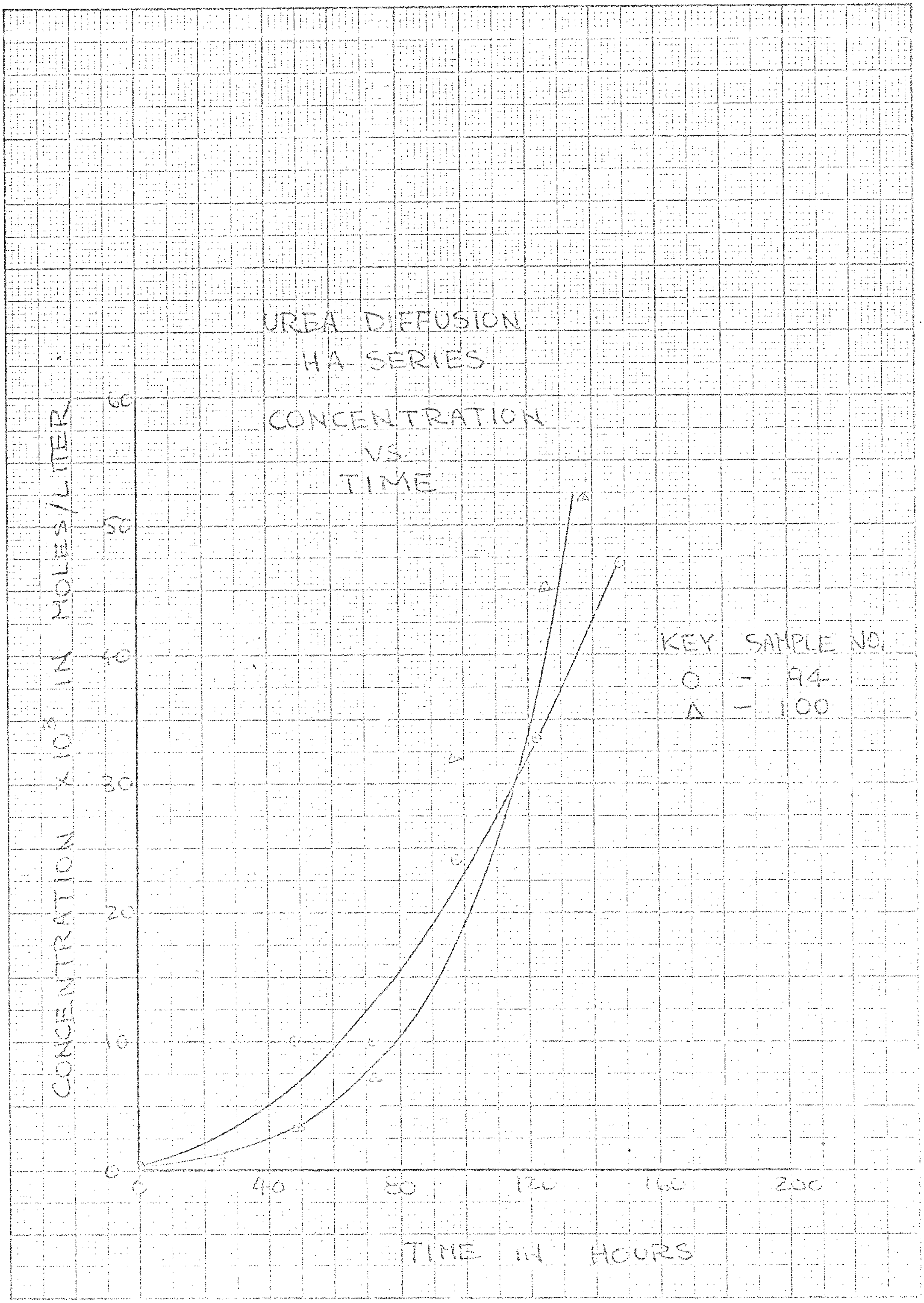

URIC ACID DIFFUSION COEFFICIENT
VS.
VARIABLE POLYMER CONTENT
URIC ACID DIFFUSION COEFFICIENT IN CM²/SEC X 10⁻⁴
KEY SAMPLE SERIES
○ - IPA
△ - HA
□ - XFHA
• - TFEA
VARIABLE POLYMER CONTENT
IN WEIGHT %

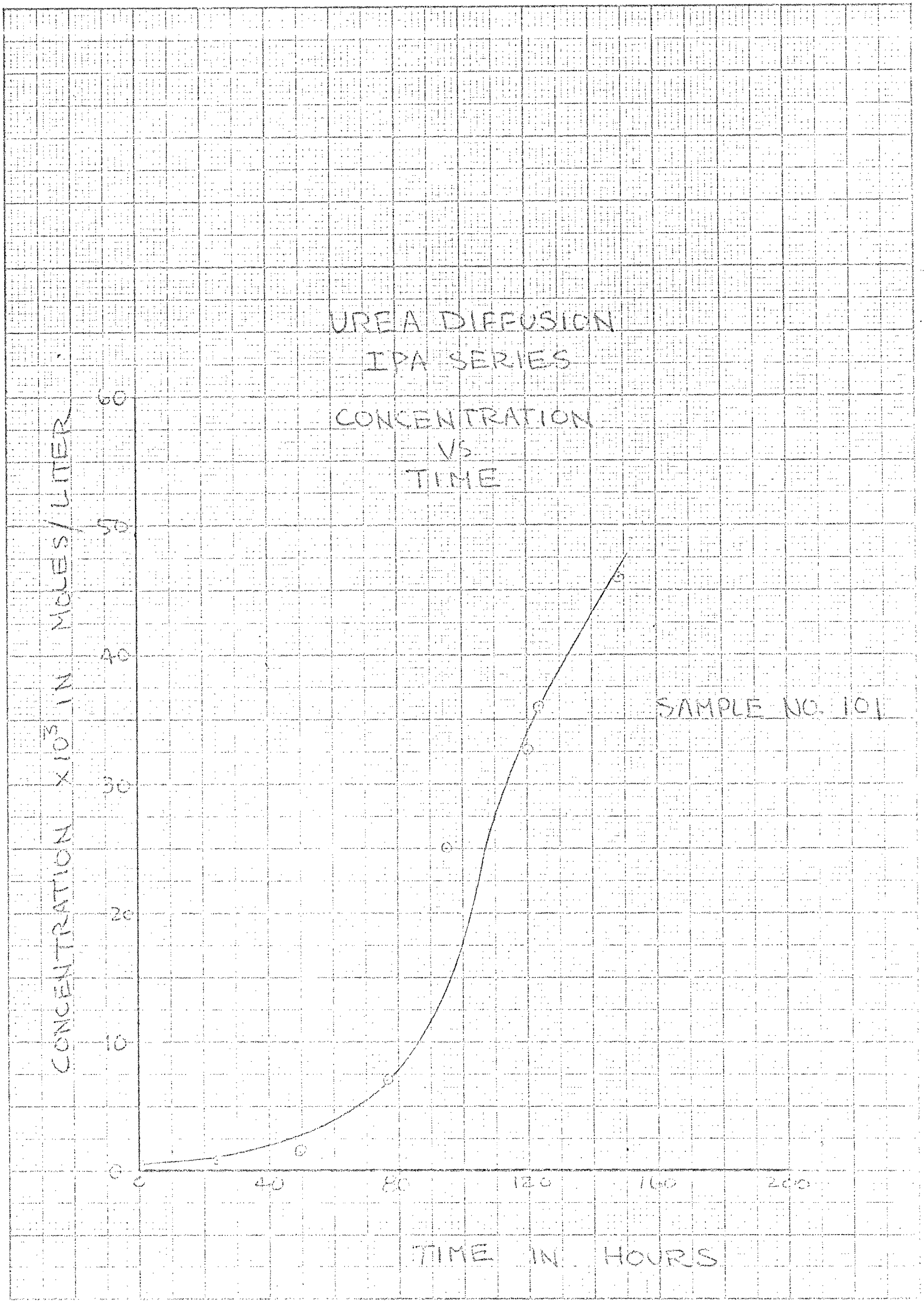

NaCl DIFFUSION
HA SERIES
CONCENTRATION
VS
TIME
CONCENTRATION X 10^4 IN MOLES/LITER
TIME IN HOURS
KEY SAMPLE NO
○ - 94
△ - 100
0
1
2
3
4
5
6
7
8
0
20
40
60
80
100

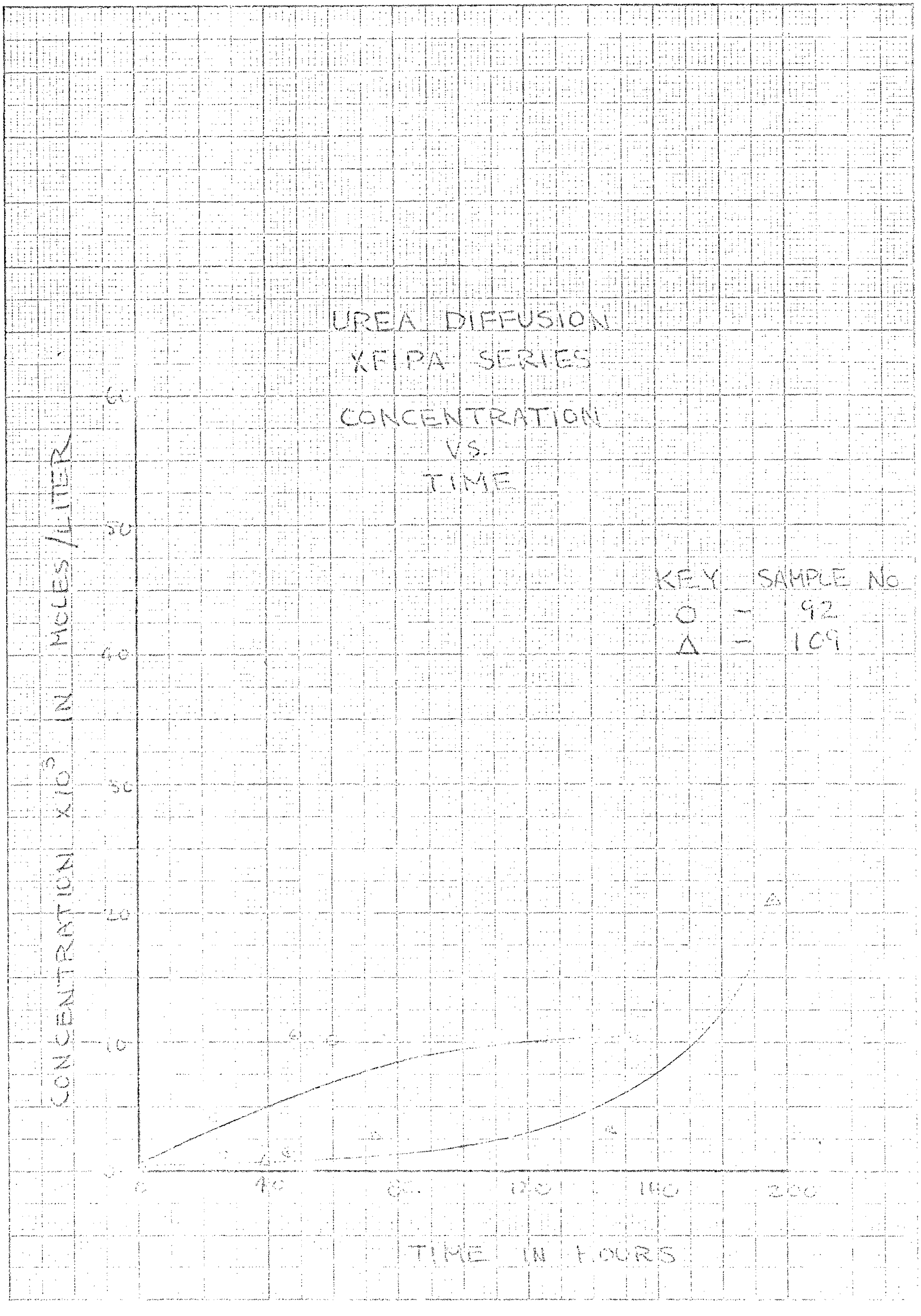

NaCl DIFFUSION
IPA SERIES
CONCENTRATION
VS
TIME
KEY SAMPLE NO
○ - 95
△ - 101
CONCENTRATION X 10^{4} IN MOLES/LITER
TIME IN HOURS
0
1
2
3
4
5
6
7
8
0
20
40
60
80
100

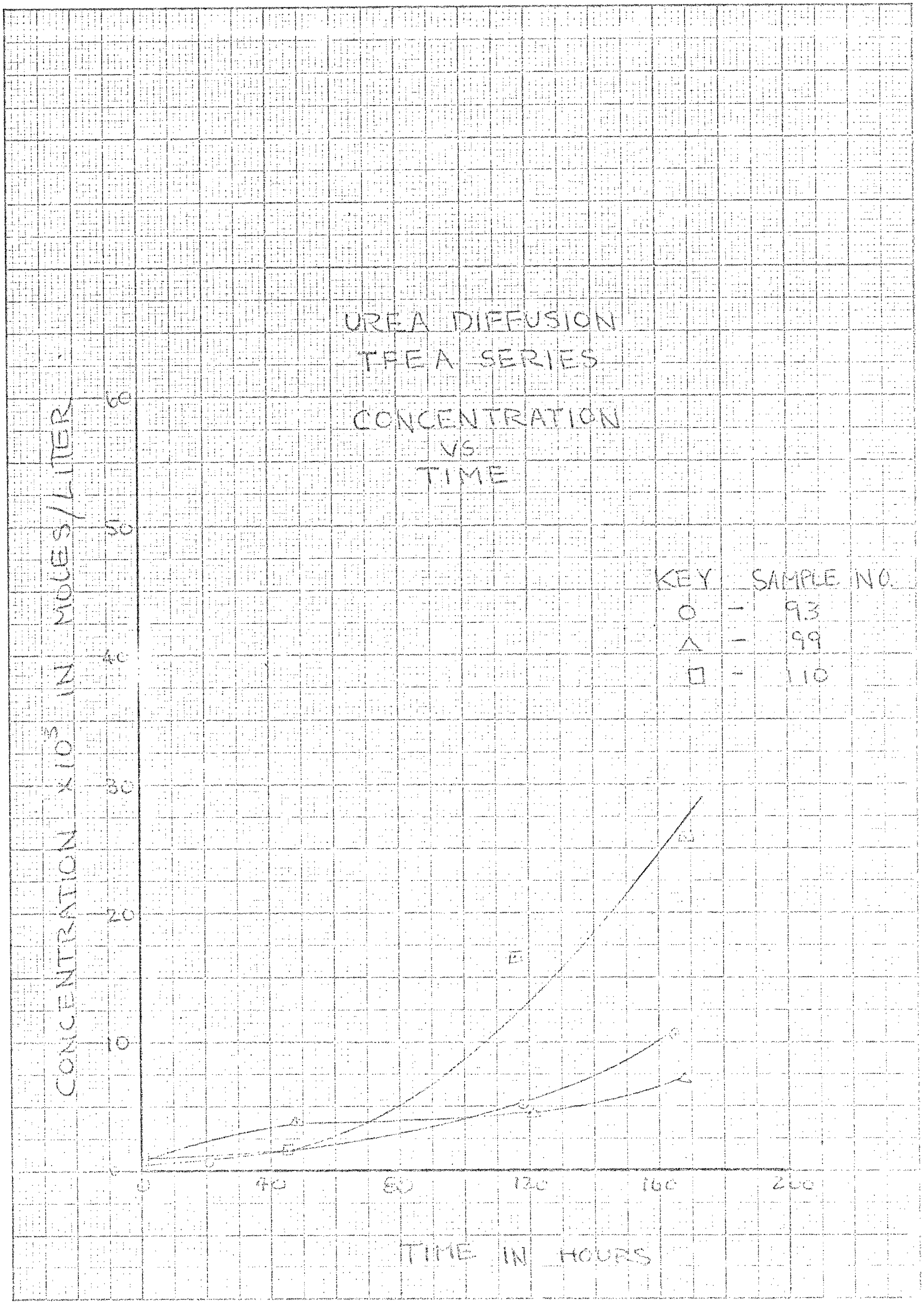

NaCl DIFFUSION
XFIPA SERIES
CONCENTRATION
VS
TIME
CONCENTRATION x 10^{-4} IN MOLES / LITER
TIME IN HOURS
0
1
2
3
4
5
6
7
8
0
20
40
60
80
100
KEY SAMPLE NO
○ — 92
△ — 98
□ — 103
— 109

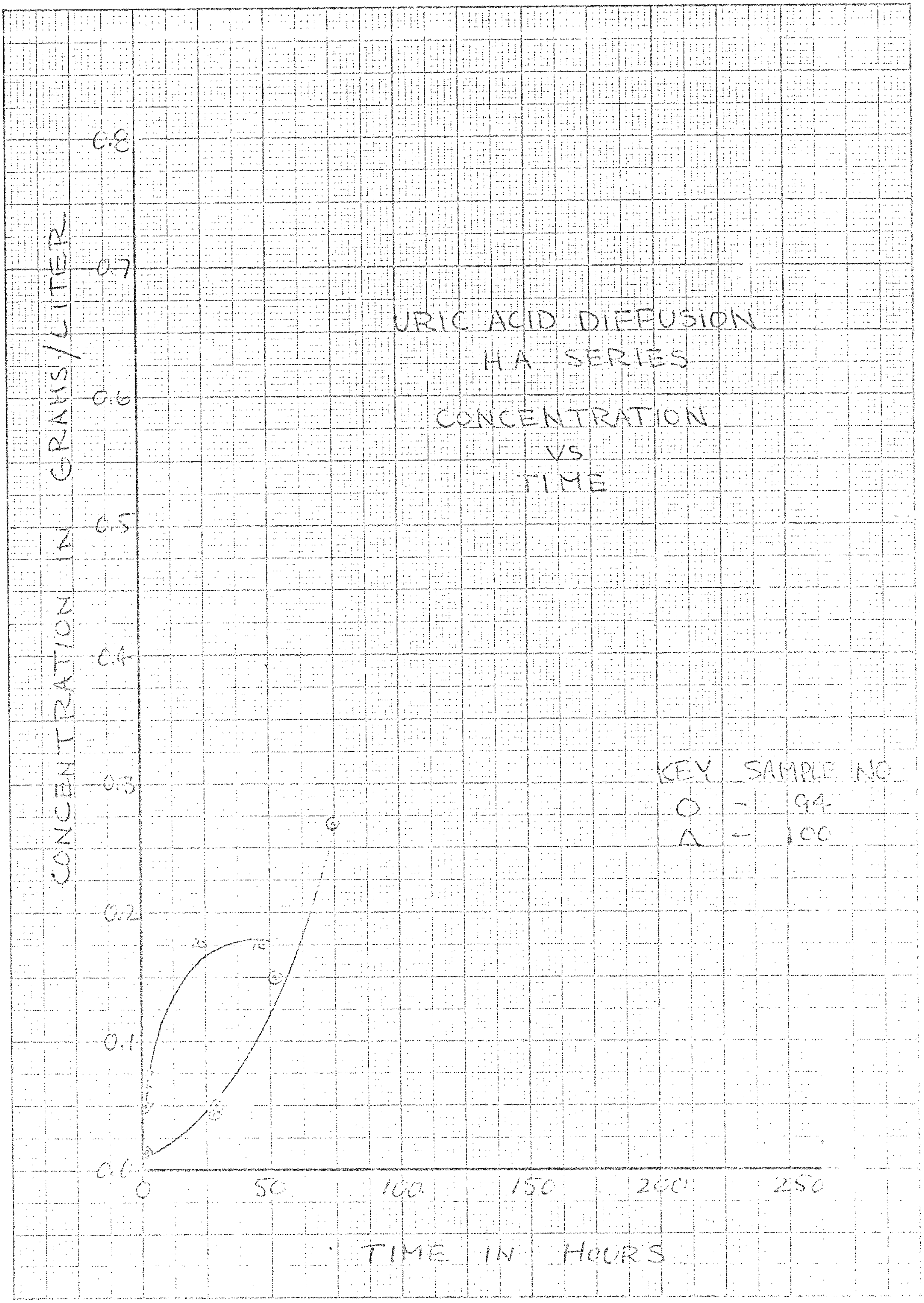

NaCl DIFFUSION
TFEA SERIES
CONCENTRATION
VS.
TIME
CONCENTRATION x 10⁴ IN MOLES/LITER
TIME IN HOURS
0
20
40
60
80
100
1
2
3
4
5
6
7
8
KEY SAMPLE NO
○ - 93
△ - 99
□ - 104
- 110

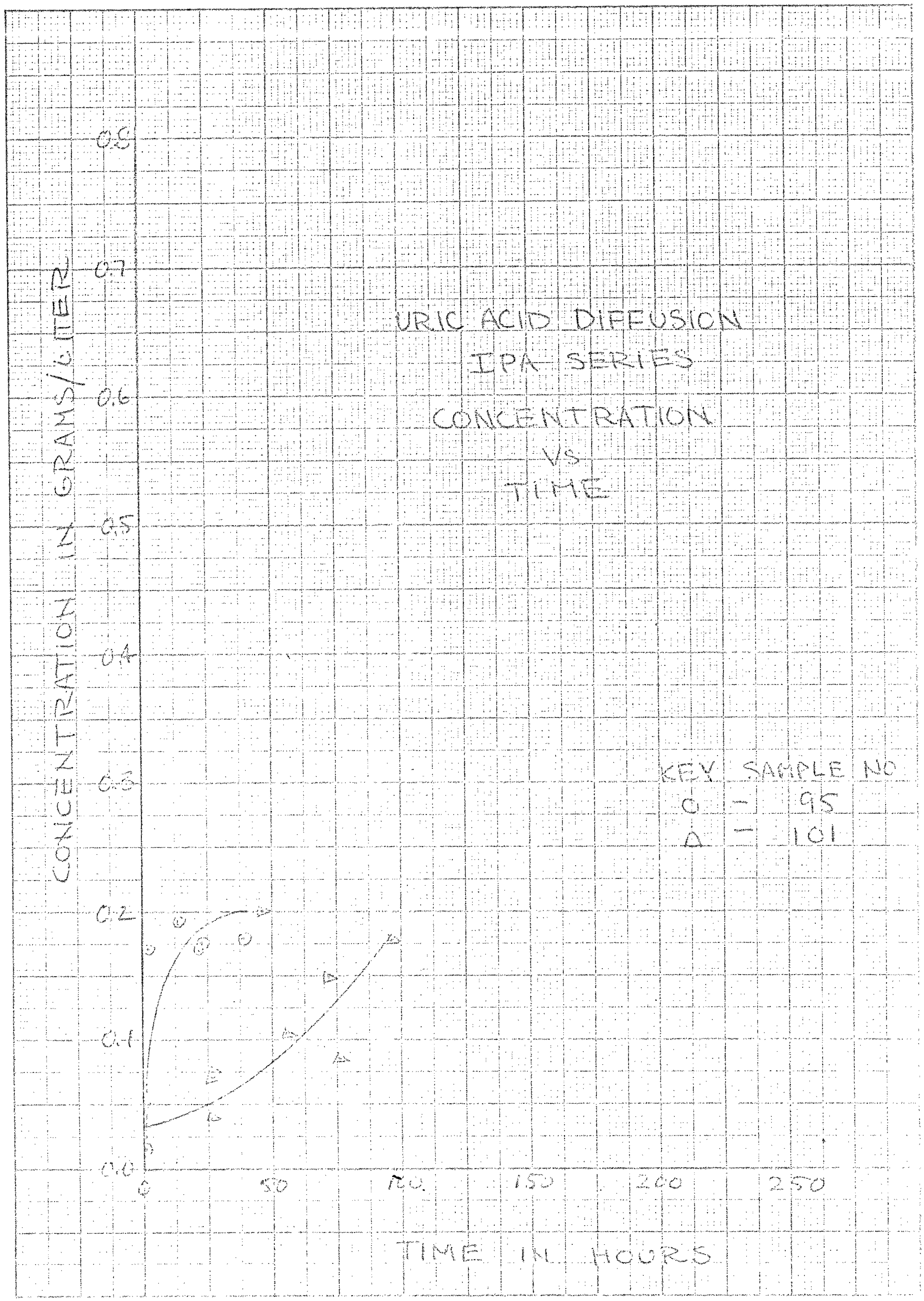

UREA DIFFUSION
HA SERIES
CONCENTRATION
VS.
TIME
CONCENTRATION X 10^3 IN MOLES/LITER
0
10
20
30
40
50
60
0
40
80
120
160
200
TIME IN HOURS
KEY SAMPLE NO.
○ - 94
Δ - 100

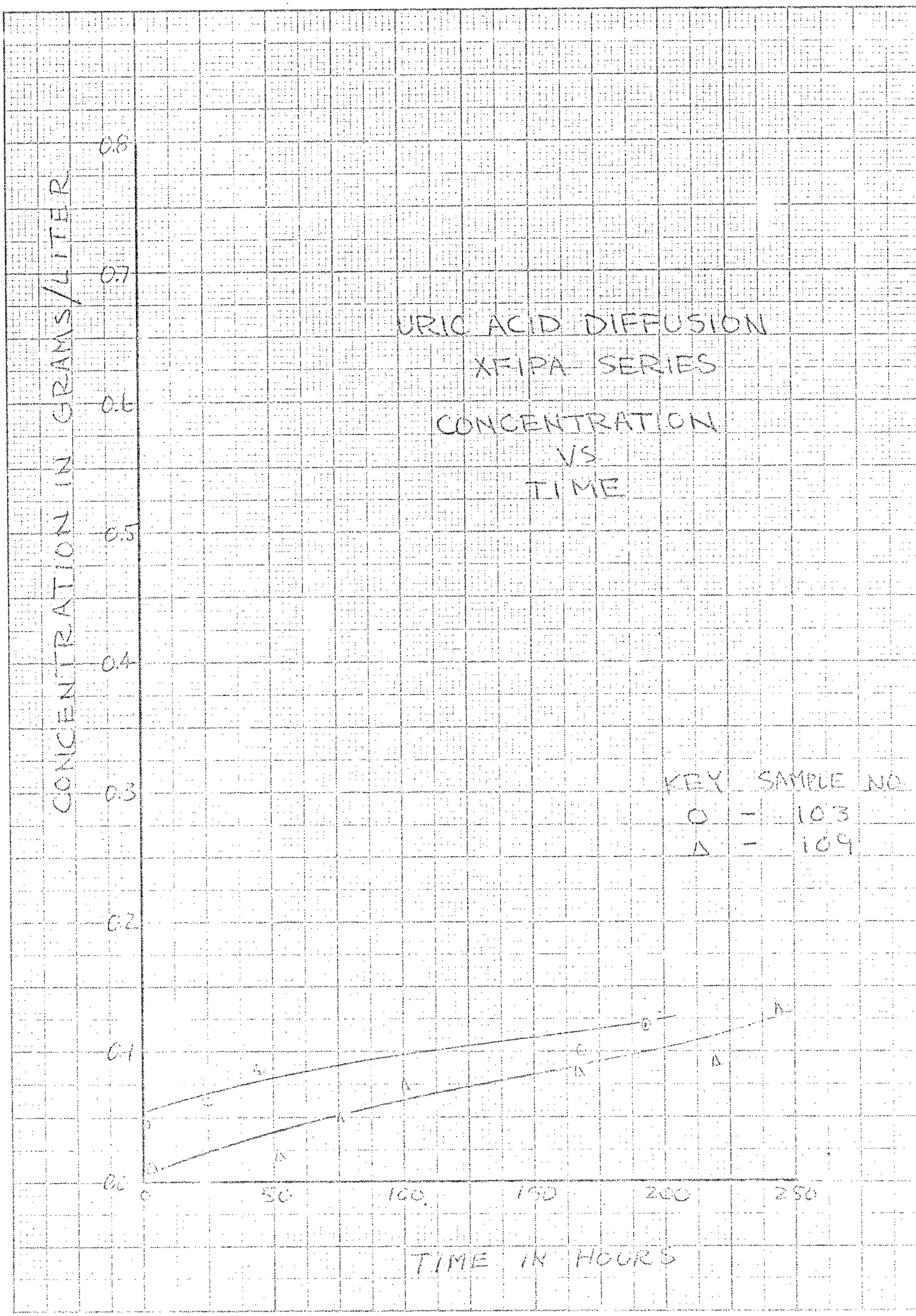

UREA DIFFUSION
IPA SERIES
CONCENTRATION
VS
TIME
SAMPLE NO. 101
CONCENTRATION X10^3 IN MOLES/LITER
60
50
40
30
20
10
0
0
40
80
120
160
200
TIME IN HOURS

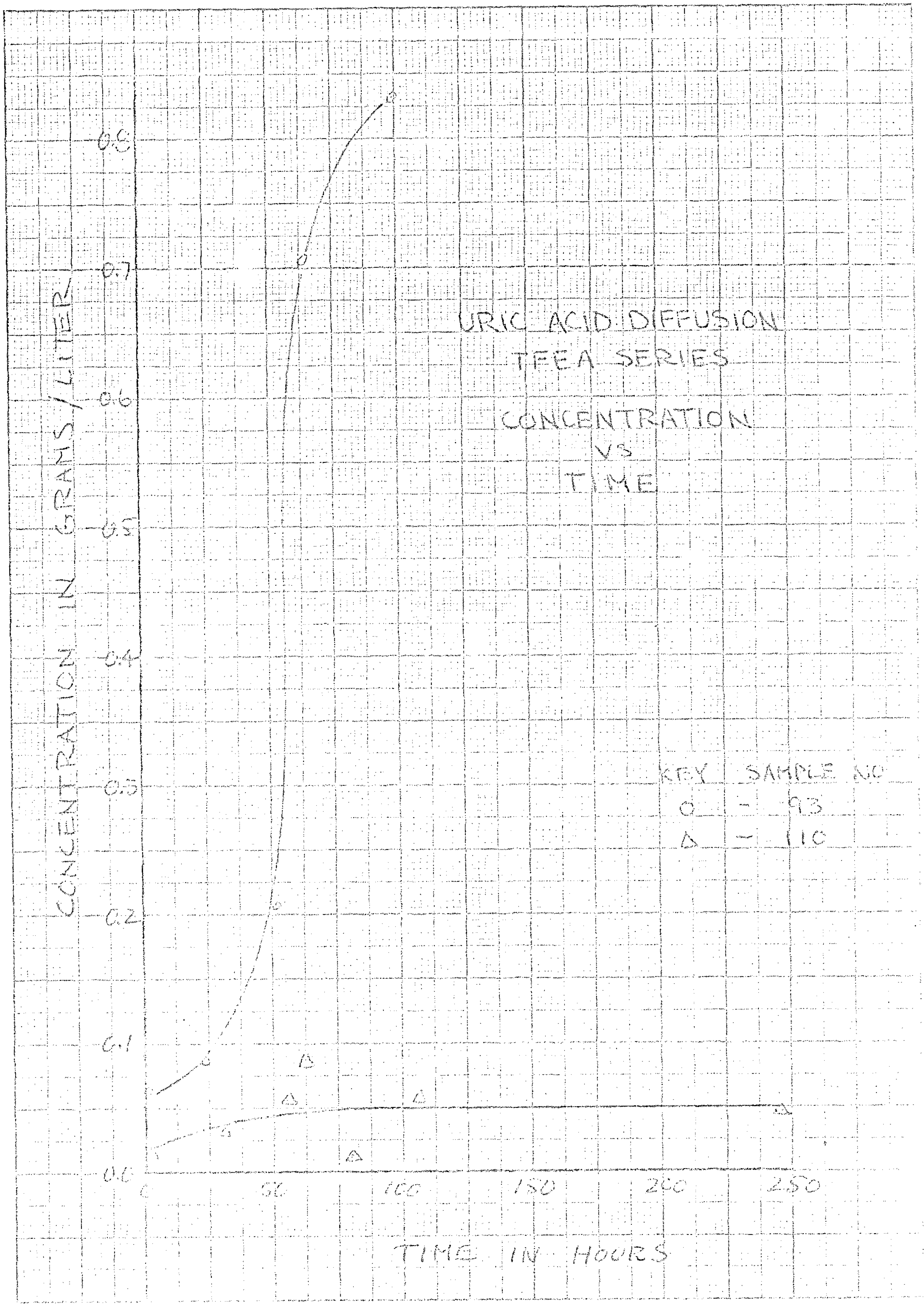

UREA DIFFUSION
XFIPA SERIES
CONCENTRATION
VS.
TIME
KEY SAMPLE No.
O - 92
Δ - 109
CONCENTRATION X10⁵ IN MOLES/LITER
TIME IN HOURS
0
10
20
30
40
50
60
40
80
120
160
200

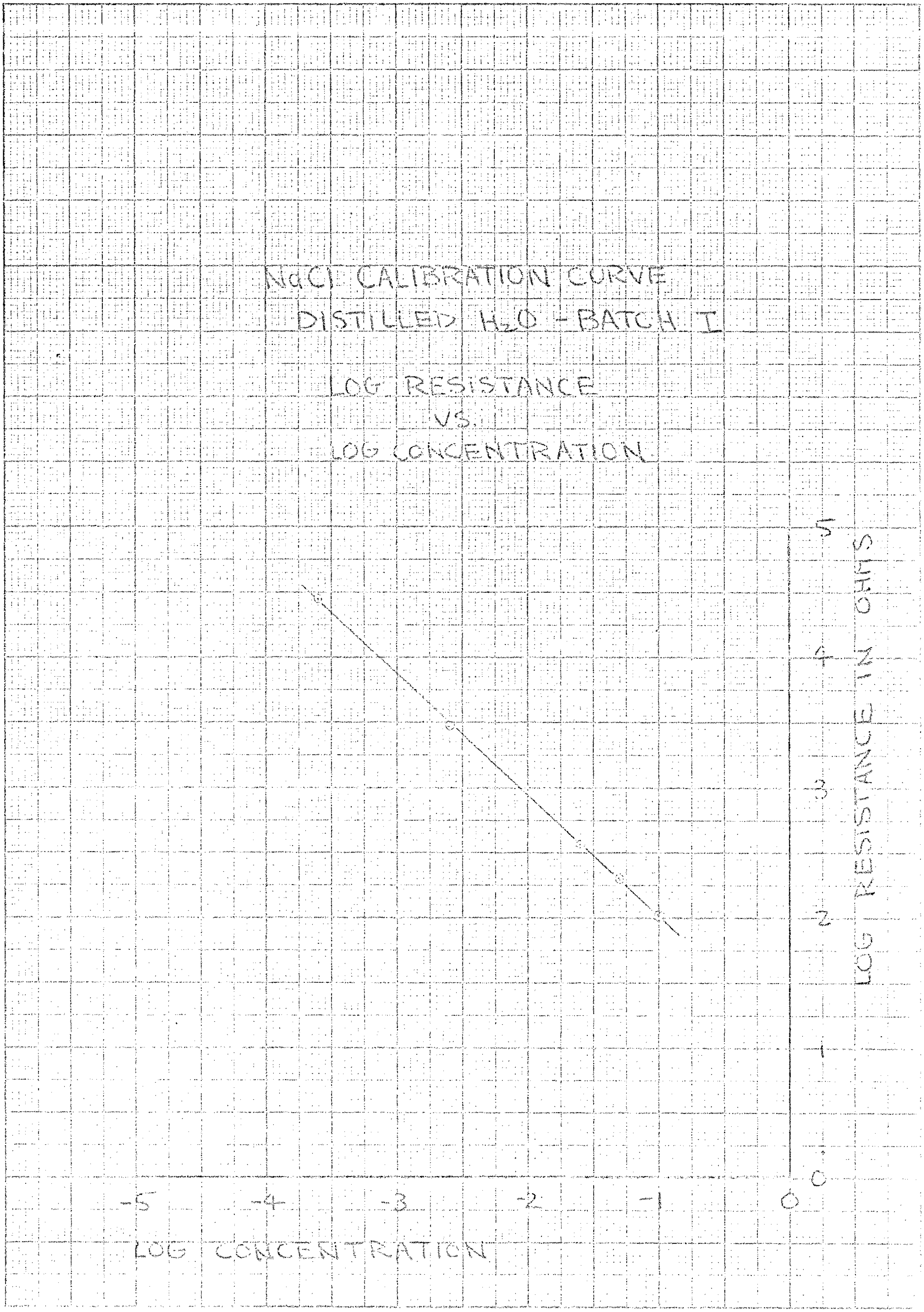

UREA DIFFUSION
TFEA SERIES
CONCENTRATION
VS
TIME
KEY SAMPLE NO.
○ - 93
△ - 99
□ - 110
CONCENTRATION X10^5 IN MOLES/LITER
0
10
20
30
40
50
60
0
40
80
120
160
200
TIME IN HOURS

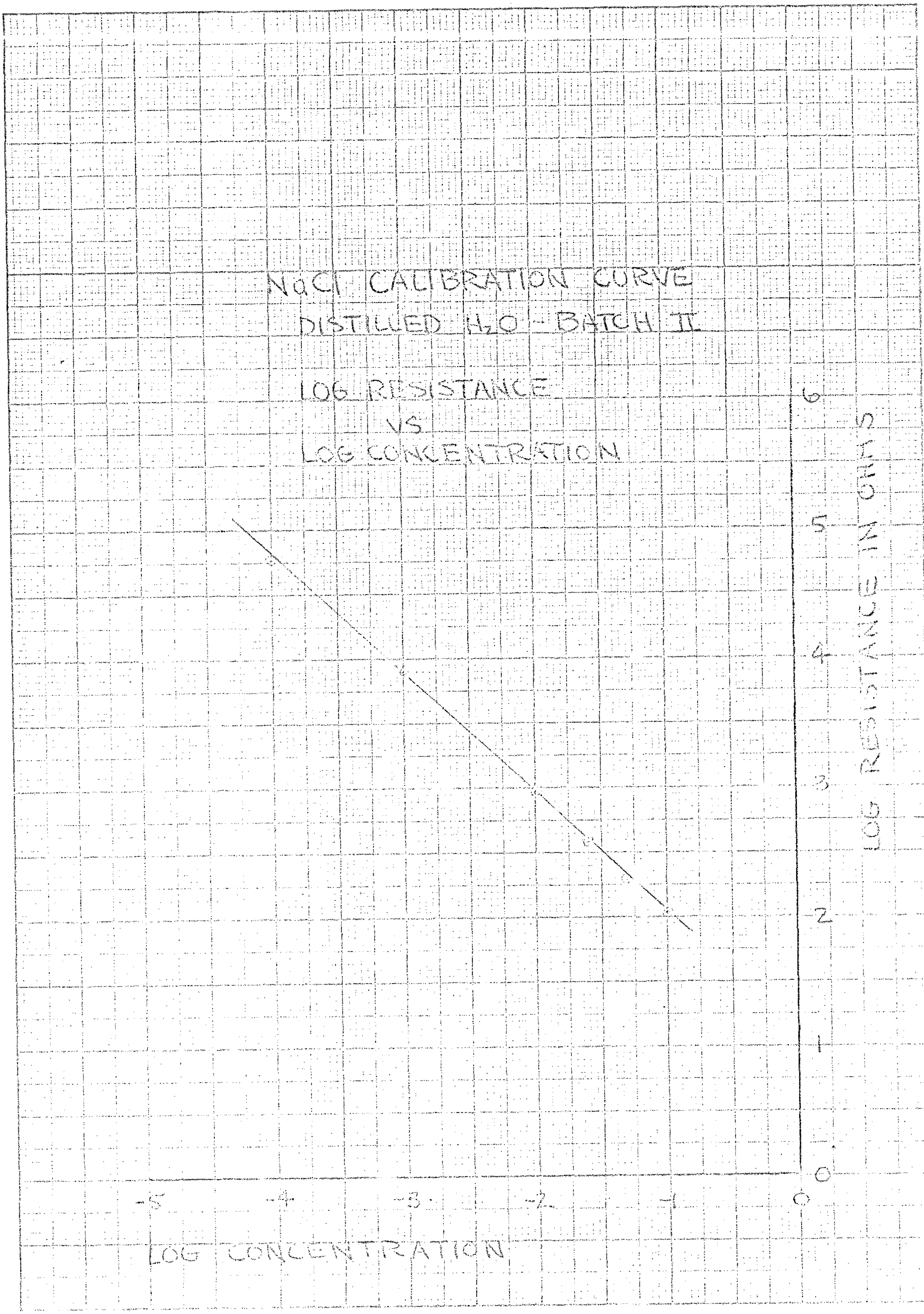

URIC ACID DIFFUSION
H A SERIES
CONCENTRATION
VS
TIME
KEY SAMPLE NO
O - 94
Δ - 100
CONCENTRATION IN GRAMS/LITER
0.0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0
50
100
150
200
250
TIME IN HOURS

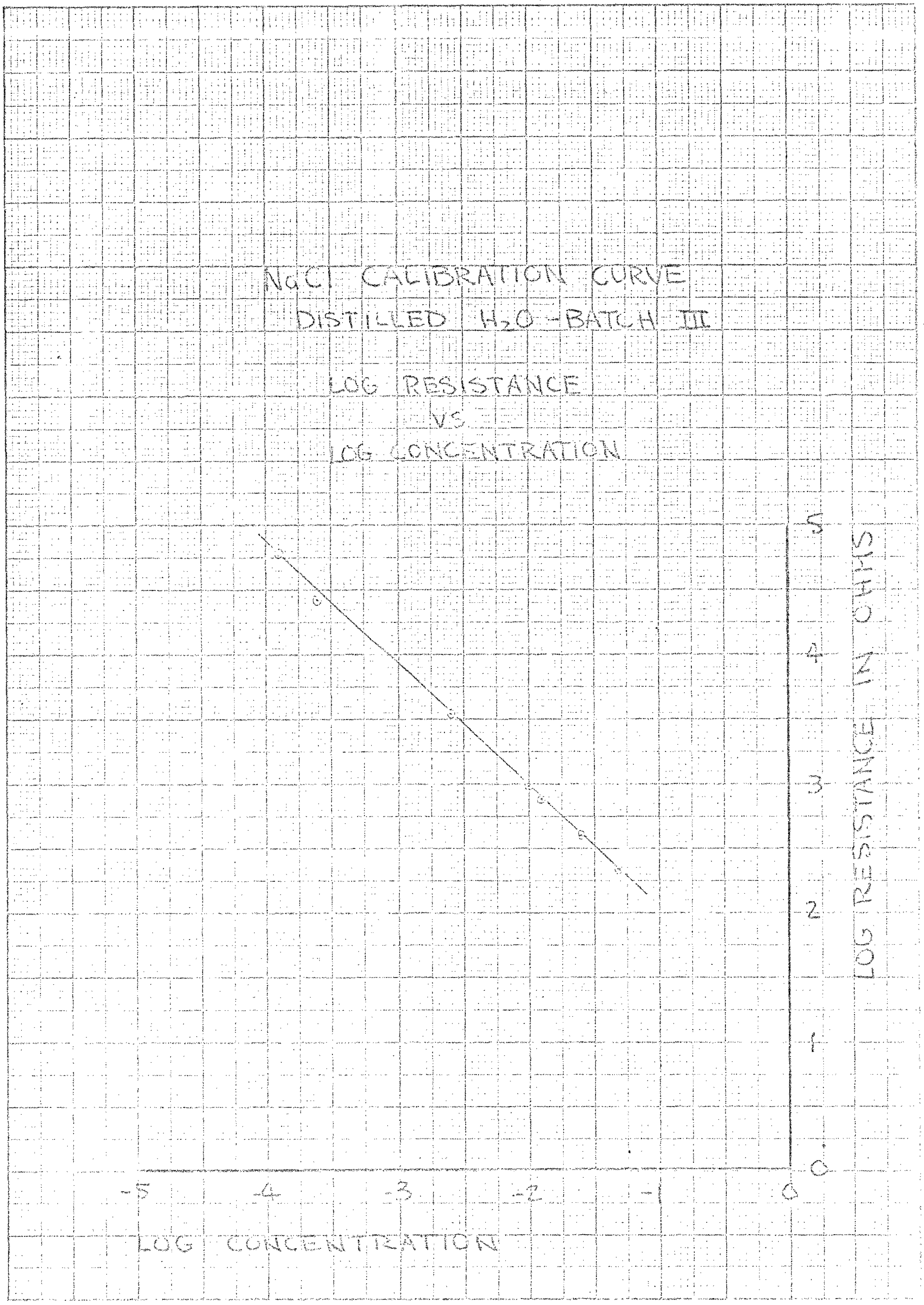

URIC ACID DIFFUSION
IPA SERIES
CONCENTRATION
VS
TIME
KEY SAMPLE NO
O - 95
Δ - 101
CONCENTRATION IN GRAMS/LITER
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0.0
0
50
100
150
200
250
TIME IN HOURS

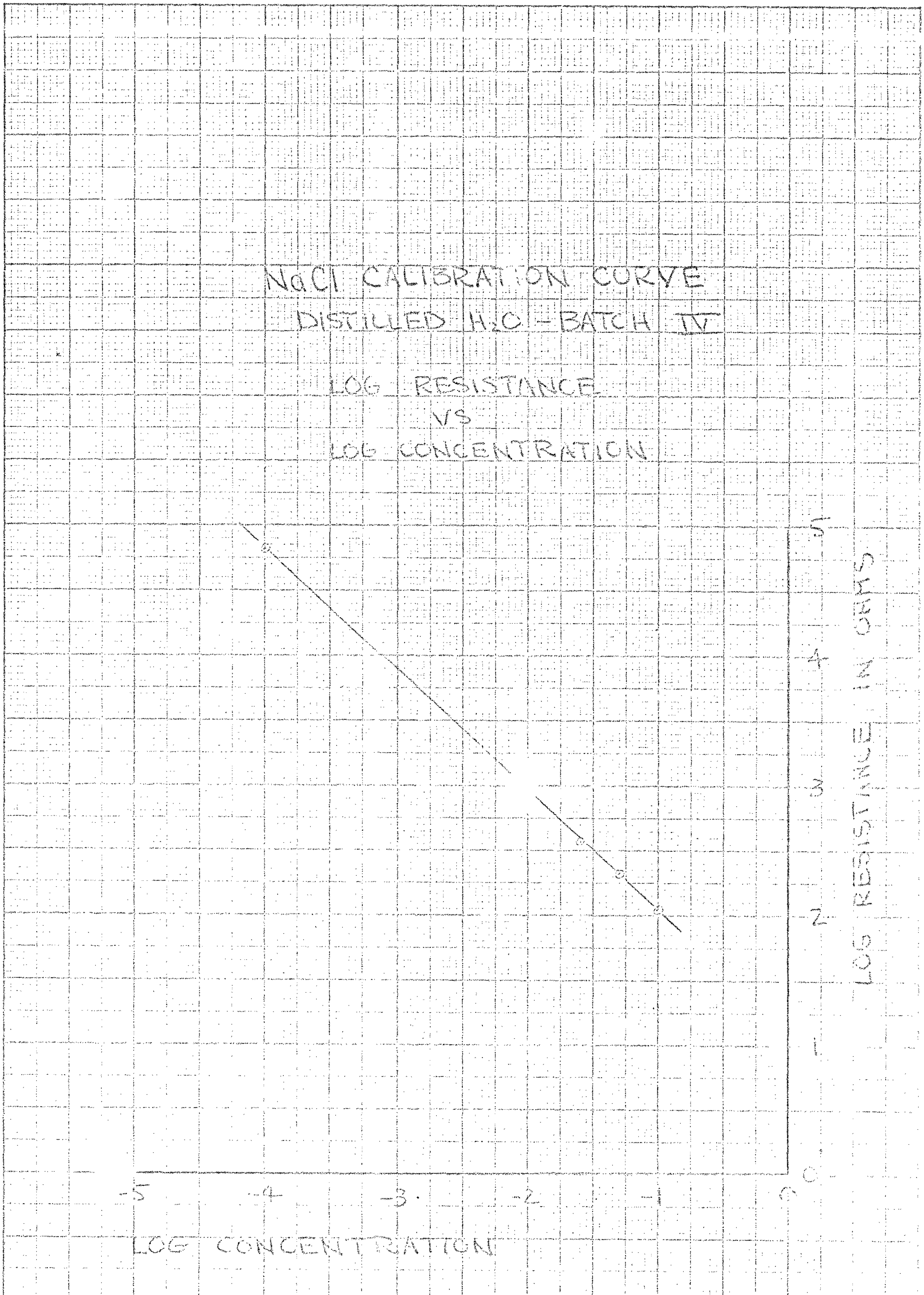

URIC ACID DIFFUSION
XFIPA SERIES
CONCENTRATION
VS
TIME
CONCENTRATION IN GRAMS/LITER
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0.0
0
50
100
150
200
250
TIME IN HOURS
KEY SAMPLE NO
O - 103
Δ - 109

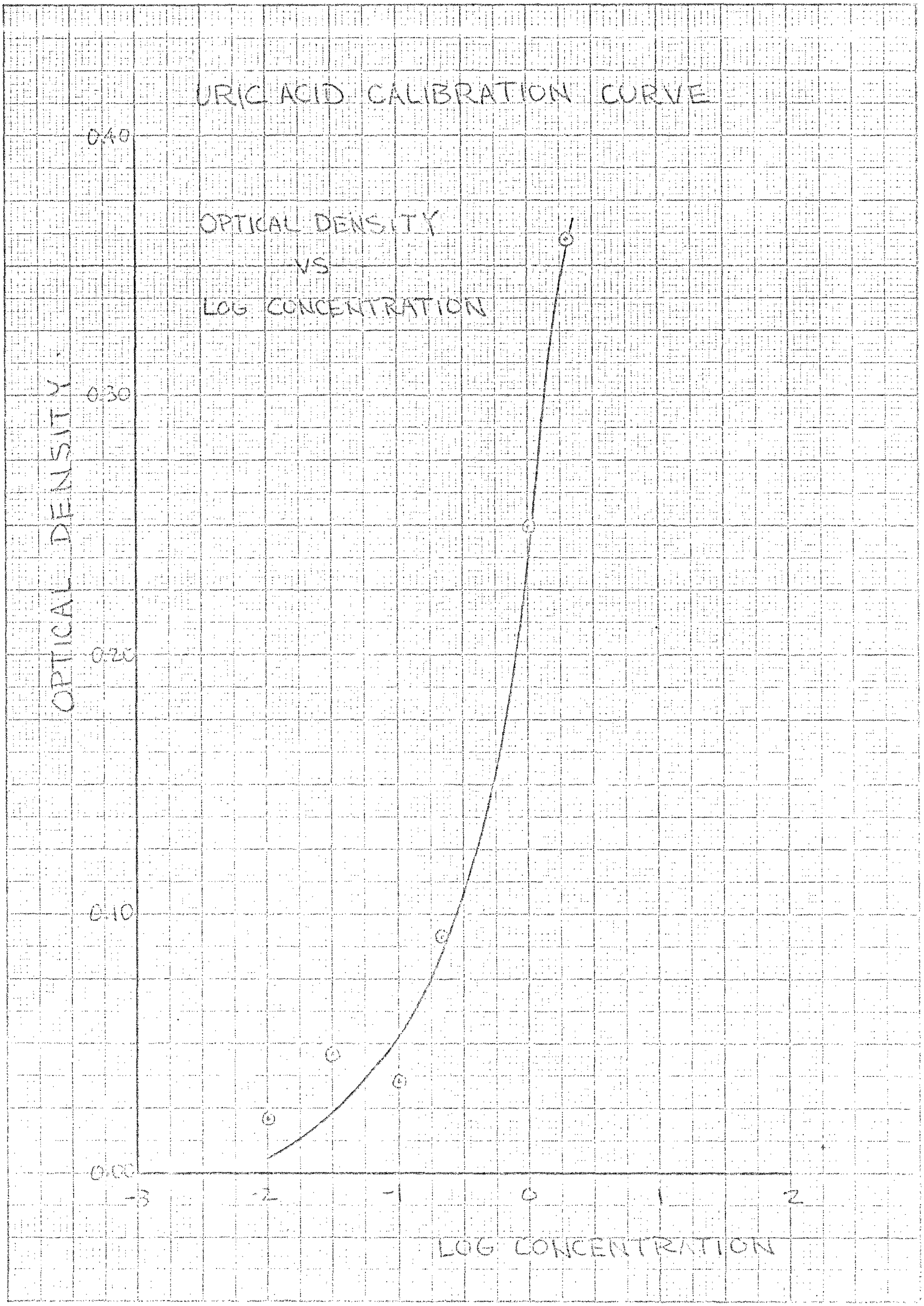

URIC ACID DIFFUSION
TFEA SERIES
CONCENTRATION
VS
TIME
CONCENTRATION IN GRAMS / LITER
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0.0
0
50
100
150
200
250
TIME IN HOURS
KEY SAMPLE NO
o - 93
Δ - 110

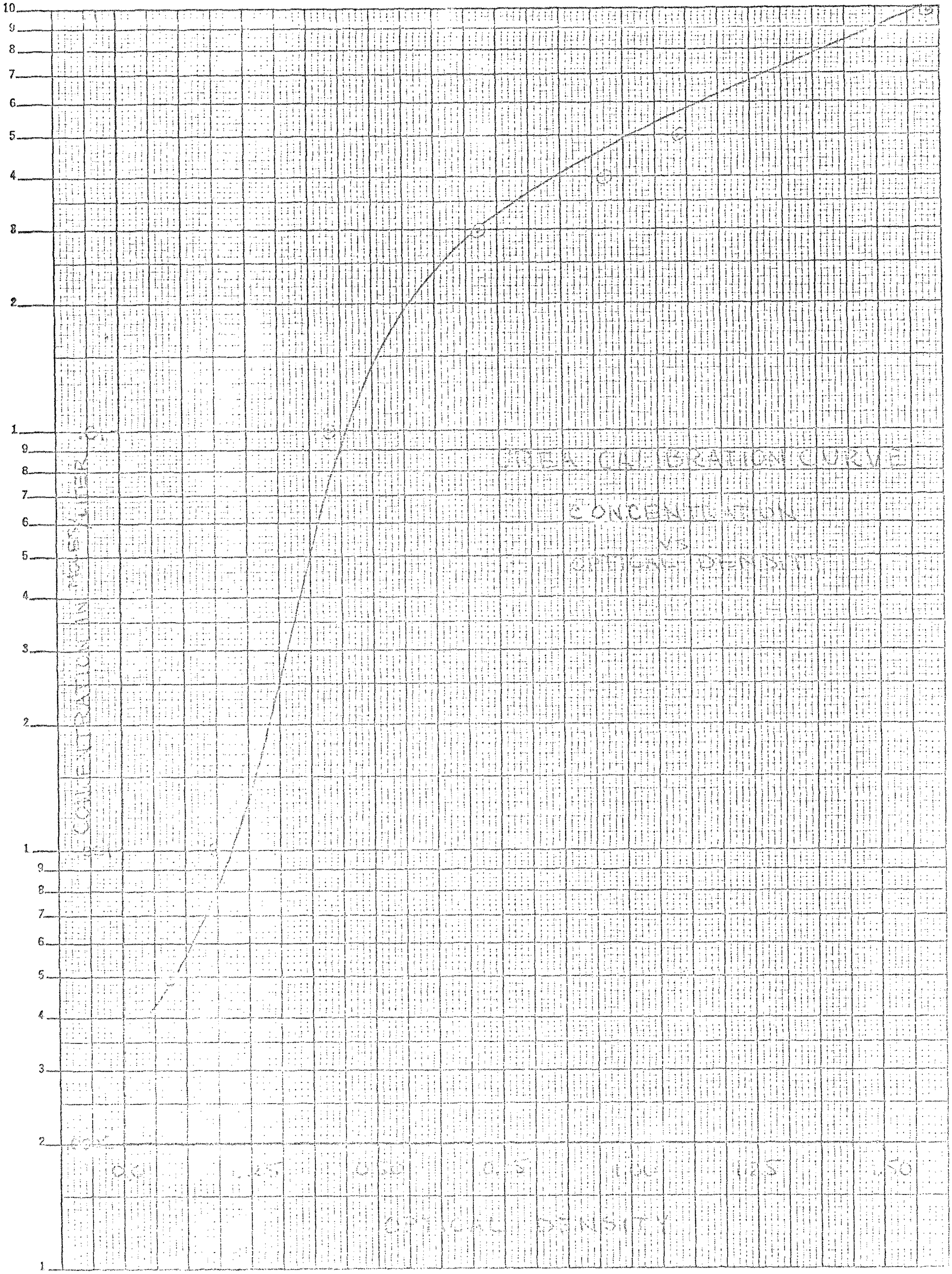

NaCl CALIBRATION CURVE
DISTILLED H_2O - BATCH I
LOG RESISTANCE
VS.
LOG CONCENTRATION
LOG RESISTANCE IN OHMS
5
4
3
2
1
0
-5
-4
-3
-2
-1
0
LOG CONCENTRATION


NaCl CALIBRATION CURVE
DISTILLED H_2O - BATCH II
LOG RESISTANCE
VS
LOG CONCENTRATION
LOG RESISTANCE IN OHMS
6
5
4
3
2
1
0
-5
-4
-3
-2
-1
0
LOG CONCENTRATION


NaCl CALIBRATION CURVE
DISTILLED H2O - BATCH III
LOG RESISTANCE
VS
LOG CONCENTRATION
LOG RESISTANCE IN OHMS
0
1
2
3
4
5
-5
-4
-3
-2
-1
0
LOG CONCENTRATION


NaCl CALIBRATION CURVE
DISTILLED H_2O - BATCH IV
LOG RESISTANCE
VS
LOG CONCENTRATION
5
4
3
2
1
0
LOG RESISTANCE IN OHMS
-5
-4
-3
-2
-1
0
LOG CONCENTRATION


URIC ACID CALIBRATION CURVE
OPTICAL DENSITY
VS
LOG CONCENTRATION
OPTICAL DENSITY
0.40
0.30
0.20
0.10
0.00
-3
-2
-1
0
1
2
LOG CONCENTRATION


UREA CALIBRATION CURVE
CONCENTRATION
VS
OPTICAL DENSITY
CONCENTRATION mgs/LITER
0.0
.25
0.50
0.75
1.00
1.25
1.50
OPTICAL DENSITY
10
9
8
7
6
5
4
3
2
1

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a	impeller radius
A	area
	factor used in Stokes-Einstein Eq. varies bet. 3π and 1
b	membrane radius
C	concentration
Cs	mean solute concentration
d	impeller diameter
F_A	unit force on a molecule of
J,Jv,Js	molecular flux; Jv = net volume flux; Js = solute flux
k	rate constant
k_{f1}, k_{f2}	liquid phase resistances or mass transfer coefficient
K	overall mass transfer coefficient
Lij	phenomenological coefficients
Lp	phenomenological coefficient = hydraulic conductivity
N	Avagadro's Number
ΔP	hydrostatic pressure difference
Pm	permeability of the membrane
R	Gas Law Constant
R_A	radius of diffusing particle
S	axial gap distance
t	time
T	absolute temperature
tm	membrane thickness
U	molecular mobility
v, v , v	velocity; in forward direction; = in backward direction
V	molar volume
V_1,V_2	volume of Chamber 1, of Chamber 2
Vc	Critical volume
x	linear distance
Tc	Critical temperature
β_{AB}	coefficient of sliding friction
λ	distance between two equilibrium positions
κ	Boltzman constant
π	osmotic pressure difference
Ω	angular velocity
Ω_D, Ω_v	generalized collision integrals for diffusion
n	stirrer speed
z	number of all the closest neighbors in all directions of a particular molecule
σ_R	Staverman reflection coefficient
σ_{AB}	Lennard-Jones distanc parameter
ζ	number of all the closest neighbors in one layer to a particular molecule
ψ	a uniform potential field applied to the diffusing molecules only
Φ	rate of entropy production
u	steady state velocity
μ	viscosity
ν	kinematic viscosity

ω	impeller rotational velocity
$\theta(S/a)$	correction factor for S/a
$\psi(b/a)$	correction factor for b/a
ψ_B	association parameter for the solvent
N_{Shw}	Sherwood Number
$\phi(N_{Shw})$	correction factor for Sherwood Number
N_{Sc}	Schmidt Number
$\eta(N_{Sc})$	correction factor for Schmidt Number
N_{St}	Stanton Number
N_{Re}	Reynolds Number

Subscripts

1	chamber 1
2	chamber 2
0,i	initial
o	overall
c	critical
m	membrane
f	fluid
A	solute
B	solvent