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SEPARATION OF GLUCOSE - FRUCTOSE - WATER
SYSTEMS VIA THERMAL PARAMETRIC PUMPING

BY

ZIKRI MOSTAFA AHMED

A THESIS
PRESENTED IN PARTIAL FULFILLMENT OF
THE REQUIREMENTS FOR THE DEGREE
OF
MASTER OF SCIENCE IN CHEMICAL ENGINEERING
AT
NEWARK COLLEGE OF ENGINEERING

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Newark, New Jersey

1973

APPROVAL OF THESIS

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ZIKRI MOSTAFA AHMED

FOR

DEPARTMENT OF CHEMICAL ENGINEERING

NEWARK COLLEGE OF ENGINEERING

BY

FACULTY COMMITTEE

APPROVED:

NEWARK, NEW JERSEY

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PREFACE

Previous research (13) indicated that fuller's earth (RVM 30-60 Mesh) was successfully used as an adsorbent with selective power of adsorption for sugar solutions, but when used in the parametric pumping experiments did not stand up the long time needed to achieve good separation.

In this research work an attempt has been made to obtain information about the capability of another kind of fuller's earth (LVM 16-30 Mesh) for adsorbing glucose and fructose from their aqueous solutions and to study the effect of different factors such as activation of adsorbent, time of contact, amount of adsorbent used, temperature and viscosity on the adsorption phenomena. This was followed by parametric pumping experiments to separate glucose and fructose using activated carbon as adsorbent. Series of tables and graphs based on experimental data are presented. Discussion and recommendations are also given to clear the way in front of other investigators who work on the same subject.

Newark College of Engineering, N.J.
May, 1973

Ahmed, Z.M.

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Newark College of Engineering

Ahmed, Z.M.

Newark, New Jersey

May, 1973

ABSTRACT

Series of experiments were carried out to determine the effect of different factors on adsorption from aqueous solutions of sugar using fuller's earth (LVM 16-30 Mesh) as an adsorbent. The equilibrium data were fitted to the Langmuir's equation, and an explanation for the deviation of some of these data has been given.

Systems of glucose-fructose and water mixtures were subjected to semi-continuous and continuous parametric pumping operations using activated carbon (400 Filterasorb) as an adsorbent. The results obtained confirm the equilibrium theory of the parametric pump and essentially fulfill the requirements established by Chen and Hill (6) to achieve high separation factors.

CONTENTS

	Page
1. Introduction.	1
2. Scope.	5
3. Theory.	6
4. Experimental:	
(A-1) Effect of Activation of Adsorbent.	9
(A-2) Adsorption Isotherms Study.	11
(B) Parametric Pumping.	13
5. Discussion.	19
6. Conclusion.	23
7. Recommendation.	25
8. Notation.	27
9. Literature Cited and References.	28
10. Tables.	30
11. Graphs.	53
12. Figures.	67
13. Appendix (A) Adsorption Isotherms and its Applications.	69
14. Appendix (B) Separation by parametric Pumping.	75
15. The Author.	78

LIST OF TABLES

No.	Page
1. Experimental results of glucose adsorption, using non activated adsorbent.	30
2. Experimental results of glucose adsorption, using activated adsorbent.	31
3. Experimental results of glucose adsorption, using activated adsorbent.	32
4. Experimental results of fructose adsorption, using non activated adsorbent.	33
5. Experimental results of fructose adsorption, using activated adsorbent.	34
6. Experimental results of fructose adsorption, using activated adsorbent.	35
7. Effect of adsorbent amount used on glucose adsorption.	36
8. Effect of adsorbent amount used on fructose adsorption.	37
9. Effect of equilibrium time on glucose adsorption.	38
10. Effect of equilibrium time on fructose adsorption.	39
11. Equilibrium data for glucose adsorption.	40
12. Equilibrium data for fructose adsorption.	41
13. Calculation of Langmuir's adsorption isotherm constants.	42
14. Parametric pumping results for glucose-water system (semi-continuous).	43
15. Parametric pumping results for fructose-water system (semi-continuous).	45
16. Parametric pumping results for glucose + fructose + water system (semi-continuous).	47
17. Parametric pumping results for glucose + fructose + water system (continuous).	50

LIST OF GRAPHS

No.	Page
1. Effect of adsorbent amount used on glucose adsorption.	53
2. Effect of adsorbent amount used on fructose adsorption.	54
3. Equilibrium time for glucose adsorption.	55
4. Equilibrium time for fructose adsorption.	56
5. Effect of temperature on glucose adsorption.	57
6. Effect of temperature on fructose adsorption.	58
7. Langmuir adsorption isotherms of glucose.	59
8. Adsorption isotherms of glucose.	60
9. Langmuir adsorption isotherms of fructose.	61
10. Adsorption isotherms of fructose.	62
11. Separation of glucose from glucose-water mixture by semi-continuous parametric pumping.	63
12. Separation of fructose from fructose-water mixture by semi-continuous parametric pumping.	64
13. Separation of glucose and fructose by semi-continuous parametric pumping.	65
14. Separation of glucose from fructose by continuous parametric pumping.	66

LIST OF FIGURES

1. Schematic diagram of parametric pumping experimental apparatus.	67
2. Regions of operations of parametric pump.	68

INTRODUCTION

History

Fructose is one of the component simple sugars of sucrose, the other being glucose. Fructose has never been produced commercially on large scale, although several projects have been proposed for this purpose. It is one of the few sugars that are sweeter than sucrose and on this score may have particular uses in some food stuffs. Ordinary sugar or molasses seems to be the most promising source for manufacturing of fructose. The production from the later origin consists simply of inverting the sucrose to glucose and fructose and then separating them. Although it is quite a simple matter to convert sucrose into its two component parts, the procedure known commercially as inversion, is the initial and almost immediate change which occurs to sucrose upon ingestion. The subsequent separation and isolation of the separate parts from the mixture are not especially easy. For this reason the supply of fructose has been quite limited. From this, the need to look for suitable method to separate fructose from glucose was obvious.

Previous Work

Dow Chemical Co. has been succeeded in separation of glucose from fructose(1). L.J. Lefeure of Dow Chemical Co. separated glucose from fructose by passage of 10-40 % aqueous solution of glucose and fructose over the Ag^+ form of a sulfonate exchange resin followed by elution with H_2O . Glucose eluted first followed by fructose. The procedure was as follows:

5 % (by volume) solution containing glucose and fructose equal to 5 % of the resin bed volume, was passed over a column of Dowex 50 W-X₄, 50-100 Mesh, the resin was in the Ag^+ form. Elution with H_2O was begun at a flow rate of 0.1 gal/minute/ft²

of column cross-section. Fractions were collected and analysed.

Roger Sargent (2) of the same company also separated glucose from fructose by passage of the solution containing both of them through a column of the salt form of either a sulfonic acid cation or quaternary ammonium anion exchange resin followed by elution with water. The glucose is eluted first, followed by the fructose.

Nitche, Ernst (3) at Laevosan-Gesellschaft Chem. Pharm. Industrie, S. Africa was able to separate glucose and fructose from each other. The procedure was as follows :

5 kg. 50 % sucrose solution with 213 c.c. N HCL was kept at 50°C for 3 hours, cooled and stirred with 150 c.c. Duolite A-7 in the OH form and then filtered. Of the invert solution 2.06 kg. was condensed in the vacuo and dissolved in MeOH. The solution containing 4.7 % H₂O was seeded with 25 gm. anhydrated glucose at 10°C and gave 276 gm. glucose containing 2 % fructose. The mother liquor and MeOH washings were added at 2 c.c. / minute, MeOH vapor from below. 31 c.c. of the dehydrated solution was collected and condensed from 24 % to 50 %. After seeding with 25 gm. fructose at 10°C, 261 gm. of fructose containing 1.1 % glucose were obtained. Additional crystalization from the mother liquors brought the yield of glucose to 90.4 % and that of fructose to 86.4 % .

Hara, Kazuo (4) of Nisshin Flour Milling Co. Ltd. Japan, succeeded in separating fructose from a mixture of fructose and glucose or from acid treated sucrose by treatment with cyanoethyl starch and Ca(OH)₂. The solution was stirred one hour in H₂O and kept one hour to give fructose of purity 94 % .

The biological technique was among the applicable techniques used to separate fructose from glucose (5). This technique based on the fact that only one member

of a homologous series is active in the catalyzed reaction, Glucose oxidase will catalyze the oxidation of glucose but not fructose. Disadvantage of this method is that the rate at which the substance is concentrated by the organism may be so slow as to rule out practical method.

Parametric Pumping

A new technique in the area of separation of solute mixtures has been recently developed. This technique despite it is still under investigation, promises a successful and economical separation technique. This is the parametric pumping technique. According to Chen, Pigford, Wilhelm et al, the basis for separation by parametric pumping lies in the ability of a solid adsorbent inside a column to retain solute adsorbed on it during the cold downflow half cycle and later to release this solute into the fluid phase stream during the hot upflow half cycle, thus setting up adsorption wave front patterns within the column. The separation here depends on the relative magnitude of penetration distances of these wave fronts through the packing during up and downflow half cycles and also the height of the column. For the parametric pump, there are three possible regions of operation: Region 1 which assure complete separation and region 2 and 3 in which the separation is finite. The equations and expressions for the concentration transients in the two product streams can be found elsewhere (6).

Because of the inherent slight differences in adsorbability of glucose and fructose, it should be theoretically possible to separate fructose from glucose by the parametric pumping technique. The advantages of this method lie in the following:-

1. It achieves high separation factor.
2. The adsorbent does not need to be

reactivated during the operation. 3. It is practical on the large industrial scale. 4. It is very economical and dynamical method.

In the subsequent pages a study of the adsorption phenomenon of glucose and fructose using fuller's earth (LVM 16-30 Mesh) as an adsorbent, followed by parametric pumping experiments to separate glucose and fructose from their aqueous solutions using activated carbon as an adsorbent (Recent research under the supervision of Dr. H.T. Chen at Newark College of Engineering indicated that activated carbon has greater capacity in adsorbing sugars from their aqueous solutions than fuller's earth) are presented.

SCOPE

This experimental work has been carried out in two parts :

1. A study of the adsorption of glucose and of fructose aqueous solutions by Fuller's earth (IVM 16-30 Mesh) to determine the effect of different factors such as the amount of adsorbent used, activation of adsorbent, temperature and viscosity on the adsorption phenomenon.
2. Semi-continuous and continuous parametric pumping experiments to separate glucose and fructose from their aqueous solutions using activated carbon as adsorbent inside the column.

The data obtained from the first part confirm the contradictory effect of temperature and viscosity on the adsorption phenomenon, and that obtained from the second part confirm the equilibrium theory of the parametric pumps and agree with results predicted from the equations of Chen et al based on this theory.

THEORY

Separation via Parametric Pumping

Very high separation factors have been obtained by Wilhelm et al (7) using cycling flow of a binary mixture upward and downward through a column packed with solid adsorbent and alternately heated and cooled. Chen and his co-workers obtained infinite separation factors by continuous (8) and semi-continuous (9) parametric pumps with feed to the top of the column. The basis for separation by parametric pumping lies in the ability of the solid adsorbent to retain solute adsorbed on it during the cold downflow half cycle and later to release this solute into the fluid phase stream during the hot upflow half cycle, thus setting up adsorption wave front patterns within the column. The separation depends on the relative magnitudes of the penetration distances of these wave fronts through the packing during up and down flow half cycles and also the height of the column. The extent of separation, of course, also depends on the operating conditions and the system involved in the parametric pumping. Prediction of separation is relatively simple if the equilibrium theory of Baker, Pigford and Blum applies. However in many systems separation is retarded by some countereffects (10) as ; (a) The axial fluid phase diffusive losses caused by molecular diffusion and by fluid mixing processes in the spaces between particles, (b) mass transfer resistance to diffusion of material between solid and fluid phases. Also, other phenomena may effect the separation. For example, it is possible that in certain temperatures ranges, the viscosity effect may override the normal adsorption phenomena .

Based on the equations of continuity and motion, and by neglecting axial diffusion inside the column, the equation of transport for the parametric pumping

system can be expressed in the modified form :

$$\epsilon \rho_f \frac{\partial y}{\partial t} + \epsilon \rho_f v \frac{\partial y}{\partial z} + (1 - \epsilon) \rho_s \frac{\partial x}{\partial t} = 0$$

where ϵ is the porosity of the adsorbent and v is the interstitial velocity inside the column, X = gm. mole solute adsorbed / gm. solid adsorbent and Y = gm. mole-solute remaining / gm. mole solution.

The above equation has been solved by Pigford et al and the transient equations for the concentration of the top and bottom streams have been obtained (11). Chen (6) also obtained the transient equations by solving a system of two internal and two external equations (Internal equation is a solute material balance inside the column and external equation is a solute material balance on streams from and to the reservoir).

For the continuous parametric pump there are three regions of operations, region 1 in which the separation factor defined as the quotient of the top and bottom concentrations approaches infinity as the number of cycles becomes large, and region 2 and 3 in which the separation factor becomes finite and separation is incomplete. However the possibility of running in any of these regions depends on the relative magnitudes of the penetration distances L_1 and L_2 where :

$$L_1 = \frac{u_1}{1 - b} \frac{\pi}{\omega} \quad \text{at the end of an upflow half cycle}$$

$$L_2 = \frac{u_2}{1 + b} \frac{\pi}{\omega} \quad \text{at the end of a downflow half cycle}$$

u_1 and u_2^* are the propagation velocities at the mean column temperature in upflow and downflow respectively, b is dimensionless equilibrium parameter and $\frac{\pi}{\omega}$ is the half cycle time. It also depends on the height of the column.

The boundaries between region 1 and 2 and between region 1 and 3 are the loci of so called switching points . If L_1 decreased until it becomes less than L_2 or L_2 increased until it exceeds h , the pump switches its original operating region to another one in which the separation factor is different than that of the original region. The crossing of the boundary $L_1 = L_2$ is due to increasing the bottom product flow rate ϕ_B and so decreasing u_1 and lowering L_1 . The crossing of the boundary $L_2 = h$ is due to increasing the reservoir displacement volume and hence decreasing L_2 .

There are three main types of parametric pumps , batch, continuous and semi-continuous (batch operation during one half cycle and continuous operation in the other). The performance characteristics of the semi-continuous with top feed is similar to that of continuous and the expressions for the transient equations are the same, the only difference is that of the switching points resulting from bottom product variation. For continuous pump the switching condition is $\phi_B = b$ whereas for semi-continuous pump, the condition is $\phi_B = \frac{2b}{1-b}$.

The separation of two component systems by parametric pumping could be extended to the multi-component systems. The degree of separation of each component depends on the rate of bottom product ϕ_B as compared with dimensionless equilibrium parameter h for the two binary pairs

$$* \quad u_1 = \frac{v_o (1 - \phi_B)}{1 + m_o}$$

$$u_2 = \frac{v_o (1 + \phi_B)}{1 + m_o}$$

EXPERIMENTAL

(A-1) The Effect of Adsorbent Activation
on Adsorption at Different Temperatures

Aqueous solutions containing 5 gms. of glucose per 100 ml. solution were prepared. 25 ml. of each solution were added to four 125 ml. Erlenmeyer flasks, each of which contained 4 gms. fuller's earth* (LVM 16-30 Mesh). The flasks were immersed in a mechanical shaker constant temperature (22° C) water bath, and were sealed with rubber stoppers. Another flask containing 25 ml. of the same solution but without fuller's earth was immersed in the bath in order to get a blank reading for purposes of comparison.

After exposure periods of 30, 60 and 120 minutes of shaking, one of the flasks was removed from the bath, filtered and the filtrate analyzed by an automatic polarimeter to determine the glucose concentration in the solution after adsorption. A jacketed polarimeter tube of 2 dm. length was used to measure the optical rotation of the sugar solution, this value divided by the rotation of the blank sample gave the amount of glucose directly. The amount adsorbed was determined by difference. These experiments were repeated at 65° C and the adsorption data for both temperatures are shown in table 1.

From the literature (4), it was found that fuller's earth can give high amount of adsorption if it has been activated by washing and heating at suitable temperature, therefore other experiments were performed using fuller's earth (LVM 16-30 Mesh) which was washed and heated for 6 hours at 250° C and at 150° C, the results are shown in Tables 2 and 3. Adsorption

values for fructose were obtained by the same procedure and under the same conditions. Results are shown in Tables 4, 5 and 6. From these experiments it was established that activating fuller's earth (LVM 16-30 Mesh) by washing and by heating at 150°C for 6 hours increased the capacity for adsorption.

* It was found later that dosage of 4 gms. fuller's earth gave us the highest amount of adsorption.

(A-2) Adsorption Isotherms Study

In the next series of experiments, the purpose was to determine the effect of using different amounts of adsorbent on adsorption.

Aqueous solutions containing 5 gms. glucose per 100 ml. of solution were prepared. 25 ml. of each was placed in 125 ml. Erlenmeyer flasks, each flask containing a specific amount of activated fuller's earth different from the other. As before, the flasks were sealed with rubber stoppers and immersed in a mechanical shaker constant temperature water bath with water up to half of its height in order to guarantee that the temperature of the solution inside each flask would be the same as that of the bath.

Another flask containing 25 ml. of the same solution but without fuller's earth was immersed in the bath for purposes of comparison. After 3 hours of regular shaking at constant temperature of 22°C , the flasks were immediately removed from the bath and filtered. The filtrate was analyzed by an automatic polarimeter to determine the glucose concentration after adsorption, and the amount of glucose adsorbed was determined as before. The procedure was repeated at temperature of 65°C . The results are shown in Table 7.

Adsorption values for fructose were obtained by the same procedure. The results are shown in Table 8. In order to study the effect of time on adsorption, series of experiments were carried out using the same method with different times of contact of 30, 60, 120, and 180 minutes respectively, and at temperatures of 22°C , 40°C and 65°C .

The results obtained for glucose and fructose are shown in Tables 9 and 10 respectively.

From the equilibrium data obtained experimentally at different concentrations and different temperatures, the isotherms for glucose and fructose were calculated (see Tables 11 and 12) and applied to the Langmuir's equation.

(B) Parametric Pumping

A parametric pumping system (Fig. 1) consists of a jacketed glass column of 1 cm. internal diameter and 90 cms. height. Two infusion-withdrawal pumps, each with two syringes, each syringe can maintain a volume of 50 m.l. are used as reservoir and feed pumps. A magnetic stirrer has to be placed in each of the reservoir pump syringes to assure homogeneous mixing. The action of the reservoir pump is automatically reversed at the end of each half cycle by means of micro-switch stops wired to the pump circuit. The sources of hot and cold water for the jacket supply are constant temperature water baths with programmed cycle timer which cycle the jacket temperature by means of two solenoid valves attached to the baths. Product streams are taken off by means of two micrometer capillary valves attached to the ends of the product lines. Rotometers are used in the feed and product lines to arrange the passage of the fluid through.

Prior to any run the following steps have to be taken:

1. The column, reservoir pump, feed pump and all lines has to be clean and dry.
2. Connect the bottom of the column.
3. Pack the column from the top with the adsorbent to be used, the packing should be slowly and carefully.
4. Connect the top of the column together with all other lines as shown in Fig. 1 .
5. Close the product and feed lines and fill the column as well as all lines through by delivering feed solution at ambient temperature to the bottom of the column by means of 50 m.l. bottom reservoir syringe of an infusion withdrawal pump (Reservoir pump).
6. Assure the elimination of air from the entire system during the operation of filling.

7. Adjust the speed of the reservoir pump and that of the feed pump to deliver the required amounts need per each half cycle.
8. Adjust the temperature of the hot water bath and that of the cold water bath to the required hot and cold temperatures, and connect the two baths to the column.
9. Two magnetic stirrers has to be used to assure homogeneous mixing inside the reservoirs.
10. Fill the bottom reservoir syringe with the amount of feed solution required to be delivered each half cycle including a dead volume, fill the top reservoir syringe with amount of feed solution equal to the dead volume.
11. Feed pump to be filled with the same solution.

Two runs were carried out, one for glucose-water system with feed concentration of 2.5 gms. glucose / 100 m.l. aqueous solution, the other for fructose-water system with feed concentration of 2.5 gms. fructose / 100 m.l. aqueous solution. The operating conditions for these two runs were the following :

Pump type	Semi-continuous
Adsorbent used	Activated carbon (400 Filterasorb) [*]
Hot temperature	333 ^o K
Cold temperature	295 ^o K
Time of half cycle	20 minutes
Reservoir pump speed	2 m.l. / minute (40 m.l. / half cycle)
Feed pump speed	0.8 m.l. / minute (16 m.l. / half cold cycle)
Dead volume in each reservoir syringe	Approximately 4 m.l.

* Activated carbon (400 Filterasorb) was manufactured by Calgon Co. Pa.

At the beginning of the run, the reservoir pumps were switched on and the timer was activated. The first half cycle was hot upflow, during which bottom reservoir syringe pumped the fluid into the bottom of the column and the timer switched the solenoids to supply hot water at 60°C to the jacket of the column. During this half cycle there is no feed and no products were collected. At the end of this 20 minutes half cycle, the timer switched the solenoids to supply cold water at 22°C to the jacket and the feed pump was switched on to feed the column from the top.** At the same time the microswitch reversed the action of the reservoir pump. This second half cycle was cold downflow during which top and bottom products were collected. At the end of every half cycle, the position of the reservoir pistons were recorded, also at the end of each half cold cycle, the amount of feed delivered was recorded. At the end of the cold half cycle, the second cycle was started and this procedure was repeated for each cycle until the required number of cycles for each run was completed (10 cycles for glucose-water system and 12 cycles for fructose-water system) . Samples for analysis were taken from the product streams during each cold half cycle and immediately analysed by an automatic polarimeter to determine the concentration in each product. Calculations and results for these two runs are shown in Tables 14 and 15 and Graphs 11 and 12.

A third semi-continuous run was carried out with feed solution consisted of 2 gms. glucose + 2 gms. fructose + 96 gms. water, the adsorbent used was activated carbon (400 Filterasorb). The reservoir pump speed was set to deliver 1.333 m.l. per minute and that of the feed pump was set to deliver 0.333 m.l. per minute. Feed was on during the half cold cycle only. Time for each half cycle was 30 minutes, temperature during hot half cycle was 60°C and that during the cold one was 20°C . Samples from the product streams were taken during the half cold cycles and

** In semi-continuous operation feed on during the cold downflow half cycle only.

analysed by an automatic polarimeter to determine fructose concentration and by glucostat method to determine that of glucose.

The fourth run was continuous with feed delivered to the top of the column and product samples collected during both hot and cold half cycles. The operating conditions for this run were as follows :

Pump type	continuous
Adsorbent used	Activated carbon (400 Filterasorb)
Hot temperature	333°K (60°C)
Cold temperature	293°K (20°C)
Feed rate	0.333 m.l. / minute
Reservoir displacement	1.333 m.l. / minute
Feed concentration	2gms.glucose + 2gms.fructose + 96gms.water
Time of half cycle	30 minutes

The results for these two runs (the third and the fourth) are shown in Tables 16 and 17 and Graphs 13 and 14.

Methods of Analysis

(1) Polarimeter Method

Fill the jacketed polarimeter tube with the solution to be measured. Measure the optical rotation of the solution by taking the reading of the polarimeter.

Calculation.

$$\frac{R_u}{R_f} C_f = C_u$$

R = Reading of Polarimeter.

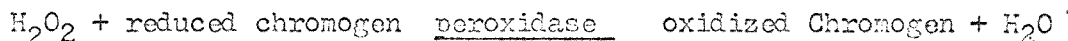
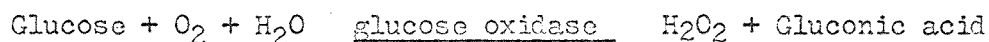
C = Concentration

f = Feed

u = Unknown

(2) Glucostat Method

Glucostat is a prepared reagent for the quantitative, colorimetric determination of glucose. It makes use of the coupled enzyme reactions represented by the following scheme:



The Glucostat method is a general method suitable for determination of glucose in aqueous solution. It can be summarized in the following:
 Standard: Add 1 m.l. feed solution to 50 m.l. graduate. Add distilled water and adjust the final volume to 50 m.l. Take 1 m.l. from the new solution and add to it 10 m.l. distilled water, this will be our standard.

Reagent: Add 30 m.l. distilled water to 50 m.l. graduate cylinder. Dissolve the cromogen in distilled water and add to the graduate cylinder. Dissolve the content of gluco-stat-s- in distilled water and add to the graduate. Adjust the final volume to 50 m.l.

Unknown: Add one m.l. unknown solution to 50 m.l. graduate cylinder. Add distilled water and adjust the final volume to 50 m.l. Take 1 m.l. from the new solution and add to it 10 m.l. distilled water.

Procedure:

To 2 m.l. standard add 2 m.l. reagent. After 10 minutes at the room temperature, add to the mixture one drop 4M HCL to stop reaction and stabilize color. Let the mixture stand for five minutes after stopping the reaction. Using a photometer in the region 400 mu, read the absorbancy of the feed sample (standard), setting the reagent blank at zero absorbancy. Repeat the same procedure using the unknown samples.

Calculation:

$$\frac{A_u}{A_s} C_s = C_u$$

A = absorbancy

C = concentration

s = standard

u = unknown

DISCUSSION

(A) Adsorption Isotherms and Its Applications

Previous research (13) indicates that fuller's earth (RVM 30-60 Mesh) has ability to adsorb glucose and fructose from their aqueous solutions. Although many authors have spoken about the capability of fuller's earth for working as an adsorbent, most of them (14) mentioned its ability to adsorb colours as the milestone of the subject. The present work, aims to get clear information about the capability of one kind of fuller's earth (LVM 16-30 Mesh) for adsorbing glucose and fructose from their binary solutions (water used as the solvent in both cases) and to determine the effect of different factors such as activation of adsorbent, amount of adsorbent used, time of equilibrium and temperature on the adsorption from sugar solutions.

Experiments have shown that washing fuller's earth (LVM 16-30 Mesh) and then heating it at 150°C for 6 hours increases its capacity for adsorption. As far as the amount of adsorbent used considered, Graphs 1 and 2 indicated that to a certain degree the larger the amount used, the higher the rate of adsorption achieved. However it depends to a certain limit on the temperature used and the sugar involves in test, fructose at 65°C showed steady increase in adsorption rate as amount of adsorbent increased.

One of the disadvantages showed by experiments when using fuller's earth (LVM 16-30 Mesh) as an adsorbent for glucose and fructose from their aqueous solutions was the lengthy time (two and half hours as indicated by Graphs 3 and 4) required to establish equilibrium between adsorbent and adsorbate. This probably would make it unpractical when used in the parametric pumping technique or when used on industrial scale.

From data obtained experimentally it was clear that aqueous solutions do not always observe the theory that the higher the temperature the lower the amount adsorbed (see Graphs 5 and 6). In adsorption we believe that the highest convenient temperature should be used during the adsorption process, because the resulting decreased liquid viscosity increases diffusion of the solute to the surface of the adsorbent and lower the resistance of the adsorbent particles to the liquid flow. In case of gases, adsorption decreases when temperature increases, but in case of liquids there is no rule (e.g. in the clay treatment of petroleum-lubricant fractions, the adsorbent oil mixture may be heated to as much as 300°F and for heavy oils even to $600^{\circ}\text{-}700^{\circ}\text{F}$). As is clear from Graphs 5 and 6, there were increase in adsorption and deviation from Langmuir's equation, when we raised our temperature up to 65°C . This could possibly from the fact that some substances after becoming adsorbed, undergo change so that they are no longer soluble and such changes may be accelerated by an elevation in temperature. The nature of such behaviour is analogous to the coagulating effect of temperature on certain proteins. It could be also a result of viscosity effect as explained before. A third possibility is possible change in other properties such as surface tension because of elevation of temperature. However the second possibility could be the explanation of our case. Anyhow, the true reasons behind this behaviour are unknown and can be left to future investigation.

As for the adsorption isotherms at temperatures 22°C and 40°C , the Langmuir's-equation has been applied properly as Graphs 7, 8, 9 and 10 indicate.

(R) Separation Via Parametric Pumping

The results obtained from the four parametric pumping runs, we have carried out support and confirm the parametric pumping theory and proved the feasibility of separating solute from solvent in binary mixtures as well as multi-component systems by parametric pumping technique.

The first two runs (semi-continuous) have been carried out to separate glucose from glucose-water mixture and fructose from fructose-water mixture. The results obtained indicated that the separation increased without limit as the number of cycles increased until the resistance to the mass transfer inside the column became important and rate of separation slowed down. This could be noticed from Graphs 11 and 12 which indicate that the rate of separation began to slow down after the seventh cycle in case of glucose and after the tenth in case of the fructose run. However the high separation factors (top product concentration divided by bottom product concentration at the same cycle) achieved were good enough to prove the significance of this technique.

With data obtained from these runs the b (equilibrium dimensionless parameter) values for glucose and fructose were computed by the method indicated by Chen et al (8) and better choice for the bottom product flow rate ϕ_B based on these values was available.

The third run was carried out (using semi-continuous parametric pump) with feed solution consisted of mixture of glucose and fructose and bottom product flow rate within the limit of running glucose and fructose in region 1. The number of cycles was extended to 16 and time of half cycle increased to 30 minutes to enable us establishing clear and definite information about the feasibility

of separation by comparing the b values obtained from this run with those obtained from the previous two pseudo runs.

Significant separation was obtained and separation factors as large as 80 for fructose and 14 for glucose were achieved. Graph 13 and Table 16 show that beginning with feed concentration = 2 % , we were able to reach bottom product concentration as low as 0.027 % in case of fructose and 0.2 % in case of glucose with number of cycles only equal to 16. The top product concentration increased steadily to reach 2.22 % in case of fructose and 2.76 % in case of glucose. Anyhow the b values obtained from this run together with those obtained from the previous runs indicated two very close b values for glucose and fructose (0.126 for glucose and 0.136 for fructose).

Based on the b values obtained from the first two runs and assured by the third run, a fourth run using continuous parametric pump with bottom product flow rate fall between these two values to assure the running of glucose and fructose in two different operating regions, was carried out to separate them from each other. However due to : 1. The very close b values they have as a result of equal powers of adsorption imposed on both of them by activated carbon and the difficulty of choosing proper bottom product flow rate. 2. The increasing flow rate of bottom product which might shift the operating region for fructose from region 1 to region 2., the separation factor was almost the same for both of them. This indicates the importance of looking for an adsorbent with noticable selective power of adsorption of these two similar components which together with this attractive separation technique could lead us to dynamical, practical and economical method for separation of glucose from fructose.

CONCLUSION

(A) Adsorption Isotherms and Its Applications

In adsorption from aqueous solutions, the Langmuir's equation does not hold well at higher temperatures, this is because the resulting decreased liquid viscosity increases the rate of diffusivity of the solute to the surface of the adsorbent, this affects the rate of adsorption and balance the effect of the higher temperature on adsorption. In case of adsorption of glucose and fructose by fuller's earth (LVM 16-30 Mesh) at higher temperatures, the adsorption phenomenon follows the Freundlich's equation more than the Langmuir's equation.

There appears to be no relation between the adsorptive power of different types of fuller's earth and their chemical analysis, fuller's earth (RVM 30-60 Mesh) showed more adsorption for glucose (13) than fructose, while fuller's earth (LVM - 16-30 Mesh) showed variant results despite the same chemical analysis they have.

Activation of fuller's earth (LVM 16-30 Mesh) by washing and heating at certain temperature increases its capacity for adsorption from sugar solutions.

(B) Parametric Pumping Technique

The parametric pumps promise successful and economical technique for separation of solute from solvent in binary and multi-component systems and the results obtained from our experiments confirm the parametric pumping theory and agree reasonably well with the equations obtained by Chen, Pigford et al.

The separation increased without limit as the number of cycles increased until the mass transfer resistance became important and the rate of separation decreased.

Activated carbon has been used successfully as an adsorbent in the parametric pumping experiments for separation of glucose and fructose from their aqueous solutions and high separation factors (80 in case of fructose and 14 in case of glucose) have been achieved, but upon used for separation of glucose from fructose from their mixture (water used as solvent), the yield of separation for both of them was approximately the same due to the very close b (dimensionless equilibrium-parameter) values they have as a result of the equal adsorption rates by which activated carbon adsorbs them.

RECOMMENDATION^{*}

(A) Adsorption Isotherms and Its Applications

1. A fine mesh fuller's earth is advantageous for rapid adsorption, but the degree of fineness for purposes of using in adsorbent column is controlled by several limitations, we have to insure a free passage for the liquid through the adsorbent and to prevent building up a set back pressure inside the column.
2. Adsorption process should be carried out at the highest convenient temperature to avoid the contradictory effect of viscosity and temperature at certain concentrations.
3. Activation of fuller's earth (LVM 16-30 Mesh) by heating at certain temperature increases its capacity for adsorption.
4. Activated carbon is of great capacity in adsorption of glucose and fructose from their aqueous solutions, but it adsorbs them approximately to the same level.

* These recommendations are based on the experimental work we carried out and the results we obtained.

(B) Parametric Pumping Operations

1. The two b values for the two components to be separated must differ from each other by noticable amount to insure better choice for the bottom product flow rate ϕ_B such that the two components would run in two different operating regions, this can be checked by carrying out the adsorption isotherms experiments before starting the parametric pumping experiments.
2. Bottom product flow rate should be less than the critical amount needs to reach the switching points to avoid any possible shifting in the operating regions.
3. Time of half cycle should be enough to establish equilibrium between adsorbent and adsorbate inside the column.
4. Air should be completely removed from the entire system of the parametric pumping apparatus before starting any run to avoid building up pressure inside the column and also, because the space air occupied decreases the amount of fluid passing through the column and hence affect the reservoir displacement which has great effect on the separation rate.

NOTATION

- a = dimensionless parameter.
 b = dimensionless equilibrium parameter.
 C_2 = dead volume / reservoir displacement.
 H = heat of adsorption , gm-cal / gm.mole solute adsorbed.
 K = adsorption equilibrium parameter defined by equation (5).
 M = equilibrium constant.
 m_0 = dimensionless equilibrium constant.
 N = Langmuir equation constant.
 n = number of cycles of pump operation.
 Q = reservoir displacement rate, cm^3 / minutes.
 R = gas constant, 1.987 gm-cal / gm.mole. K° .
 T = temperature in K° .
 X = gm-mole of solute adsorbed / gm solid adsorbent.
 Y = concentration of solute in the liquid phase, in
 gm-mole solute / gm-mole solution.
 $\langle \rangle$ = average value.

Greek Letters:

- ϕ = product volumetric flow rate / reservoir displacement.
 $\frac{\pi}{\omega}$ = duration of half cycle, minutes.
 α = slope of the line represented by $\log \frac{\langle Y_P \rangle}{Y_F}$ versus n .

Subscripts:

- F = feed conditions.
 BP = bottom product.
 TP = top product.

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Table 1: Experiment Result of Glucose Adsorption
 Using Nonactivated Fuller's Earth LVM*
 16-30 Mesh

Test No.	Temperature	Time of contact	Co	C	D
1	22 ^o C	30 Minutes	5 gm/100 c.c.	4.9200	0.0800
2	"	60 "	"	4.9200	0.0800
3	"	120 "	"	4.9113	0.0887
1	65 ^o C	30 Minutes	5 gm/100 c.c.	4.9956	0.0044
2	"	60 "	"	4.9950	0.0050
3	"	120 "	"	4.9890	0.0110

Co = Initial concentration of Glucose solution gm glucose/100 c.c. glucose solution.

C = Equilibrium concentration of Glucose solution gm glucose/100 c.c. glucose solution.

D = Amount of Glucose adsorbed in grams/100 c.c. = Co-C

Volume of solution used for every test = 25 c.c.

Amount of adsorbent used for every test = 4 gms.

* Manufactured by Englehard Minerals N.J.

Table 2: Experimental Results of Glucose Adsorption

Using activated Fullers' Earth LVM 16-30 Mesh*

Test No.	Temperature	Time of contact	Co	C	D
1	22 ^o C	60 Minutes	5gm/100 c.c.	4.9535	0.0465
2	"	120 "	"	4.9403	0.0597

* Fullers' Earth LVM 16-30 Mesh has been activated by being washed and then heated at 250^o C for 6 hours.

* Volume of solution used for every test = 25 c.c.

Amount of adsorbent used for every test = 4 gms.

Table 3 : Experimental Results of Glucose Adsorption

Using activated Fullers' Earth LVM 16-30 Mesh*

Test No.	Temperature	Time of contact	Co	C	D
1	22 ^o C	30 Minutes	5 gm/100 c.c	4.8956	0.1044
2	"	60 "	"	4.8904	0.1096
3	"	120 "	"	4.8872	0.1128
1	65 ^o C	30 Minutes	5 gm/100 c.c.	4.8892	0.1108
2	"	60 "	"	4.8652	0.1348
3	"	120 "	"	4.8912	0.1088

* Fullers' Earth LVM 16-30 Mesh has been activated by being washed and then heated at 150^o C for 6 hours.

* Volume of solution used for every test = 25 c.c.

Amount of adsorbent used for every test = 4 gms.

Table 4: Experimental Results of Fructose Adsorption
Using Non activated Fullers Earth LVM 16-30 Mesh

Test No.	Temperature	Time of contact	Co	C	D
1	22 °C	30 Minutes	5 gm/100 c.c.	4.9320	0.0680
2	"	60 "	"	4.9100	0.0900
3	"	120 "	"	4.9120	0.0880
1	65 °C	30 Minutes	5 gm/100 c.c.	4.9600	0.0400
2	"	60 "	"	4.9540	0.0460
3	"	120 "	"	4.9280	0.0720

Volume of solution used for every test = 25 c.c.

Amount of adsorbent used for every test = 4 gms.

Table 5: Experimental Results of Fructose Adsorption
Using activated Fuller's Earth 16-30 Mesh*

Test No.	Temperature	Time of contact	Co	C	D
1	22 ^o C	60 Minutes	5 gm/100 c.c.	4.8700	0.1300
2	"	120 "	"	4.9410	0.0590

* Fuller's earth LVM 16-30 Mesh has been activated by being washed and then heated at 250^oC for 6 hours.

Volume of solution used for every test = 25 c.c.

Amount of adsorbent used for every test = 4 gms.

Table 6: Experimental Results of Fructose Adsorption
Using activated Fuller's Earth 16-30 Mesh*

Test No.	Temperature	Time of contact	Co	C	D
1	22°C	30 Minutes	5 gm/100 c.c.	4.9360	0.0640
2	"	60 "	"	4.9344	0.0656
3	"	120 "	"	4.8672	0.1228
1	65°C	30 Minutes	5 gm/100 c.c.	4.9460	0.0540
2	"	60 "	"	4.9228	0.0772
3	"	120 "	"	4.9208	0.0792

* Fuller's earth LVM 16-30 Mesh has been activated by being washed and then heated at 150°C for 6 hours.

Volume of solution used for every test = 25 c.c.

Amount of adsorbent used for every test = 4 gms.

(a) Effect of Adsorbent Amount Used for Test

Table 7: Experimental Results of Glucose Adsorption
Using activated Fuller's Earth (LVM 16-30)

Temperature	Co	C	D	M
22 °C	5 gm/100 c.c.	4.9772	0.0228	2
"	"	4.9390	0.0610	3
"	"	4.8747	0.1253	4
"	"	4.9754	0.0246	6
"	"	4.9734	0.0266	7
"	"	4.9734	0.0266	8
65 °C	5 gm/100 c.c.	4.9490	0.0510	2
"	"	4.9208	0.0792	3
"	"	4.8928	0.1072	4
"	"	4.9376	0.0624	6
"	"	4.9447	0.0553	7
"	"	4.9432	0.0568	8

M = Amount of Fuller's earth used in gms.

Total volume of Glucose solution used for every test = 25 c.c.

Time of contact for every test = 3 hours

*Adsorbent has been washed and heated at 150 °C for 6 hours before used.

Effect of Adsorbent Amount Used for Test

Table 8: Experimental Results of Fructose Adsorption
Using activated Fuller's Earth (LVM 16-30)

Temperature	Co	C	D	M
22 °C	5 gm/100 c.c.	4.9158	0.0842	2
"	"	4.8815	0.1185	3
"	"	4.8712	0.1288	4
"	"	4.8614	0.1386	6
"	"	4.8488	0.1512	7
"	"	4.8592	0.1408	8
65 °C	5 gm/100 c.c.	4.9397	0.0603	2
"	"	4.9028	0.0972	3
"	"	4.8796	0.1204	4
"	"	4.8554	0.1466	6
"	"	4.8173	0.1827	7
"	"	4.7752	0.2248	8

Total volume of Fructose solution used for every test = 25 c.c.

Time of contact for every test = 3 hours.

(b) Effect of Equilibrium Time

Table 9: Experimental Results of Glucose Adsorption
Using activated Fuller's Earth (LVM 16-30)

Test No.	Temperature of contact	Time of contact	Co	C	D	X
1	22 °C	30 Minutes	5 gm/100 c.c.	4.8956	0.1044	0.0000363
2	"	60 "	"	4.8904	0.1096	0.0000380
3	"	120 "	"	4.8872	0.1128	0.0000413
4	"	180 "	"	4.8747	0.1253	0.0000435
1	40 °C	30 Minutes	5 gm/100 c.c.	4.9600	0.0400	0.0000139
2	"	60 "	"	4.9443	0.0557	0.0000193
3	"	120 "	"	4.9388	0.0612	0.0000213
4	"	180 "	"	4.9028	0.0972	0.0000338
1	65 °C	30 Minutes	5 gm/100 c.c.	4.8892	0.1108	0.0000385
2	"	60 "	"	4.8652	0.1348	0.0000468
3	"	120 "	"	4.8912	0.1088	0.0000378
4	"	180 "	"	4.8928	0.1072	0.0000373

Co = Initial concentration gm/100 c.c.

C = Equilibrium concentration gm/100 c.c.

D = Amount of Glucose adsorbed in gm/100 c.c.

X = gm mole Glucose adsorbed/gm adsorbent

Volume of solution used for every test = 25 c.c.

Amount of adsorbent used for every test = 4 gms.

Effect of Equilibrium Time

Table 10: Experimental Results of Fructose Adsorption

Test No.	Temperature	Time of contact	Co	C	D	X
1	22 °C	30 Minutes	5 gm/100 c.c.	4.9360	0.0640	0.0000222
2	"	60 "	"	4.9344	0.0656	0.0000226
3	"	120 "	"	4.8672	0.1328	0.0000461
4	"	180 "	"	4.8712	0.1288	0.0000447
1	40 °C	30 Minutes	5 gm/100 c.c.	4.9320	0.0680	0.0000236
2	"	60 "	"	4.9493	0.0507	0.0000176
3	"	120 "	"	4.9459	0.0541	0.0000188
4	"	180 "	"	4.9356	0.0644	0.0000228
1	65 °C	30 Minutes	5 gm/100 c.c.	4.9460	0.0540	0.0000187
2	"	60 "	"	4.9228	0.0772	0.0000268
3	"	120 "	"	4.9208	0.0792	0.0000275
4	"	180 "	"	4.8796	0.1204	0.0000418

Table 11: Experimental Results of Glucose Adsorption

Temperature	Co	C	X	Y	Y/X
22 °C	2.5 gm/100 c.c.	2.37184	0.0000445	0.002500	56.2
"	5 gm/100 c.c.	4.87472	0.0000435	0.004994	114.8
"	7.5 gm/100 c.c.	7.34820	0.0000527	0.007620	144.6
"	10 gm/100 c.c.	9.87200	0.0000445	0.010350	232.6
"	15 gm/100 c.c.	14.63520	0.0001267	0.015725	124.2
40 °C	2.5 gm/100 c.c.	2.41212	0.0000305	0.002442	80.07
"	5 gm/100 c.c.	4.90280	0.0000338	0.005030	148.8
"	7.5 gm/100 c.c.	7.34232	0.0000548	0.007190	131.3
"	10 gm/100 c.c.	9.88520	0.0000398	0.010380	260.00
"	15 gm/100 c.c.	14.96372	0.0000128	0.016180	1260.7
65 °C	2.5 gm/100 c.c.	2.30320	0.0000683	0.002333	34.1
"	5 gm/100 c.c.	4.89280	0.0000373	0.005020	134.6
"	7.5 gm/100 c.c.	7.22400	0.0000958	0.007573	79.1
"	10 gm/100 c.c.	9.57040	0.0001490	0.010046	67.1
"	15 gm/100 c.c.	14.61400	0.0001338	0.015820	112.00

Co = gm Glucose/100 c.c. before the test.

C = gm Glucose/100 c.c. after the test.

X = gm mole Glucose adsorbed/gm adsorbent

Y = gm mole Glucose remaining/gm mole solution.

Table 12: Experimental Results of Fructose Adsorption.

Temperature	C_0	C	X	Y	Y/X
22 °C	2.5 gm/100 c.c.	2.4482	0.0000180	0.002478	137.8
"	5 gm/100 c.c.	4.8712	0.0000448	0.005000	111.6
"	7.5 gm/100 c.c.	7.3728	0.0000441	0.007650	173.5
"	10 gm/100 c.c.	9.8072	0.0000670	0.010310	153.9
"	15 gm/100 c.c.	14.5252	0.0001645	0.015750	95.7
40 °C	2.5 gm/100 c.c.	2.45288	0.0000163	0.002490	152.7
"	5 gm/100 c.c.	4.93560	0.0000223	0.004992	224.1
"	7.5 gm/100 c.c.	7.42240	0.0000269	0.007776	288.4
"	10 gm/100 c.c.	9.88920	0.0000385	0.010375	269.5
"	15 gm/100 c.c.	14.97704	0.000008	0.016250	2206
65 °C	2.5 gm/100 c.c.	2.44320	0.0000198	0.002476	125.00
"	5 gm/100 c.c.	4.87960	0.0000418	0.005001	119.6
"	7.5 gm/100 c.c.	7.26880	0.0000805	0.007620	94.7
"	10 gm/100 c.c.	9.73400	0.0000923	0.010220	110.6
"	15 gm/100 c.c.	14.60080	0.0001388	0.015850	114.2

Table 13: Calculation of Langmuir's Adsorption Isotherm Constants.

(a) Constants for Glucose Isotherms.

Temperature	N	1/NK	K
40° C	0.0000441	25	905.6
22° C	0.0000441	5	4528

(b) Constants for Fructose Isotherms.

Temperature	N	1/NK	K
40° C	0.00006	132	126.2
22° C	0.00006	50	333

Table (14) (continued)

8-UP	36	7	---	---	---	-----	-----
8-DOWN	5	36	2	14	16	1.040	0.132
9-UP	35	7	---	---	---	-----	-----
9-DOWN	5	37	2	14	16	1.090	0.123
10-UP	32	8	---	---	---	-----	-----
10-DOWN	6	35	2	14	15.8	1.092	0.118

Y_{TP} = Concentration of Top product in
gm/100 c.c. solution .

Y_{BP} = Concentration of Bottom product in
gm/100 c.c. solution .

Y_F = Concentration of Feed in
gm/100 c.c. solution
= 2.5 %

* Concentrations of feed and products have been determined by using
Polarimeter methods.

Table (15)

Parametric Pumping Experiment Observation

Pump type	Semi-continuous Top feed
System	Fructose + Water
$Q \frac{\pi}{\omega}$	Approximately 40 c.c.
$\frac{\pi}{\omega}$	20 Minutes
T_h	333°K
T_c	295°K
Adsorbent	Activated carbon

Cycle No.	Position of Top Reservoir	Position of Bot. Reservoir	Bottom Product	Top Product	Feed Amount	$\frac{Y_{BP}}{Y_F}$	$\frac{Y_{TP}}{Y_F}$
1-UP	42	6	—	—	—	—	—
1-DOWN	5	42	—	12	11	—	0.180
2-UP	40	5	—	—	—	—	—
2-DOWN	4	40	2	14	16	0.620	0.198
3-UP	38	6	—	—	—	—	—
3-DOWN	3	40	1.8	14	16	0.500	0.332
4-UP	38	4	—	—	—	—	—
4-DOWN	3	38	1.9	13.6	16	0.400	0.405
5-UP	39	4	—	—	—	—	—
5-DOWN	2	40	1.9	13	15	0.323	0.510
6-UP	36	4	—	—	—	—	—
6-DOWN	3	38	1.9	14	16	0.253	0.675

Table (Continued) (15)

7-UP	36	4	—	—	—	—	—
7-DOWN	3	38	2	14	16	0.214	0.813
8-UP	35	4	—	—	—	—	—
8-DOWN	2.5	37	1.9	13	16	0.177	0.910
9-UP	37	4	—	—	—	—	—
9-DOWN	2.5	36	1.9	14	16	0.146	1.010
10-UP	35	6	—	—	—	—	—
10-DOWN	2	39	2	14	16	0.136	1.070
11-UP	37	5	—	—	—	—	—
11-DOWN	3	38	1.9	14	16	0.131	1.110
12-UP	34	6	—	—	—	—	—
12-DOWN	3	38	1.8	14	15.9	0.123	1.095

Table (16)

Parametric Pumping Experiment Observations

Pump Type	Semi-continuous Top Feed
System	Glucose + Fructose + Water
$Q \frac{\pi}{\omega}$	Approximately 40 c.c.
$\frac{\pi}{\omega}$	30 Minutes
T_h	333° K
T_c	293° K
Feed Concentration	2 gms. Glucose + 2 gms. Fructose + 96 gms. Water
Adsorbent Used	Activated Carbon

Cycle No.	Position of Top Reservoir	Position of Bot. Reservoir	Top Product	Bottom Product	Feed Amount
1 UP	45	4	---	---	---
1 DOWN	5	44	7	1.8	10
2 UP	45	5	---	---	---
2 DOWN	4	47	8	2	10
3 UP	45	5	---	---	---
3 DOWN	5	45	8	2.1	10
4 UP	45	5	---	---	---
4 DOWN	5	45	8	1.9	10
5 UP	45	5	---	---	---
5 DOWN	4	46	7.5	1.9	10

Table (16) continued.

6 UP	44	5	---	---	---
6 DOWN	4	45	7	1.9	10
7 UP	44	5	---	---	---
7 DOWN	4	45	7.6	1.9	10
8 UP	44	5	---	---	---
8 DOWN	4	45	5.5	2	9
9 UP	44	5	---	---	---
9 DOWN	4	45	7.6	2	10
10 UP	45	5	---	---	---
10 DOWN	5	45	7	1.8	10
11 UP	46	5	---	---	---
11 DOWN	5	46	8	1.9	10
12 UP	46	5	---	---	---
12 DOWN	5	46	8.1	1.9	10
13 UP	46	5	---	---	---
13 DOWN	5	45	6	2	9
14 UP	45	5	---	---	---
14 DOWN	5	45	8	2	10
15 UP	45	5	---	---	---
15 DOWN	5	45	6	1.9	9
16 UP	45	5	---	---	---
16 DOWN	5	45	8	1.9	10

Table (16) Continued.

Glucose			Fructose		
Cycle No.	$\frac{Y_{BP}}{Y_F}$	$\frac{Y_{TP}}{Y_F}$	Cycle No.	$\frac{Y_{BP}}{Y_F}$	$\frac{Y_{TP}}{Y_F}$
1	0.7200	0.2820	1	0.5980	0.1500
2	0.5400	0.3810	2	0.5211	0.1530
3	0.4291	0.5601	3	0.4320	0.3800
4	0.3260	0.6622	4	0.3203	0.4601
5	0.2582	0.7140	5	0.2700	0.5822
6	0.1982	0.9301	6	0.2771	0.6420
7	0.1750	1.0201	7	0.1504	0.8051
8	0.1587	1.1120	8	0.1240	0.8920
9	0.1381	1.1600	9	0.0905	0.9882
10	0.1360	1.2720	10	0.0724	1.0581
11	0.1334	1.3501	11	0.0320	1.0850
12	0.1301	1.3610	12	0.0556	1.0790
13	0.1270	1.3330	13	0.0251	1.1301
14	0.1261	1.3800	14	0.0250	1.1021
15	0.1182	1.3800	15	0.0261	1.1500
16	0.1111	1.3801	16	0.0139	1.1101

Table (17)

Parametric Pumping Experiment Observations

Pump Type	Continuous Top Feed
System	Glucose + Fructose + Water
$Q \frac{\pi}{\omega}$	Approximately 40 c.c.
$\frac{\pi}{\omega}$	30 Minutes
T_h	333°K
T_c	293°K
Feed Concentration	2gms. Glucose + 2gms. Fructose + 2gms. Water
Adsorbent Used	Activated Carbon

Cycle No.	Position of Top Reservoir	Position of Bot. Reservoir	Top Product	Bottom Product	Feed Amour
1 UP	45	5	3.5	3.8	9
1 DOWN	5	46	4	2.7	9
2 UP	45	5	5.5	4.6	8
2 DOWN	5	40	5.2	4.7	10
3 UP	40	5	5.2	4.6	10
3 DOWN	5	40	3.5	3.5	8
4 UP	40	5	5.3	4.3	10
4 DOWN	5	40	5	4.5	10
5 UP	41.5	4.5	5.5	4.3	10
5 DOWN	5	41	5.4	4.5	10

Table (17) Continued.

6 UP	41	5	5.5	4.5	10
6 DOWN	5	41	5.3	4.6	10
7 UP	42	4.5	5.2	4.7	10
7 DOWN	5	41	5.1	4.8	10
8 UP	41	5	5.5	4.6	10
8 DOWN	5	40	5	4.7	10
9 UP	40.5	4.5	5	4.6	9.5
9 DOWN	5	40	4	4.6	10
10 UP	40	5	5	4.9	10
10 DOWN	4	40	4.5	4.5	10
11 UP	40	4	4.7	4.7	9.5
11 DOWN	4.5	40	4.2	4.5	10
12 UP	40.5	4.5	5.5	4.6	10
12 DOWN	4.5	40.5	4.8	4.5	9.5
13 UP	40	4.5	5.3	4.6	9.5
13 DOWN	4	39	5	4.5	10
14 UP	39	4	5.3	4.7	9
14 DOWN	3.5	39	5	4.6	10

Table (17) Continued.

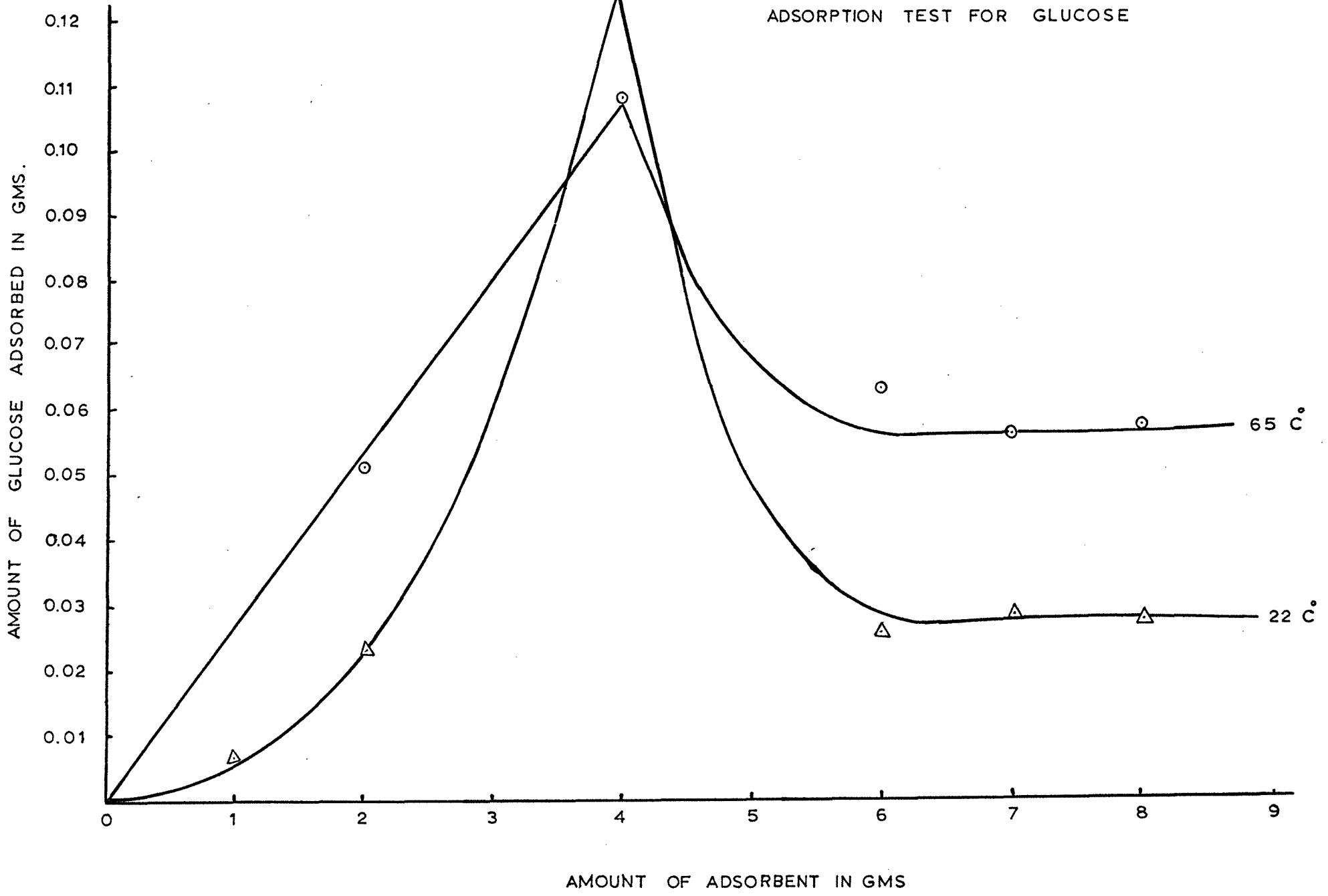
Glucose			Fructose		
Cycle No.	$\frac{Y_{B2}}{Y_F}$	$\frac{Y_{T2}}{Y_F}$	Cycle No.	$\frac{Y_{B2}}{Y_F}$	$\frac{Y_{T2}}{Y_F}$
1	0.7360	0.1690	1	0.7410	0.1038
2	0.4540	0.4182	2	0.5890	0.4671
3	0.3251	0.5590	3	0.3675	0.5152
4	0.2522	0.7600	4	0.3093	0.6690
5	0.1812	0.9220	5	0.2033	0.8200
6	0.1285	1.1251	6	0.1684	0.9371
7	0.1132	1.1621	7	0.1497	1.0620
8	0.0875	1.2720	8	0.1145	1.1450
9	0.0845	1.4000	9	0.1064	1.2021
10	0.0861	1.4922	10	0.0877	1.2110
11	0.0755	1.4565	11	0.0877	1.2662
12	0.0831	1.5020	12	0.0835	1.2815
13	0.0861	1.6020	13	0.1102	1.3400
14	0.0845	1.5830	14	0.0746	1.3401

B2 = Bottom product of cold half cycle .

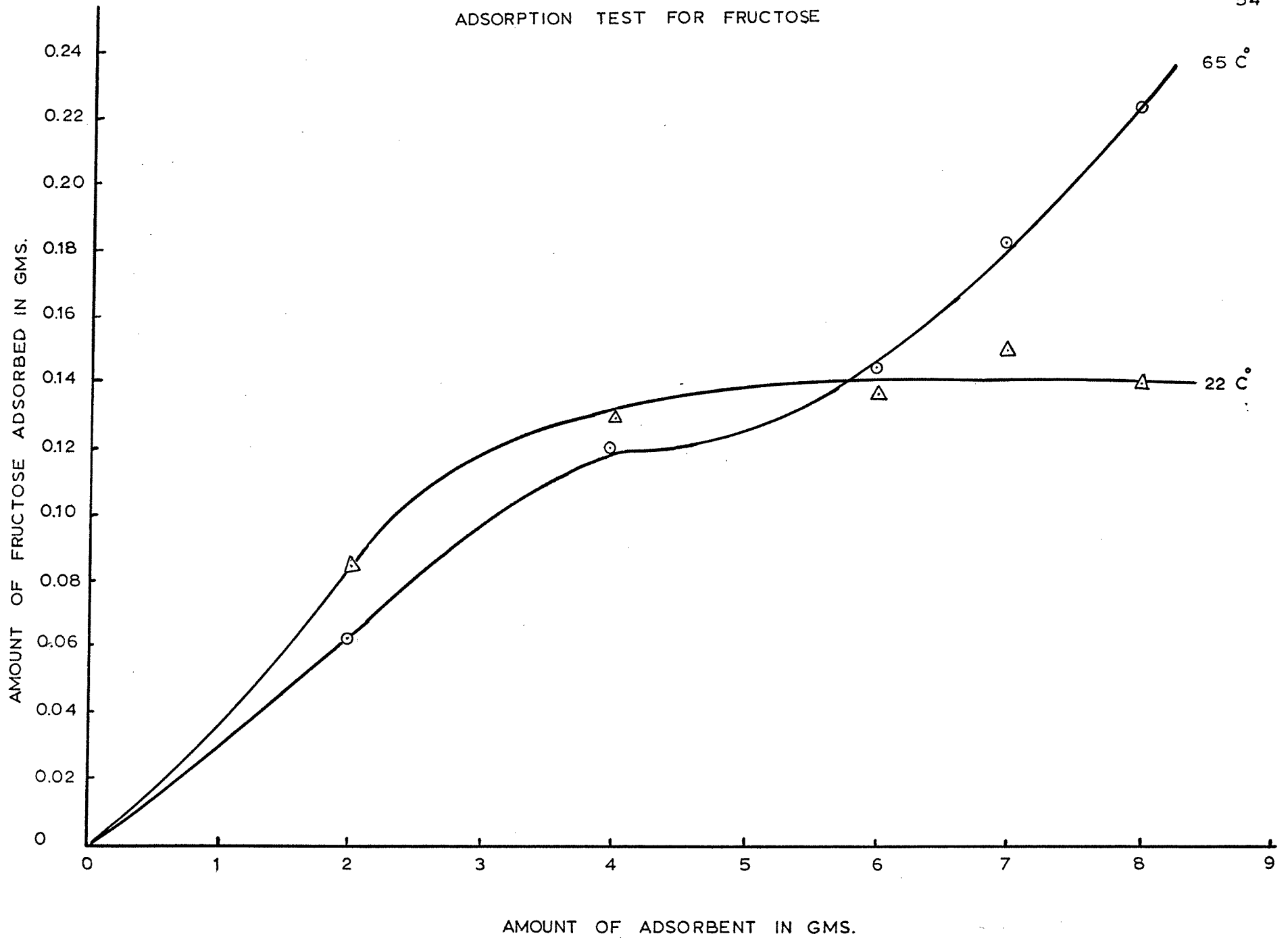
T2 = Top product of cold half cycle .

GRAPH (1)

EFFECT OF ADSORBENT AMOUNT USED ON ADSORPTION TEST FOR GLUCOSE

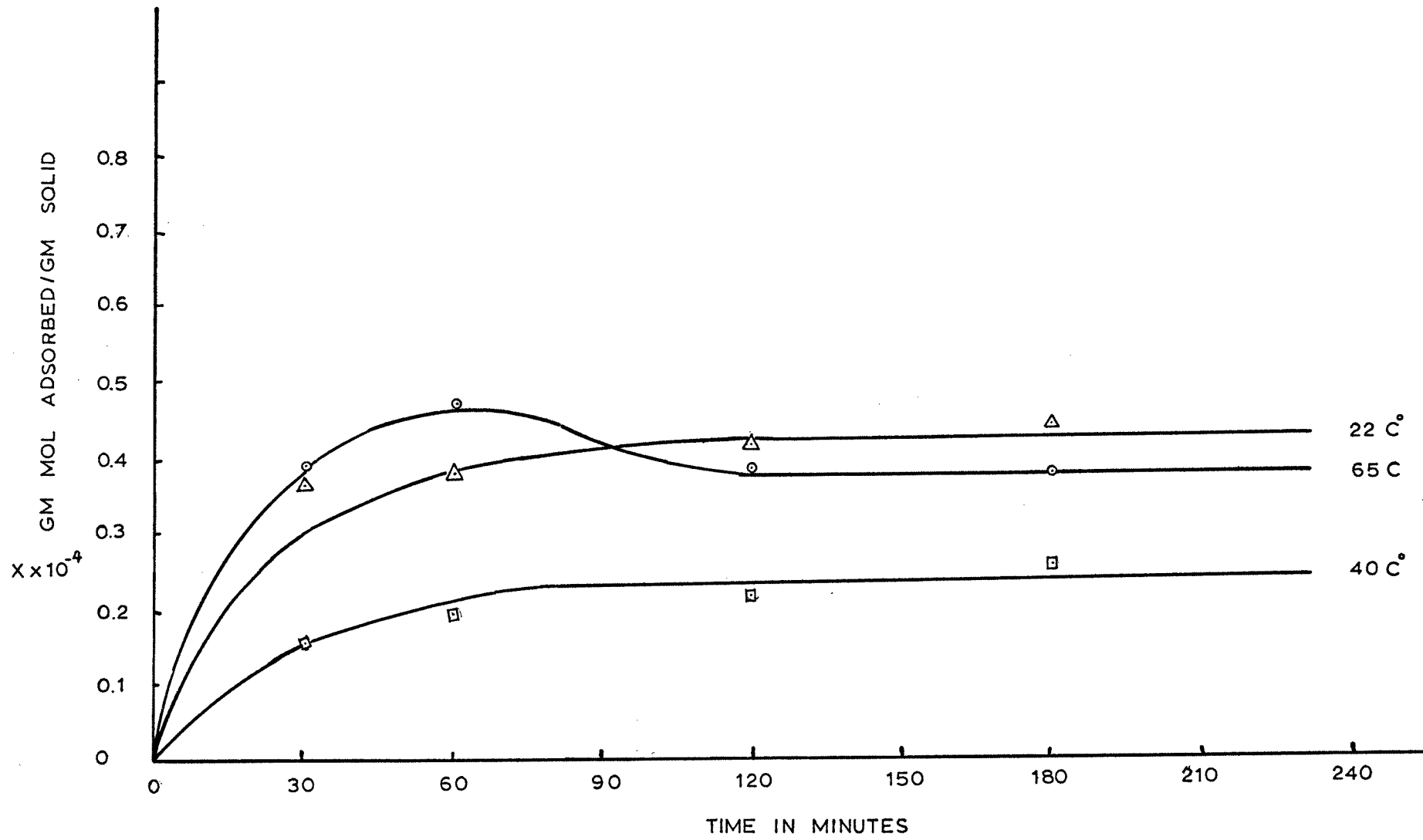


EFFECT OF ADSORBENT AMOUNT USED ON
ADSORPTION TEST FOR FRUCTOSE



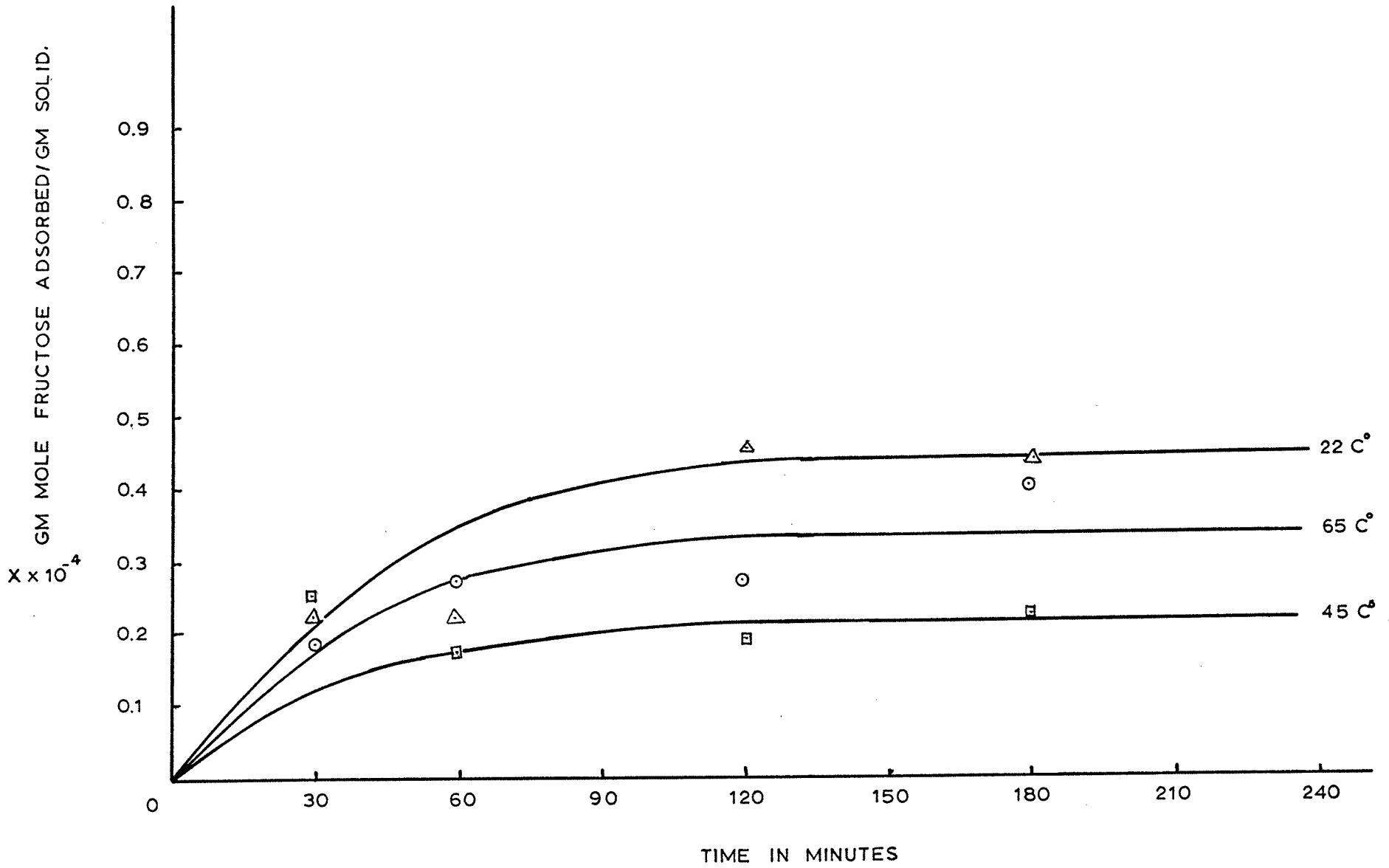
GRAPH (3)

EQUILIBRIUM TIME FOR GLUCOSE ADSORPTION



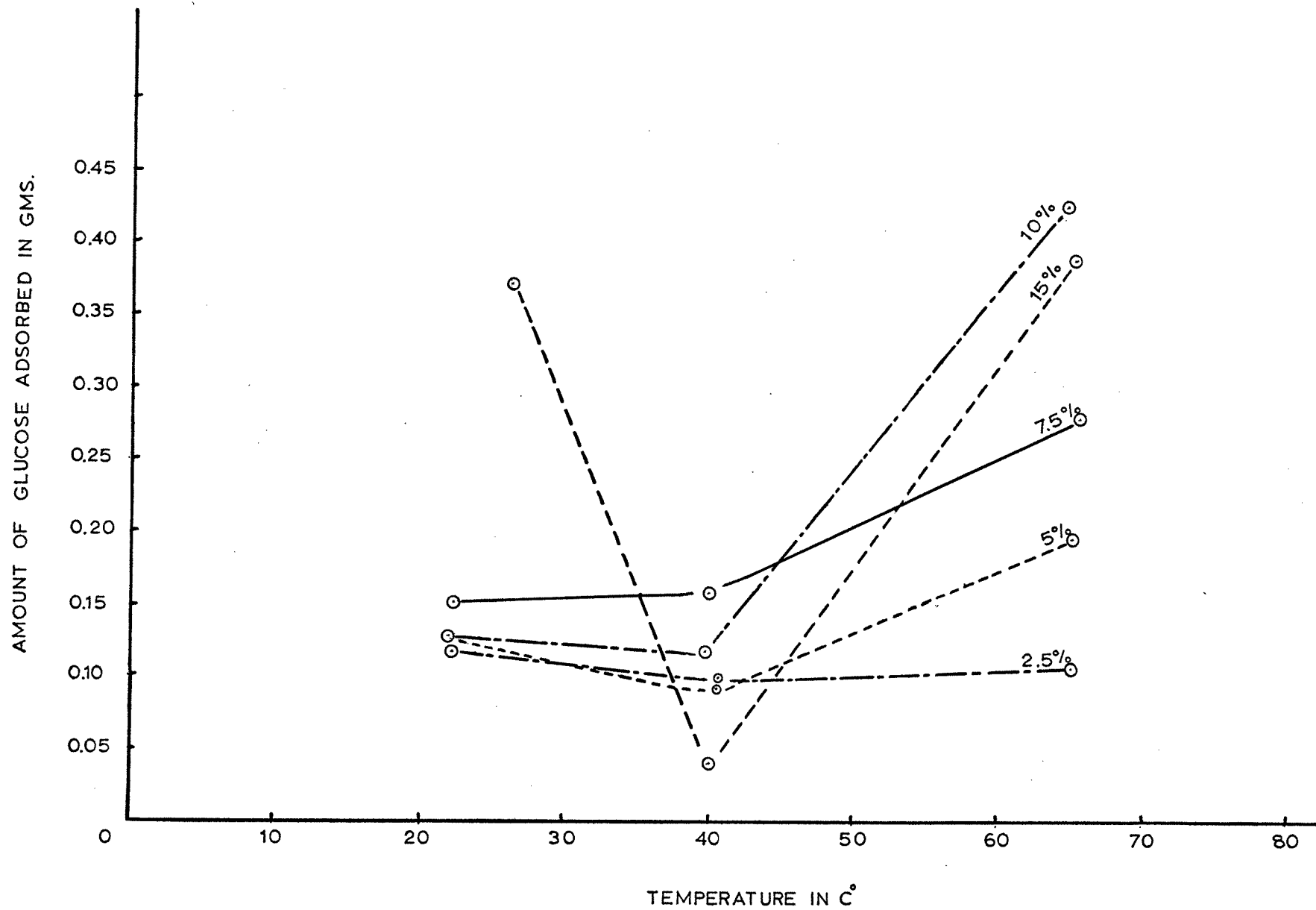
GRAPH (4)

EQUILIBRIUM TIME FOR FRUCTOSE ADSORPTION



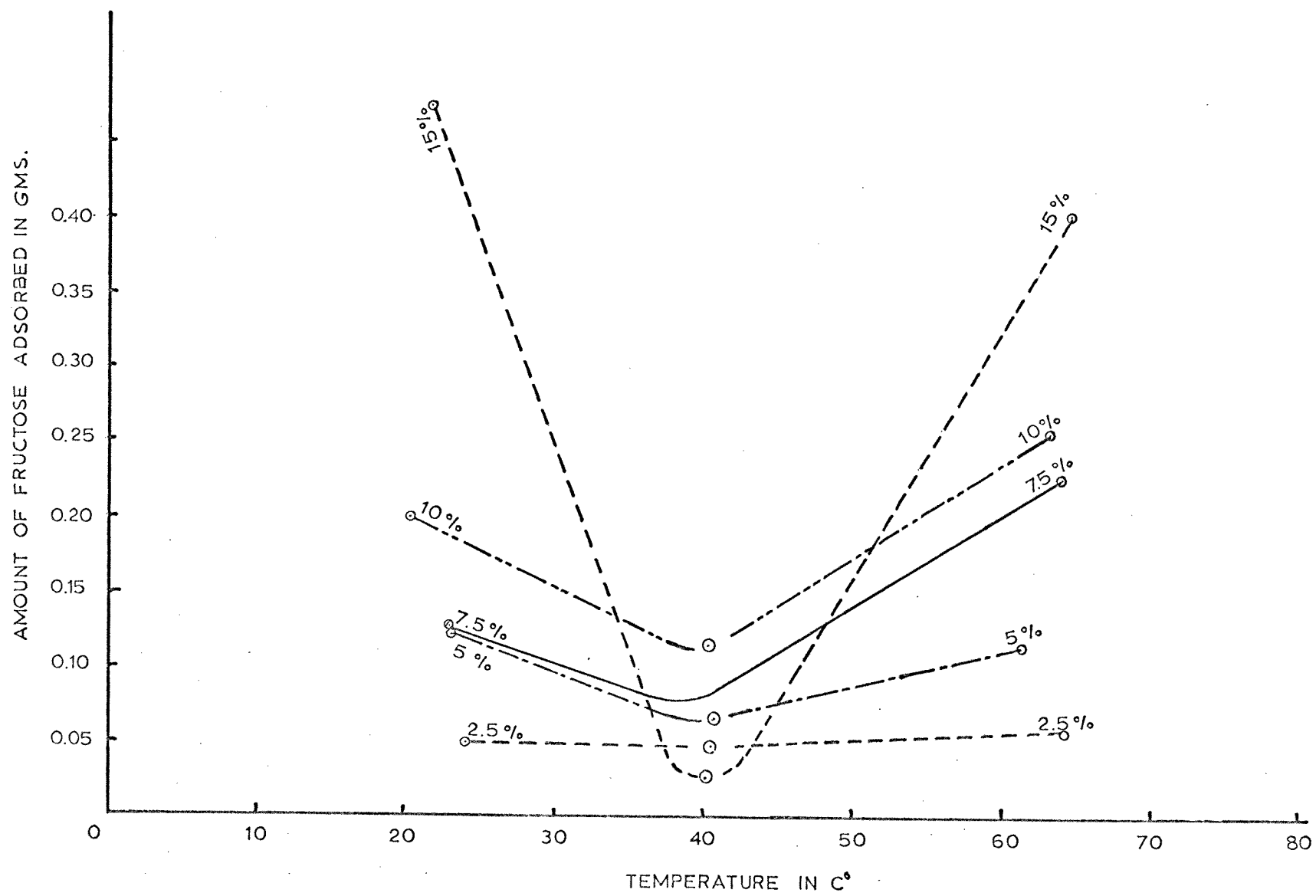
GRAPH (5)

EFFECT OF TEMPERATURE ON ADSORPTION



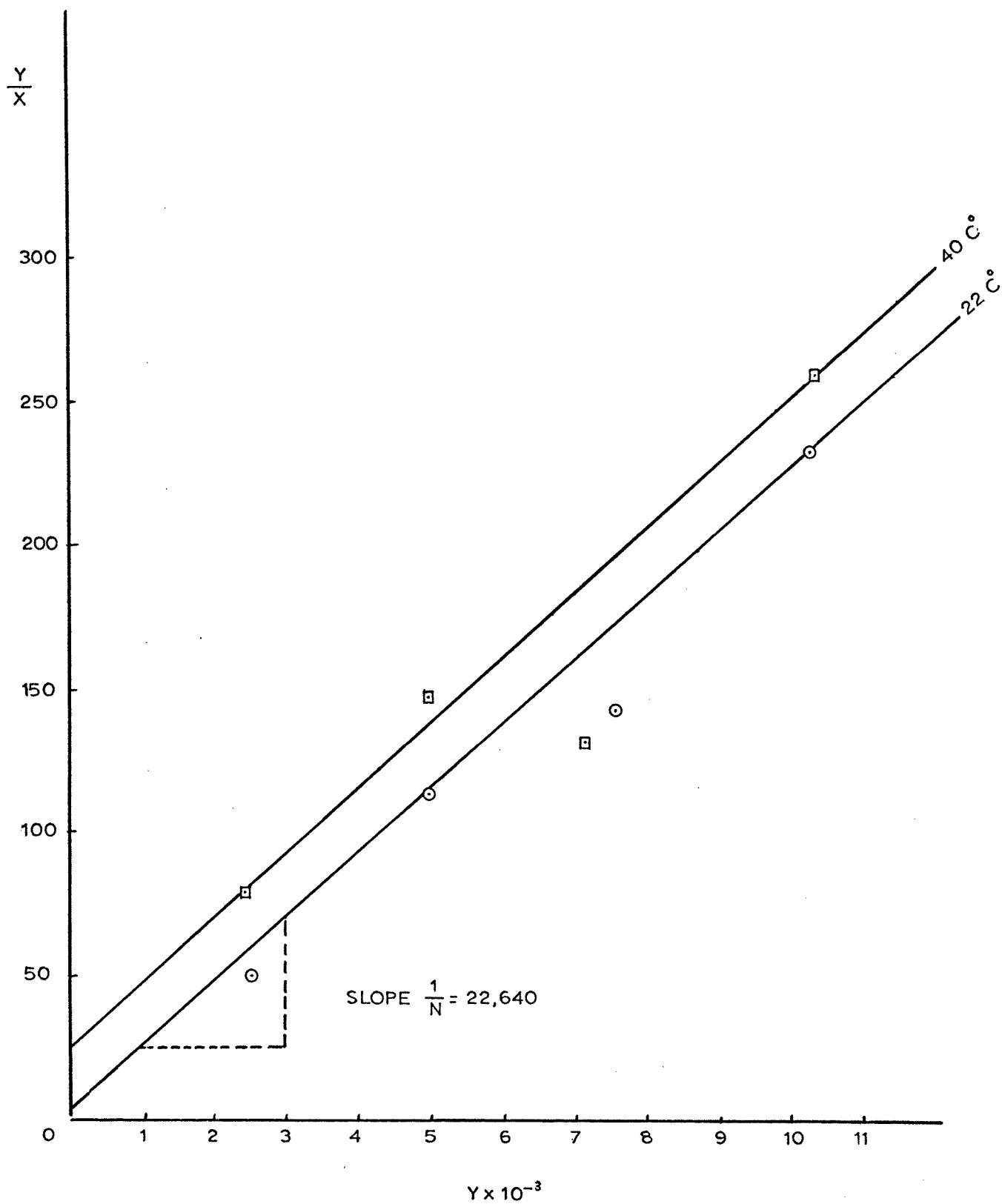
GRAPH (6)

EFFECT OF TEMPERATURE ON ADSORPTION



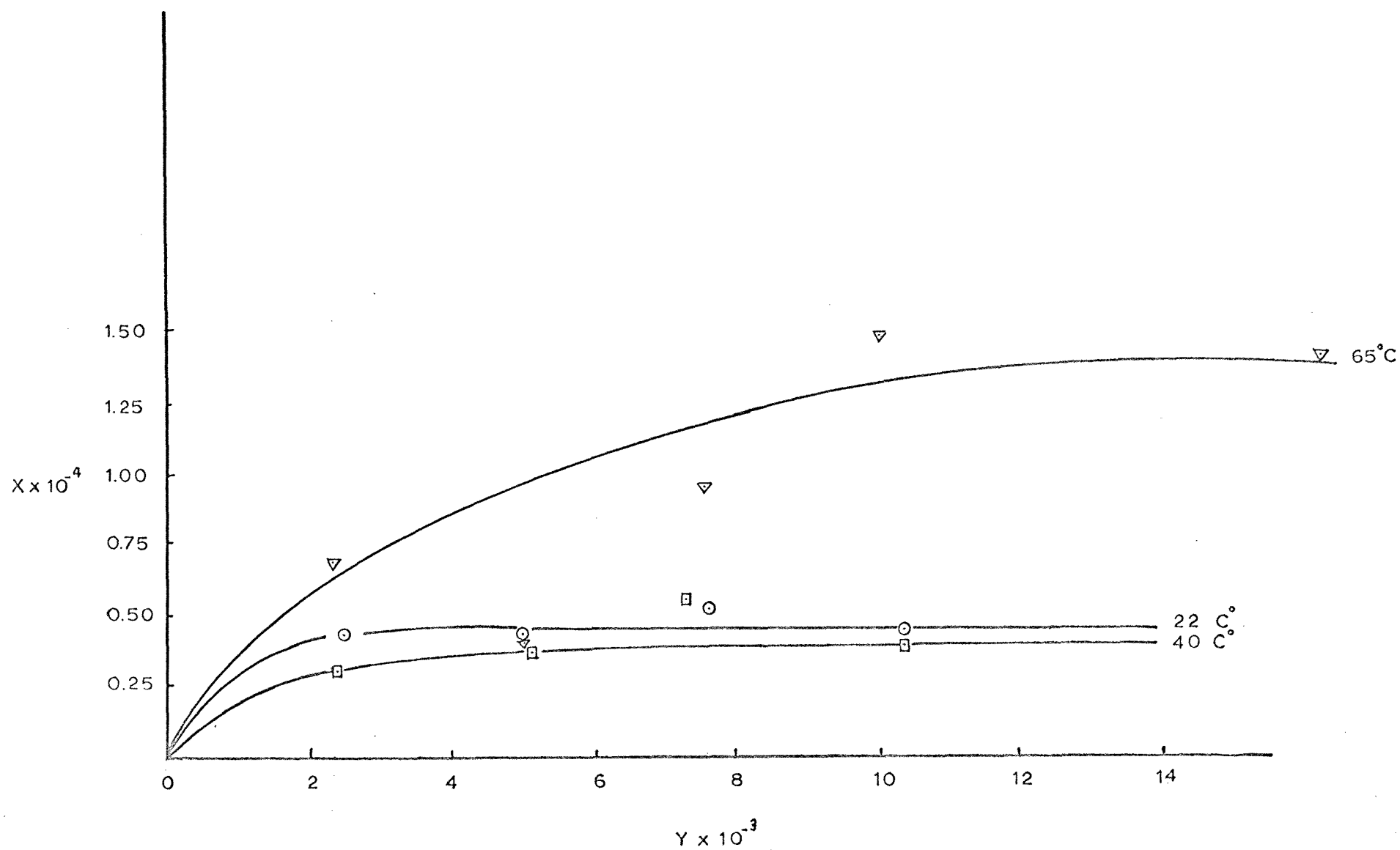
LANGMUIR ADSORPTION ISOTHERM OF GLUCOSE

$$\frac{Y}{X} = \frac{1}{NK} + \frac{Y}{N}$$



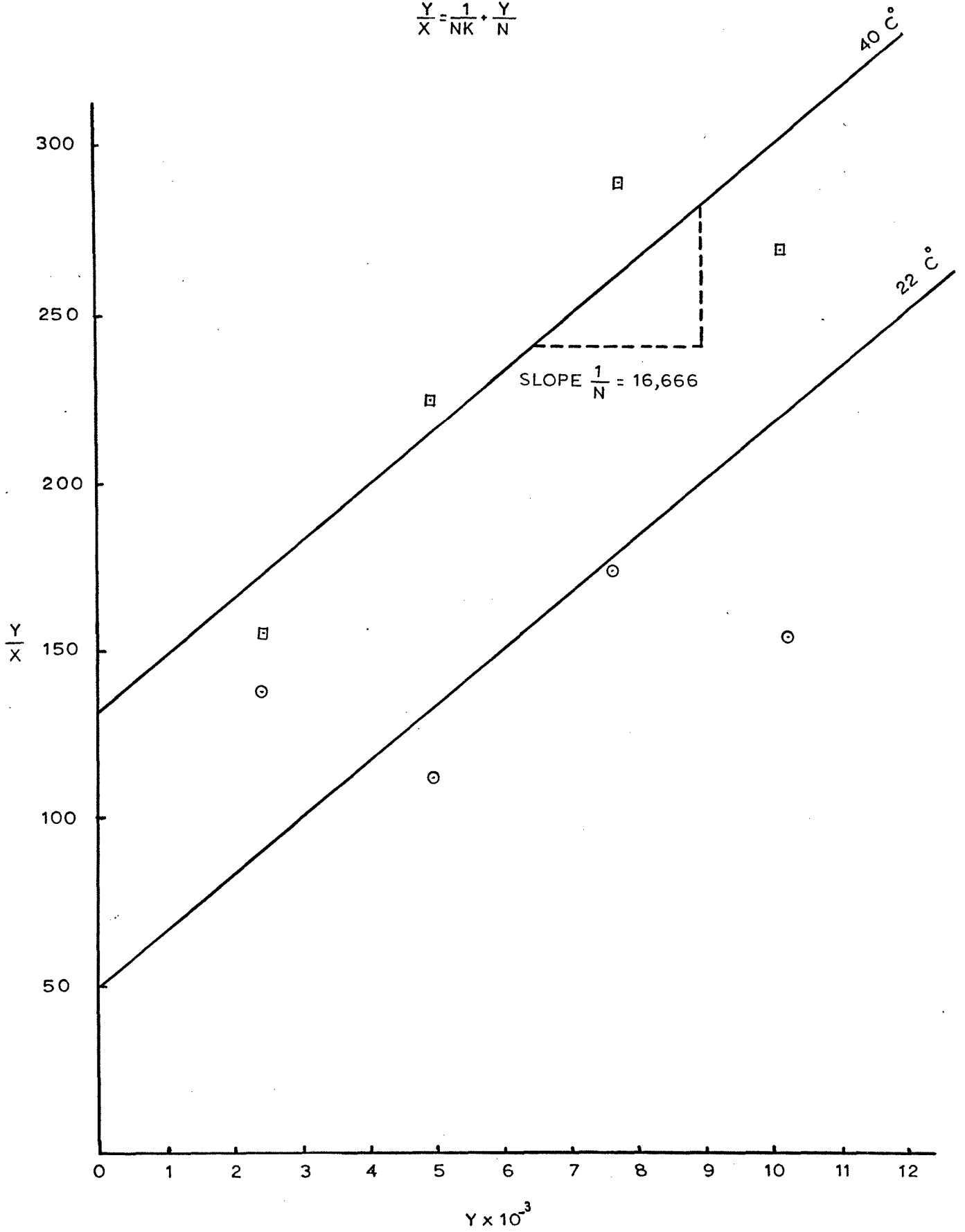
GRAPH (8)

ADSORPTION ISOTHERMS OF GLUCOSE

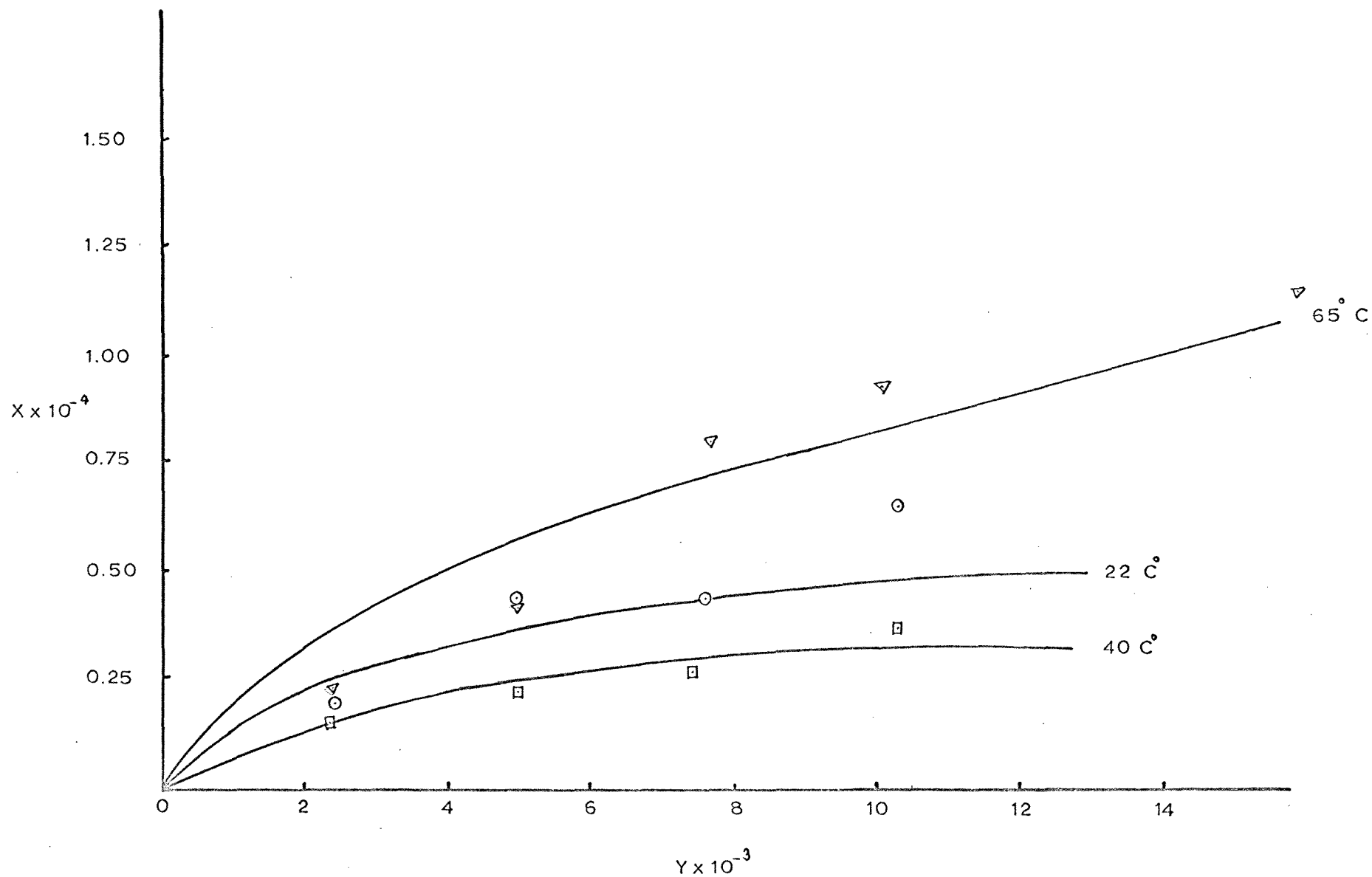


LANGMUIR ADSORPTION ISOTHERMS OF FRUCTOSE

$$\frac{Y}{X} = \frac{1}{NK} + \frac{Y}{N}$$

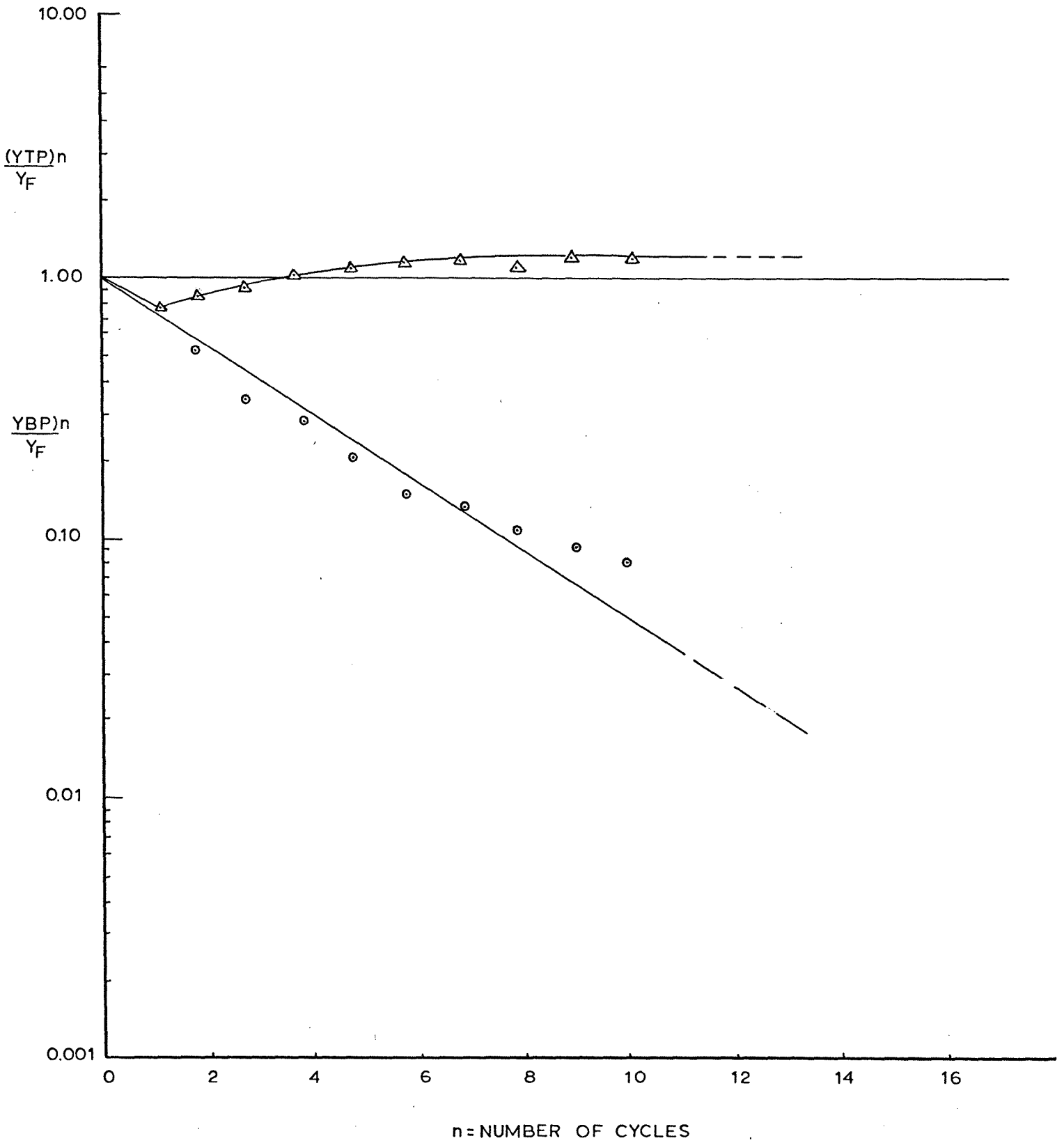


ADSORPTION ISOTHERMS OF FRUCTOSE

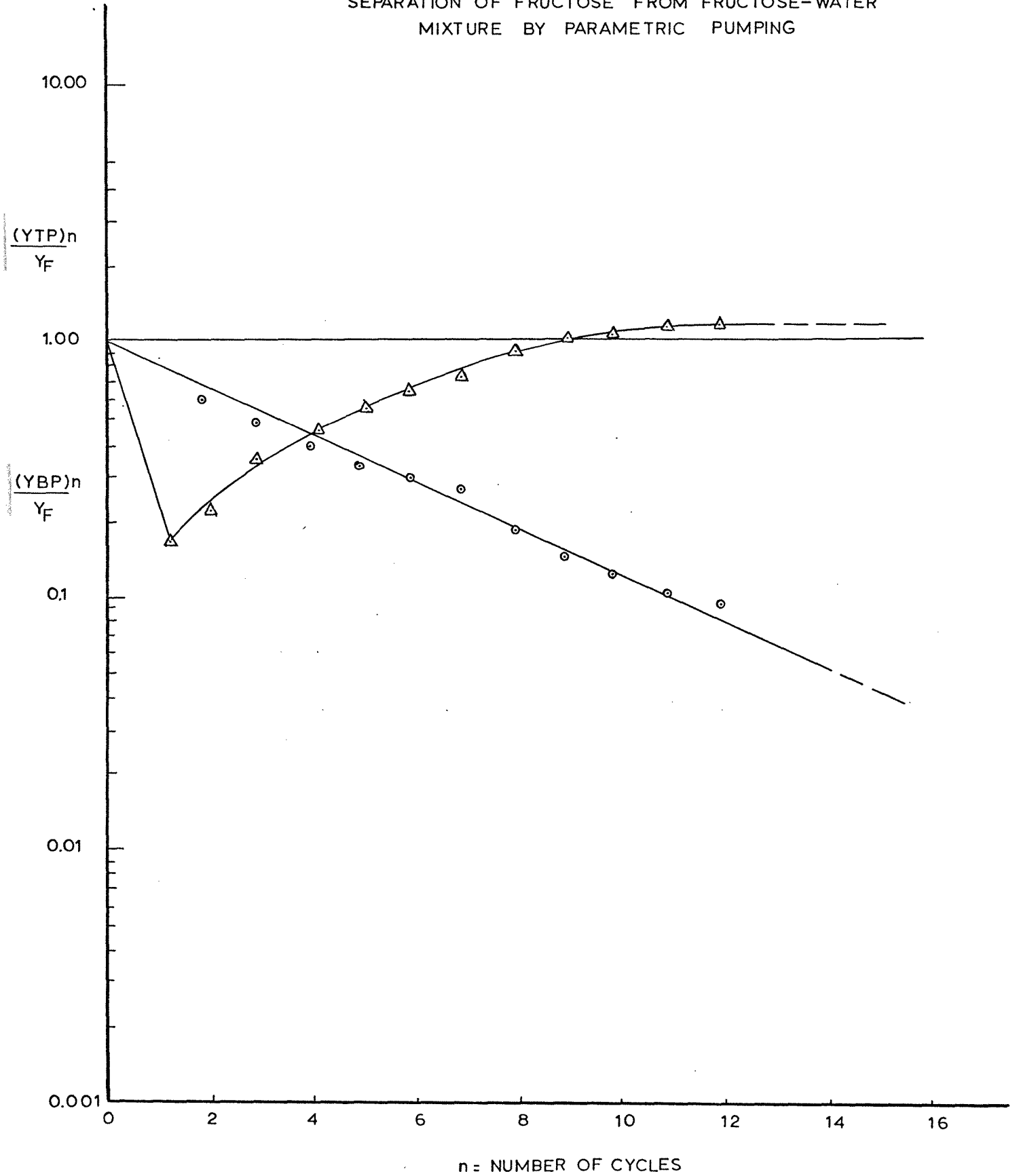


GRAPH (11)

SEPARATION OF GLUCOSE FROM GLUCOSE-WATER MIXTURE BY PARAMETRIC PUMPING

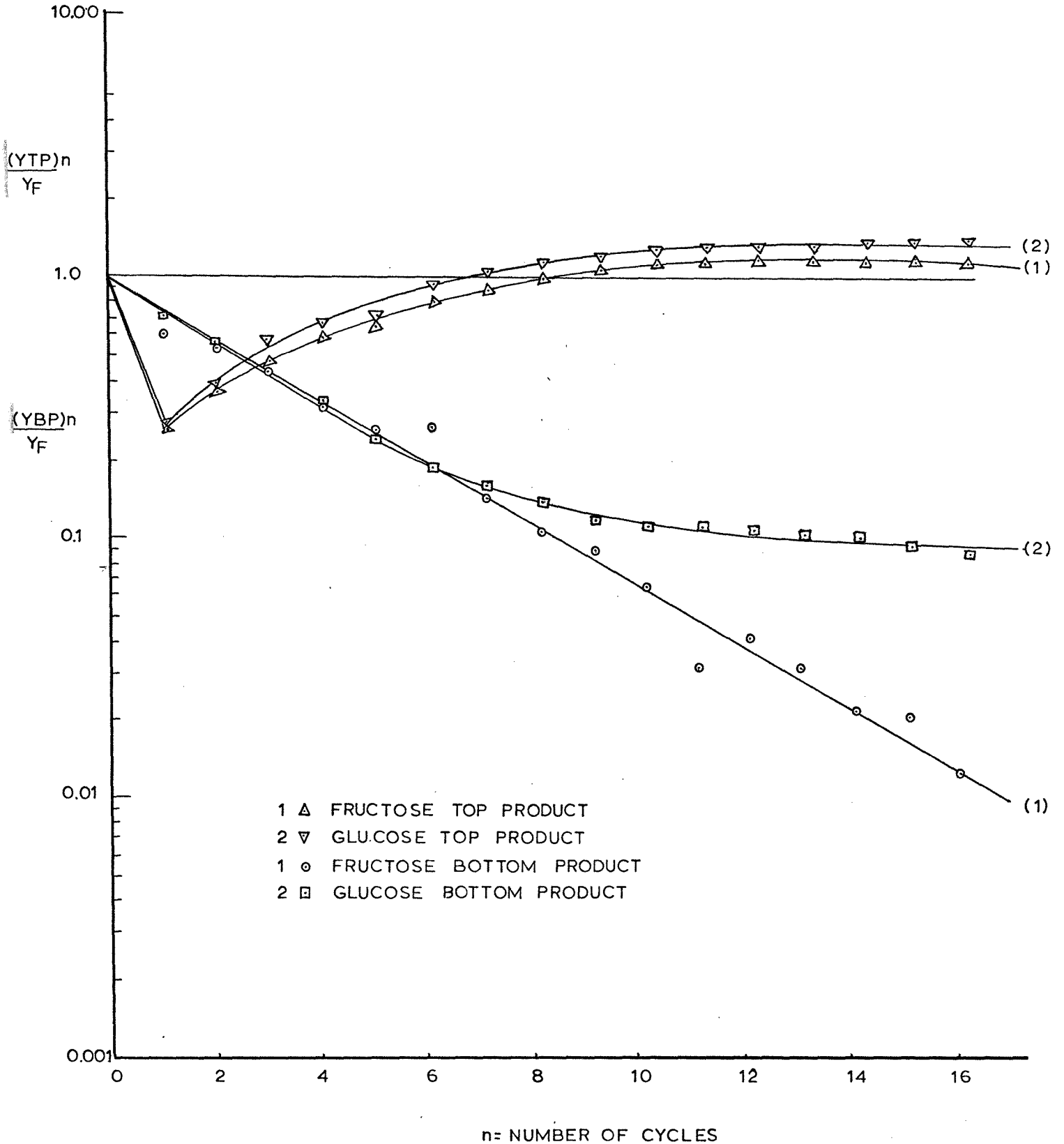


GRAPH (12)

SEPARATION OF FRUCTOSE FROM FRUCTOSE-WATER
MIXTURE BY PARAMETRIC PUMPING

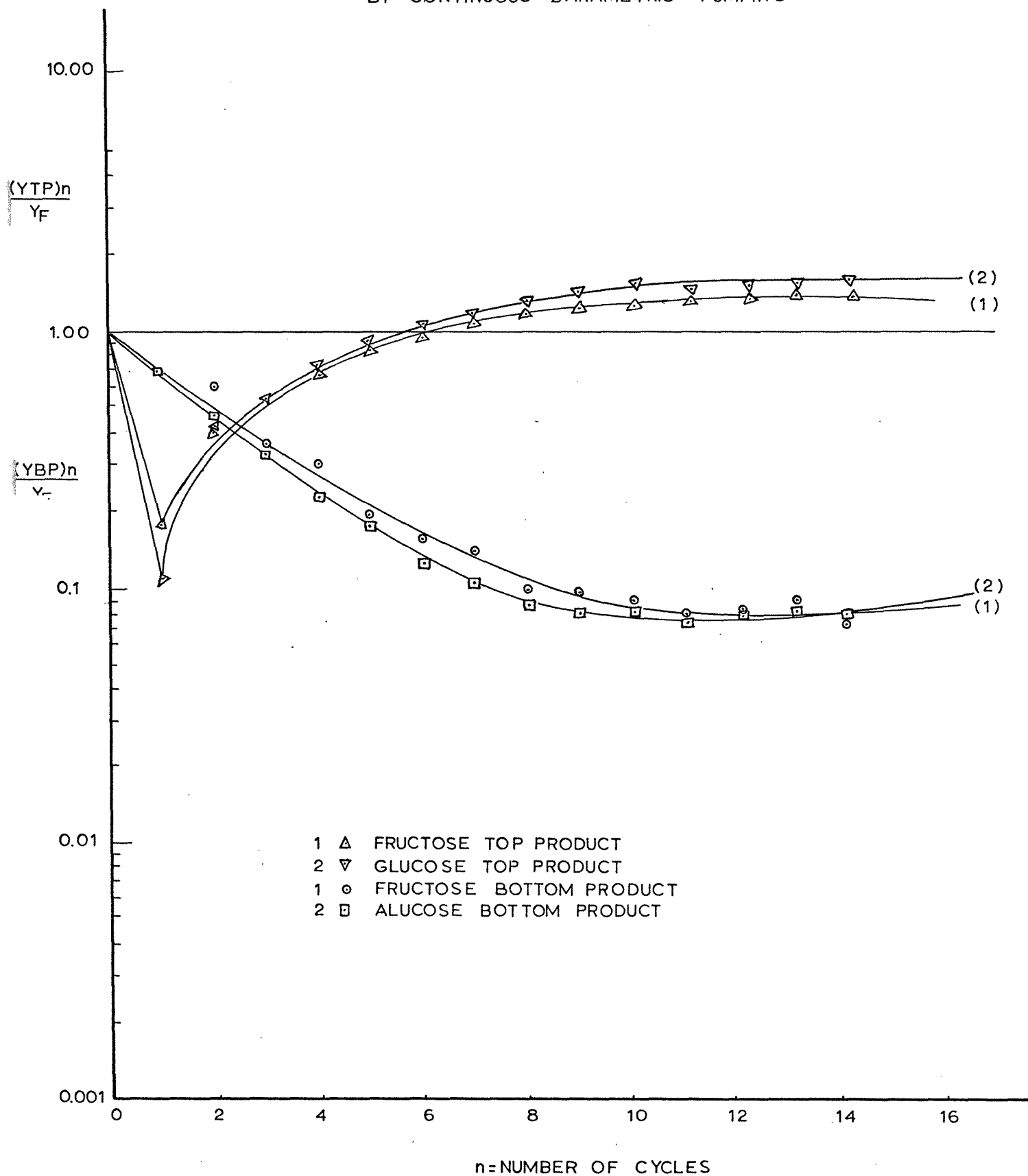
GRAPH (13)

SEPARATION OF GLUCOSE AND FRUCTOSE
BY SEMI-CONTINUOUS PARAMETRIC PUMPING



GRAPH (14)

SEPARATION OF GLUCOSE FROM FRUCTOSE
BY CONTINUOUS BARAMETRIC PUMPING



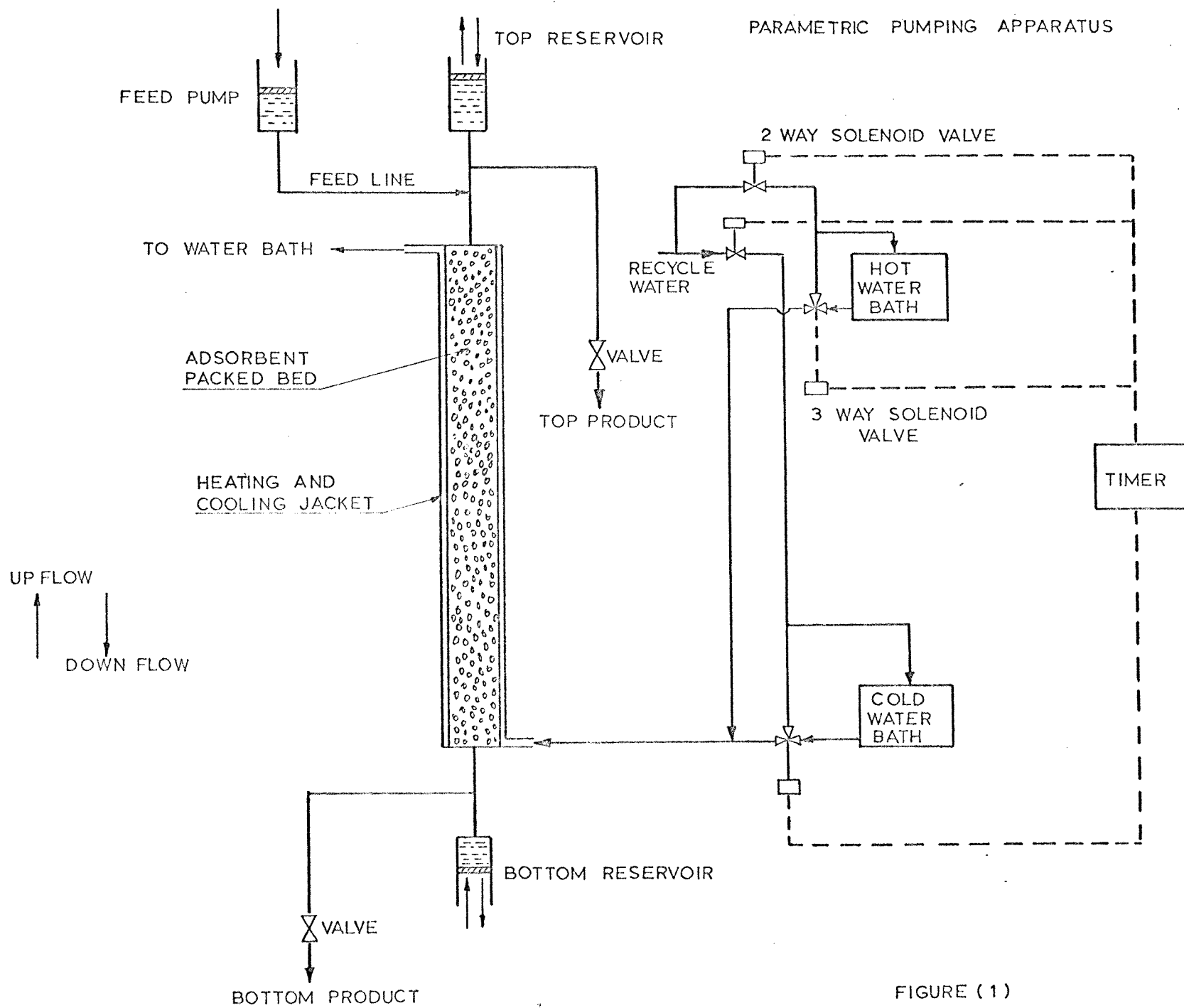


FIGURE (1)

OPERATING REGIONS OF PARAMETRIC PUMP

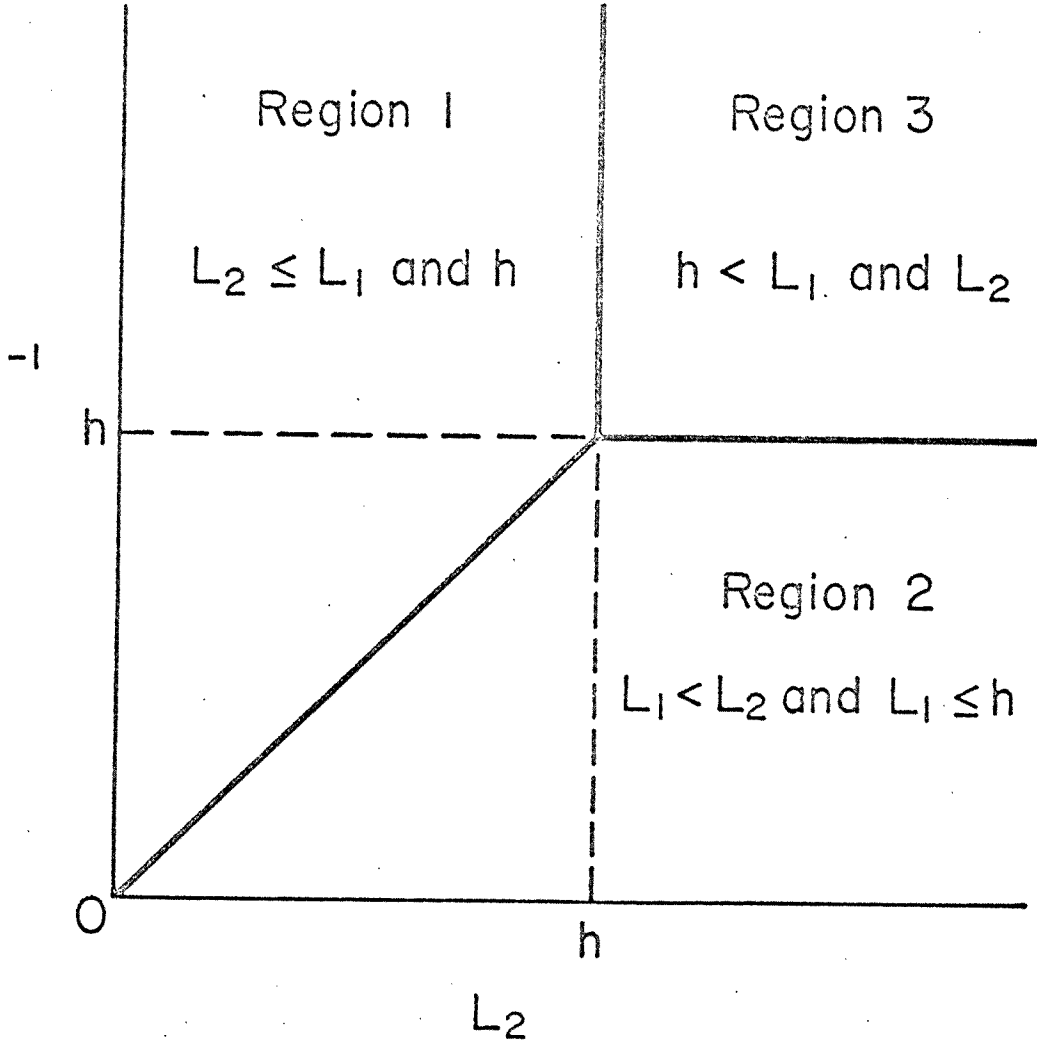


Figure 2

APPENDIX (A)

THEORY

(A) Adsorption Isotherms for Aqueous solution

The ability of certain solids preferentially to concentrate specific substances from solutions onto their surfaces is called adsorption.

Adsorption has for some time been recognized in the chemical industries as an effective process for a wide range of solute-solvent separation.

There are two types of adsorption, (a) Physical adsorption which is reversible phenomena and it is a result of intermolecular forces of attraction between molecules of solid and substance adsorbed, (b) Chemisorption which is a result of chemical interaction between the solid and substance adsorbed.

The amount adsorbed in an adsorption process is a function of many factors, some of which are interrelated. Some of these are: (a) The number of adsorbable molecules (i.e. the concentration in the solution), (b) The number of layers of adsorbed molecules, (c) The total area of the solid surface, (d) The time required to reach the equilibrium between the solute and the adsorbent, (e) The temperature under which the process is carried out; (f) The viscosity of the solution.

One of the oldest attempted explanations of adsorption is that known as the exponential equation by Freundlich and can be expressed as

$$X = KC^{\frac{1}{n}}$$

X = the amount adsorbed per the amount of adsorbent used.

C = The equilibrium concentration of solute.

n and K are constants.

Magnus (15) proposed a theory of unimolecular adsorption on the assumption that the forces of interaction between the surface of adsorbent and solute were electrostatic in nature. De Boer proposed the polarization theory.

Langmuir (16) produced the first theoretical treatment of an isothermal adsorption equilibrium. According to Langmuir, the rate of adsorption u is proportional to: (a) The number of molecules that strike 1 cm.^2 of surface per second, (b) To the fraction f_1 of that number that remain on the surface long enough for an exchange of kinetic energy to take place, (c) To the fraction of the 1 cm.^2 of surface not already occupied by adsorbed molecules.

This can be expressed in the form.

$$u = (PN/2 \pi MRT) f_1 (1-\theta) \quad (1)$$

M = molecular weight of adsorbate gm/mole.

P = equilibrium pressure.

θ = fraction of the adsorbent surface covered with adsorbate.

N = Avogadro's number (6.02×10^{23})

On the other hand the rate of adsorption v is proportional to the fraction of the surface occupied by adsorbate and to the fraction of the total number of adsorbed molecules that have enough energy to leave the attractive forces of the surface which are expressed as a uniform adsorption energy of U cal/mole.

Hence.

$$v = k_0 \theta e^{-U/RT} \quad (2)$$

at equilibrium

$u = v$, i.e. from equation (1) and (2) we obtain

$$P = k \left(\frac{\theta}{1-\theta} \right)$$

$$k = \left(\frac{k_0}{f_1} \right) (2 \pi MRT/N) e^{-U/RT}$$

$$K = Ae^{-U/RT}$$

A is constant for any given temperature.

f_1 = fraction of molecules striking a surface that remain long enough to change their kinetic energy.

The concept underlying the use of θ which has defined before implies that when $\theta = 1$, the whole surface of the solid is covered with a monomolecular film.

Let $\theta = \frac{V}{V_m}$ where V is the amount of gas adsorbed at an equilibrium pressure P and V_m is the amount adsorbed at surface saturation.

$$\text{Then } P = k \left(\frac{V}{V_m - V} \right) \quad (4)$$

$$\begin{aligned} V &= \frac{PV_m}{P + k} \\ \text{i.e. } V &= \frac{PV_m K}{1 + PK} \end{aligned} \quad (5)$$

$$\text{Where } K = \frac{1}{k}$$

For solid-liquid adsorption equation (5) is written as

$$X = \frac{NKY}{1 + KY} \quad (6)$$

in which the experimentally measured quantities are X and Y, and K and N are constants that can be evaluated if the experimental data are capable of being described by the previous equation.

The goal of this part of the present work is to examine fuller's earth (LVM 16-30 Mesh) and to determine its capacity for adsorping Glucose and Fructose from their binary mixtures, solvent in both cases is water.

APPENDIX (A)

Adsorption Isotherms and its Applications.

Previous work (13) indicated that fuller's earth (RVM 30-60 Mesh) adsorbed glucose more than fructose, but when used as an adsorbent in the parametric pump experiments to separate glucose from fructose it broke down after 6 cycles (36 hours) and created a high back pressure inside the column. From this the need to look for another kind of fuller's earth which can stand up under the parametric pumping operation was obvious. Fuller's earth (LVM 16-30 Mesh) was examined to determine its capacity for glucose and fructose adsorption and to examine its ability to withstand the tendency to breakdown in the parametric pumping operation. The results obtained for the adsorption process using fuller's earth (LVM 16-30 Mesh) as purchased and after special treatment were compared. It was found (as Tables 1, 2 and 3 for glucose and 4, 5 and 6 for fructose indicated) that activating this kind of fuller's earth by washing and then heating for 6 hours at 150°C increased its capacity for adsorption. A series of experiments were made to determine the equilibrium time and the concentration of adsorbent necessary to reach equilibrium.

Aqueous solutions of 5 grams glucose / 100 c.c. solution were placed in Erlenmeyer flasks and different amounts of activated fuller's earth were added. The flasks were sealed and immersed in a mechanical shaker constant temperature water bath. After 3 hours of constant shaking (the time needed to reach equilibrium), the slurries were centrifuged and then filtered and the amounts of glucose adsorbed were determined by comparing the concentration of the solution before and after adsorption. An automatic polarimeter was used to determine the concentrations in each case. The same procedure was carried out for fructose. It was

found (as shown in Table 7 and Graph 1) that 4 grams of fuller's earth for a 25 m.l. solution containing 1.25 grams of glucose gave the highest amount of adsorption. For comparison, the same dosage was used for the subsequent series of fructose experiments despite the fact (shown in Table 8 and Graph 2) that higher amounts of adsorbent would increase the amounts of fructose adsorbed.

Series of experiments were carried out to establish the time needed to reach equilibrium between the adsorbent and adsorbate, hence determining the time needed for the half cycle period in the parametric pumping runs for separating glucose and fructose from their binary solutions. Tables 9 and 10 and Graphs 3 and 4 indicated that two and half hours would be adequate. On this basis 3 hours was selected as the time period and used for the rest of the experiments. Those remaining experiments were carried out using the previously described procedure to obtain equilibrium data at concentrations of 2.5, 5, 7.5, 10 and 15 % and at temperatures of 22°C, 40°C and 65°C. From these experiments the X-Y data were calculated (Tables 11 and 12). From Graphs 5 and 6 it was clear that data at 65°C did not fit the Langmuir's isotherms because of the opposing effects of high temperatures and resulting lower viscosities on the adsorption process. Therefore only the data at 22°C and 40°C were applied to the Langmuir equation:-

$$\frac{Y}{X} = \frac{1}{NK} + \frac{Y}{N}$$

Values of $\frac{Y}{X}$ were plotted against Y in Graphs 7 and 9. The best straight lines were drawn through the points, and their slope $\left(\frac{1}{N}\right)$ was calculated. Values of K were determined at both temperatures from the intercept $\frac{1}{NK}$ which was the same procedure used by previous investigator (13) and repeated here for the reader

APPENDIX (B)

Parametric Pumping Experiments

A parametric pumping system (Fig. 1) consists of a jacketed glass column of 1 cm. internal diameter and 90 cms. height . Two infusion-withdrawal pumps, each with two syringes, each syringe can contain a volume of 50 ml. were used as reservoir and feed pumps. A magnetic stirrer was placed in each of the reservoir pump syringes to assure homogeneous mixing. The action of the reservoir pump was automatically reversed at the end of each half cycle by means of micro-switch stops wired to the pump circuit. The sources of hot and cold water for the jacket supply were constant temperature water baths with programmed cycle timer which cycle the jacket temperature by means of two solenoid valves attached to the baths. Product streams were taken off by means of two micrometer capillary valves. Rotometers were used in the feed and product lines.

Prior to each run, the column was packed with activated carbon (400 Filter-*asorb*, manufactured by The Calgon Co. Pa.) and the entire system including the column, the bottom reservoir and the feed syringes were filled with feed mixture at ambient temperature. The reservoir syringes were adjusted to deliver about 40 c.c. per each half cycle with a dead volume of approximately 4 c.c. in each syringe.

At the beginning of a run, the reservoir pump was switched on and the timer was activated. Hot water at 60°C was circulated through the jacket. At the end of this 20 minutes hot up flow half cycle, the reservoir pump reversed its direction, the feed pump switched on and the jacket was switched to cold water bath of 22°C. During this twenty minutes cold down flow half cycle, samples for purpose of

analyses were taken from the product streams and analysed by an automatic polarimeter to determine concentration. The concentrations of the top and bottom products were compared with that of the feed and the ratios of the two concentrations were put in the form $\frac{Y_{TP}}{Y_F}$ and $\frac{Y_{BP}}{Y_F}$.

Graphs of $\log \frac{Y_{TP}}{Y_F}$ and $\log \frac{Y_{BP}}{Y_F}$ versus number of cycles n were plotted.

Dimensionless concentrations greater than one are top product concentrations, while those less than one are bottom product concentrations. The slope (α) of $\log \frac{Y_{BP}}{Y_F}$ versus n was determined and the computed b value was obtained from the relation:-

$$b = \frac{(1-10^\alpha) + C_2 (1-10^{\alpha})}{(1+10^\alpha) - C_2 (1-10^\alpha)} \quad (\text{see reference 8})$$

The ratio for $\frac{L_1}{L_2}$ was calculated from the relation :-

$$\frac{L_1}{L_2} = \frac{(1 + b)}{(1 - b) (1 + \phi_B)}$$

$\frac{L_1}{L_2}$ for the glucose-water system and for the fructose-water system were found to be more than one, this indicated that the operating region in the first and the second runs was region 1 (see Fig 2). Expressions for region 1 can be obtained from the equations derived by Chen et al (6).

The concentration transients $\frac{Y_{TP}}{Y_F}$ and $\frac{Y_{BP}}{Y_F}$ were computed from these expressions and plotted versus n . The computed results were compared with the experimental and are shown in Graphs 11 and 12.

Based on these results a third run for the mixture (glucose + fructose + water) was carried out to separate fructose and glucose. The ϕ_B chosen was

less than $\frac{2b}{1-b}$ for both components to assure their removal from the bottom product stream. This third run was followed by fourth one , that one was continuous (feed on during both hot and cold half cycles) and products were collected during both half cycles and analysed. Results and calculations for these four runs are shown in Tables 14, 15, 16 and 17 and Graphs 11, 12, 13, and 14 .

THE AUTHOR

Mr. Zikri M. Ahmed was born in _____ He received B.Sc. in Chemical Engineering from Cairo University in June 1966. He worked as process engineer from 1966 until 1969 in Isnadye Co. (Egypt) for manufacturing of dyestuffs and chemicals, then he joined the Rheinlutte Co. (West Germany) for manufacturing of chemical pumps as research engineer from 1969 until 1970. During 1970, he received graduate studies in Mathematics at Bochum University (West Germany).

In Feb. 1971 he joined Newark College of Engineering for graduate studies in Chemical Engineering.

This research was begun in Sep. 1971 and completed in March 1973 under the supervision of Dr. H.T. Chen in the parametric pumping research laboratory at Tiernan Hall, Newark College of Engineering, Newark, New Jersey.