1967

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Recommended Citation

Desai, Surendra V., "Molecular diffusion in polymer solutions by a microinterferometric method" (1967). *Masters Theses*. 2934.
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MOLECULAR DIFFUSION IN POLYMER SOLUTIONS BY A MICROINTERFEROMETRIC METHOD

BY

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A

THESIS

submitted to the faculty of

THE UNIVERSITY OF MISSOURI AT ROLLA

in partial fulfillment of the requirements for the

Degree of

MASTER OF SCIENCE IN CHEMICAL ENGINEERING

Rolla, Missouri

1967

Approved by

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ABSTRACT

The object of this investigation of molecular diffusion in aqueous polymer solutions was to study the effect of solute concentration on the differential diffusion coefficient and also to study the effect of polymer concentration on the mean integral diffusion coefficient. For this purpose a microinterferometric method was used. Two non-ionic, water soluble polymers, Carboxymethylcellulose (CMC) and Carboxypolymethylene (Carbopol), were used in the study with D-Glucose as a solute.

The differential diffusion coefficient was found to increase with increases in solute concentration in all cases. For CMC, the integral diffusion coefficient at first decreased with increasing polymer concentration but became constant after a certain value of polymer concentration has been reached. For Carbopol, the integral diffusion coefficient decreased with increasing polymer concentration.

It appears that the Wilke-Chang correlation may approximately predict the differential diffusivity of the solute at very low solute concentrations in the polymeric solutions with a probable error of ± 10%.

ACKNOWLEDGEMENT

The author is deeply indebted to Dr. R. M. Wellek, Associate Professor of Chemical Engineering, who suggested this investigation and served as a research advisor. His help, guidance and encouragement are sincerely appreciated.

The author is also grateful to Dr. G. L. Lewis, Associate Professor of Ceramic Engineering and Associate Professor of Materials, for the help and guidance in the vacuum metallization of the glass slides. Special thanks are extended to the Materials Research Center for allowing the author to use the Ultek Model TNB high vacuum system.

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I. INTRODUCTION

A quantitative measurement of the rate at which a diffusion process occurs is usually expressed in terms of a diffusion coefficient. In this work, attention will be centered on molecular diffusion. Little attention has previously been given to diffusion in non-homogeneous media in which the diffusion coefficients vary with the distances measured in the direction of diffusion, apart from the special cases relating to composite sheets, cylinders and spheres.

A case of great practical interest is that in which the diffusion coefficient depends only on the concentration of the diffusing substances. Such a concentration dependence exists in most systems, but often (e. g., in dilute solutions) the dependence is slight, and the diffusion coefficient can be assumed constant for practical purposes. In other cases, however, such as the diffusion of solutes in high polymer substances, the concentration dependence is a very marked characteristic feature.

The purpose of this investigation is to study the effect of solute concentration on the diffusion coefficient in polymer solutions and also to determine the effect of polymer concentration on the diffusion coefficient. The non-ionic, water-soluble polymers Carboxymethylcellulose (CMC) and Carboxypolymethylene (Carbopol) were used to study this effect, with D-Glucose as the solute.

Diffusion coefficients of the polymeric systems were determined by a microinterferometric method. The change in solution refractive index with solute concentration was used to measure the rate of molecular diffusion. This technique is very well suited to the low diffusion rates encountered in high viscosity liquids. According to the theory of Brownian movement (7, 8) the average of the square of the distance over which a particle is randomly wandering is proportional to the time during which it travels. In other words, the time varies inversely with the square of the distance traveled. Therefore, if the diffusion process is observed over a small distance, it should be possible to reduce the time required for observation by the square of the magnification factor. Thus, if the diffusion measurement is observed under a microscope (as was done in this work) with a magnification factor of 10, the time scale is reduced by 100. Distinct advantages of this method over conventional and other interferometric methods are that the time required is reduced by an order of about 100 if a magnification of 10X is used, the equipment is less expensive, and only microgram amounts of solution are required. It is estimated that the method employed has a probable error of from ±5 to ±10 per cent (25), which is comparable to conventional interferometric methods.

II. LITERATURE REVIEW

This chapter reviews briefly the important field of diffusion in liquids. The first part deals with the theory of molecular diffusion and the second part discusses various experimental techniques for the measurement of the molecular diffusivity.

A. Theory of Diffusion

Mass transfer operations involving polymer solutions are often controlled by molecular diffusion. A basic law for one-dimensional diffusion was proposed by Fick (9). For diffusion at constant temperature and pressure in two-component systems which show no change in volume on mixing, Fick's first law for one-dimensional transport of the solute is*

$$J_{ix} = -D\left[\frac{\partial C_i}{\partial x}\right]_t \tag{2.1}$$

where the subscript 'i' denotes the solute.

This equation shows that at any time, t, and position x in the 'x' direction, the flux, J_{ix}, of the solute is directly proportional to the first power of the solute concentration gradient $\left[\frac{\partial C_i}{\partial x}\right]_t$. The flux J_{ix} is positive in the direction of increasing x and can be defined as the amount of solute crossing a unit area perpendicular to the direction of the flow per unit time.

Fick's first law for one-dimensional transport of the

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* All symbols are also defined in the Nomenclature section, Appendix G, page 112.

solute, considering the solute transfer by bulk flow, can be written as follows:

$$N_{ix} = (N_{ix} + \sum_{\substack{j=1 \\ j\neq i}}^{n} N_{jx})\frac{C_i}{C} + J_{ix} \qquad (2.2)$$

The above equation shows that the diffusion flux N_{ix} of the ith component in the 'x' direction relative to stationary coordinates is the resultant of two vector quantities: the vector $(N_{ix} + \sum_{\substack{j=1 \\ j\neq i}}^{n} N_{jx}) \frac{C_i}{C}$, which is the molar flux of the ith component resulting from the bulk motion of the fluid, and the vector $J_{ix} = -D\left[\frac{\partial C_i}{\partial x}\right]_t$, which is the molar flux of the ith component resulting from the diffusion superimposed on the bulk flow. In this study it is assumed that

$$J_{ix} \gg (N_{ix} + \sum_{\substack{j=1 \\ j\neq i}}^{n} N_{jx}) \frac{C_i}{C}$$

That is to say, the flux related to bulk flow is very negligible and all the transport of the solute is taking place by molecular diffusion due to the concentration gradient.

Fick's second law for three-dimensional systems may be written for unsteady state mass transfer with no chemical reaction as follows:

$$\frac{\partial C_i}{\partial t} = -\left[\frac{\partial N_{ix}}{\partial x} + \frac{\partial N_{iy}}{\partial y} + \frac{\partial N_{iz}}{\partial z}\right] \qquad (2.3)$$

In some cases, e. g., diffusion in dilute solutions, D can be taken as being reasonably constant. For such cases when mass transfer by bulk flow can be neglected, N_{ix}, N_{iy} and N_{iz} are given by equation (2.1) for each direction, then equation (2.3) becomes after letting $N_{ij} = J_{ij}$

$$\frac{\partial C_i}{\partial t} = D \left[\frac{\partial^2 C_i}{\partial x^2} + \frac{\partial^2 C_i}{\partial y^2} + \frac{\partial^2 C_i}{\partial z^2} \right] \qquad (2.4)$$

Considering molecular diffusion only in the 'x' direction, one obtains the following relation

$$\frac{\partial C_i}{\partial t} = D \frac{\partial^2 C_i}{\partial x^2} . \qquad (2.5)$$

B. Prediction of Diffusion Coefficients

Several empirical methods for estimating the value of D in dilute Newtonian solutions of non-electrolytes are presented by Reid and Sherwood (23). One of the most successful empirical correlations has been suggested by Wilke (34) which later was extended by Thaker and Othmer (30) and Wilke and Chang (35).

The form suggested by Wilke and Chang is

$$D_{AB} = 7.4 \times 10^{-8} \frac{(\psi_B M_B)^{1/2} T}{\mu V_A^{0.6}} \qquad (2.6)$$

where

D_{AB} = diffusivity of solute A in dilute solutions of solvent B, sq. cm./second.

M_B = mol. wt. of solvent.

T = temperature $^{\circ}$K.

μ = viscosity of solution, centipoise.

V_A = solute molal volume at the normal boiling point, cc/gm mole.

ψ_B = an association factor for the solvent (2.6 for water).

This equation is surprisingly good for low concentrations of the solute and usually is accurate to within 10 per cent for the low viscosity non-polymer systems (i.e., $\mu < 4$ centipoise). This correlation fails to handle systems which are very viscous (31).

While experimental determinations of diffusivities are recommended whenever high accuracy is desired, methods of prediction are improving. These developments have been based primarily upon the extension of the hydrodynamic and Eyring models rather than on the more general expression of Enskog (2) and Kirkwood (14). In these models, diffusion coefficients are estimated from more easily measured properties such as viscosity and heat of vaporization. Among the recent developments are the analysis of Pyun and Fixman (21, 22) which allows the extension of the hydrodynamic model to concentrated systems and the analyses of Olander (19) and of Grainer and Metzner (10) which extend the Eyring model to dilute solutions of high viscosity. These two methods and their recent modifications are discussed in greater detail in reference (15).

In many systems, e.g., in high polymer solutions, D is frequently dependent on the solute concentration. In such cases, D varies from point to point in the solution, and equation (2.3) then becomes,

$$\frac{\partial c}{\partial t} = \frac{\partial}{\partial x}\left[D \frac{\partial c}{\partial x}\right] + \frac{\partial}{\partial y}\left[D \frac{\partial c}{\partial y}\right] + \frac{\partial}{\partial z}\left[D \frac{\partial c}{\partial z}\right] \qquad (2.7)$$

where D is a function of concentration. For one-dimensional diffusion, the above equation may be written

$$\frac{\partial c}{\partial t} = \frac{\partial}{\partial x}\left[D \frac{\partial c}{\partial x}\right] . \qquad (2.8)$$

The derivation of such concentration-dependent molecular diffusivity from equation (2.8) and the experimental concentration profile is given in the Appendix (A). In this development it is assumed that the system is binary, i.e., the solvent and the dissolved polymer are treated as one component and the solute is the second component.

C. Techniques for the Measurement of Diffusivity

Since no completely adequate theory for predicting the diffusion coefficients exists, experimental measurements are generally required. Though Fick's first law equation (2.1) defines the diffusion coefficient in terms of the flux of solute and its concentration gradient, it is not possible to calculate 'D' by direct measurement of these two quantities. It is possible to measure the concentration gradient, but the flux of the solute can not usually be measured. The steady state method is the closest approach to a direct determination of the flux. This method is not useful for the variable, solute concentration dependent molecular differential diffusion coefficient of a solute in polymer solutions. This has been fully described in reference (5). All other methods of determining 'D' utilize integrated forms of Fick's second law, i.e., equation (2.5). For systems in which 'D' is very concentration dependent, e.g., in high polymeric systems, integrated forms of equation (2.8) are generally used to calculate 'D'.

A very brief review of the pseudo-steady state method (the diaphragm cell) and some of the optical methods for studying infinite or free diffusion is given below. The microinterferometric method which has been used for determining the differential diffusion coefficient of a solute in polymer solutions is fully described.

1. Pseudo-steady State Diffusion (the diaphragm cell)

In pseudo-steady state diffusion through a diaphragm, a nearly steady concentration gradient is established across a porous diaphragm separating two miscible solutions of different composition. After a known period of diffusion, the concentrations of the two solutions are analyzed to determine the diffusion coefficient. Because of simple apparatus and potentially high accuracy the diaphragm cell technique is an outstanding method of measuring diffusion. The diaphragm cell may be used for any system where a suitable method of analyzing the solution concentration is available. This method is not useful for the variable, solute concentration-dependent, molecular differential diffusion coefficient of a solute in polymer solutions.

2. Infinite or Free Diffusion

Infinite diffusion by interferometric means is one of the most accurate current methods of measuring molecular diffusion coefficients. This consists essentially of the measurement of the concentration distribution and/or the concentration gradient distribution at any particular time during the unsteady state diffusion process. The diffusion coefficient, 'D', can be calculated as a function of concentration from the shape of either or both curves (the concentration distribution and/or the concentration gradient distribution) at a given time. Such a method should be considered if a serious long-range study of a molecular diffusion process is planned. However, the apparatus is large, expensive and difficult to construct, and it is only useful for systems whose species have significantly different refractive indices.

3. Refractive Index Profile

The interferometric methods are based on a phase difference due to different propagation rates of light. Phase difference is detected by interference of one wave with another wave, which may be a reference beam or another part of the same beam. The interference fringes formed in this way permit a precise determination of the shape of refractive index gradient curve. So the diffusion in an infinite geometry is best studied interferometrically.

The binary concentration profile, with constant diffusion coefficient and constant partial specific volume assumed, is

$$\frac{C_A - C_{Ao}}{C_{A\infty} - C_{Ao}} = \operatorname{erf} \frac{Z}{\sqrt{4D_{AB}t}} \tag{2.9}$$

This relation applies for "slight solute penetration" into a semi-infinite medium.

If the refractive index is a linear function of composition, that is, $n = R_o C_A + R_1$, then the refractive index profile is

$$\frac{n-n_o}{n_\infty - n_o} = \operatorname{erf} \frac{Z}{\sqrt{4D_{AB}t}} \qquad (2.10)$$

Binary diffusion, which obeys the three assumptions of constant diffusion coefficient, constant partial molar volume and linear concentration dependence of refractive index, is called "ideal" diffusion.

By differentiating the above equation (2.10) with respect to Z, an expression for the refractive index gradient is obtained.

$$\frac{\partial n}{\partial z} = \frac{(n_\infty - n_o)}{\sqrt{\pi D_{AB}t}} \; e^{\frac{-z^2}{4D_{AB}t}} \qquad (2.11)$$

This gradient may be measured by a number of optical systems. Although Svennsson's (28) modification of the Rayleigh interferometer accomplishes this purpose, the outstanding system is the Gouy interferometer (15).

4. Gouy Interferometer

This highly developed optical system is capable of measuring values of the diffusion coefficient to 0.1 per cent. Although the optical theory is complex, it is highly developed (12). The interference fringes formed by the optical systems permits a precise determination of the shape of the refractive index gradient curve. The curve should be symmetrical and have only one maximum. Such symmetrical curves are not obtained for all the systems under consideration but to the author's knowledge this symmetrical nature of the curve of refractive index gradient vs. distance, rather depends upon the time at which the diffusion process is observed.

5. Rayleigh Interferometer

This method produces fringes which have a shape directly proportional to n versus x in the cell. Therefore, from a single experiment on a two-component system, one may obtain the diffusion coefficient and also obtain information about its dependence on concentration. All analyses of data from this method have to be done in terms of n versus x curve, since the refractive index gradient can not be calculated from the integral curve without appreciable loss of accuracy. However, Svensson (27, 28) and Svensson, Forsberg and Lindstrom (29) have developed a modification of the optical system which automatically performs the equivalent of a numerical differentiation of the n versus x curve. Its accuracy is considerably greater than that of the Schliesen and Lamm scale methods but not quite as great as the Gouy and Rayleigh methods.

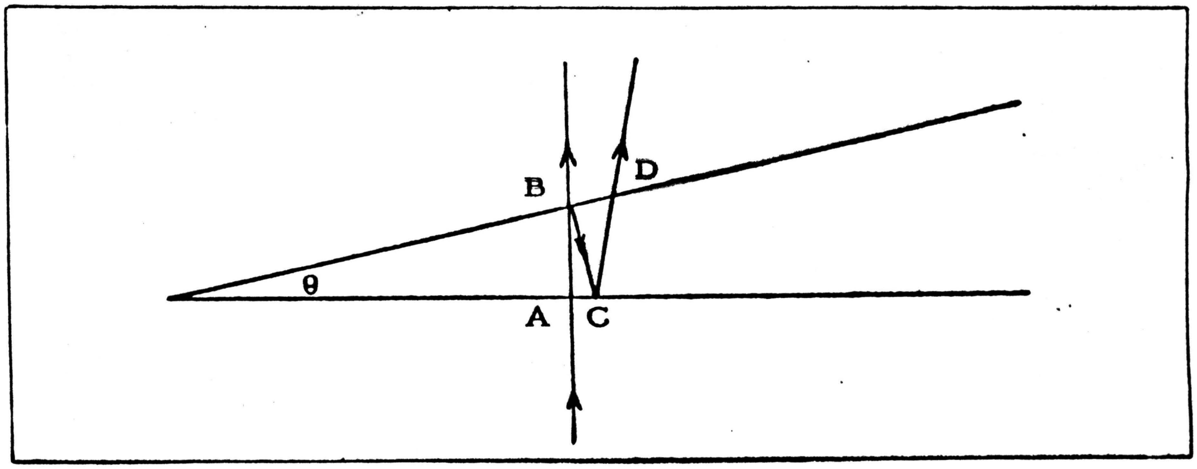
A review of different techniques used in the determination of diffusion coefficients, which are of potential interest for the study of mass transfer in solutions, is given by Muller (16). A number of additional references are also provided.

D. The Optical Wedge Technique

The microinterferometric method used in this work was adapted from the method used for studying concentration profiles around growing crystals (1), for measurements of local viscosities (18), and for the study of diffusion (17). It has also been used successfully by Secor (25) to study the effect of concentrations on diffusion coefficients in polymer solutions.

The diffusion cell consists of a wedge made from two partially metallized, plate glass microscope slides separated by a thin spacer at one end. In order to produce sharper fringes, the slides are partially metallized on one side so that they become partly transmitting and partly reflecting. The monochromatic light passes through the wedge, producing interference fringes that were viewed and photographed through a microscope.

The principle on which the optical wedge works is illustrated in Figure 1. A ray of monochromatic light AB, enters the wedge at point A and is partly transmitted and partly reflected at point B. The reflected ray travels along the path BCD. When the difference in the lengths of the optical paths of the reflected and transmitted rays is an integral number of wave lengths, reinforcement occurs, and a bright fringe is observed. Between the bright fringes formed by this reinforcement, where the paths of the two rays differ by an odd number of half wave lengths, destructive interference occurs and a dark fringe is observed. When a



$$d = \frac{\lambda}{2n\theta}$$

d = Distance between adjacent bright fringes.

n = Refractive Index of medium in wedge.

λ = Wavelength of light.

θ = Wedge angle.

Figure 1. The Optical Wedge

material of constant refractive index is in the wedge, the fringes are parallel and are equally spaced at a distance, d, given by

$$d = \lambda/2\,n\theta \tag{2.12}$$

The wedge angle shown in Figure 1 is greatly exaggerated. Actually, it is very small -- about 20 to 40 minutes of an arc.

The interference pattern has two important characteristics upon which the experimental technique depend:

1. Along any line drawn parallel to the original interface, the distance between any two adjacent fringes is constant; and

2. Along any line drawn perpendicular to the original interface, the change in refractive index between any two adjacent fringes is constant.

From the interference pattern photographed at some time, t, and knowing the refractive index as a function of concentration, the curve of C versus x can be obtained. From this curve, the concentration gradient curve can be obtained and subsequently the diffusion coefficient, D, can be calculated as a function of concentration, C, by the relation

$$D_C = \frac{-\int_0^C x\,dC}{2t\left[\frac{dC}{dx}\right]_C} \tag{2.13}$$

The experimental apparatus, procedure and computation technique are explained in detail in the next section.

The major advantages of using the micronterferometric method (as is done in this thesis) rather than the interferometric method are (1) the former equipment is less expensive; (2) the time required to obtain the data is much less; (3) only microgram amounts of solution are required in this method; (4) the diffusion cell is very thin and so convection currents are not important and hence good temperature control as required in macroscopic apparatus is not essential here provided the ambient temperature can be controlled.

III. EXPERIMENTAL

The purpose of this investigation is to study the effect of solute concentration on the molecular diffusion coefficient in polymer solutions and also to determine the effect of polymer concentration on the molecular diffusion coefficient. For this purpose, water soluble polymers, Carboxymethylcellulose (CMC) and Carboxypolymethylene (Carbopol) were selected. D-Glucose was selected as a solute for both the systems as it dissolved rapidly in polymer solutions and the difference in refractive index between the solute-free solution and solution with solute was large enough so that the interferometric method could be used. The micro-interferometric method was used to measure the diffusion coefficient as a function of concentration. The difference in the index of refraction of the solute-free polymer solution and various solute-polymer solutions was measured as a function of solute concentration over the range of solute concentrations encountered.

The Experimental Chapter is essentially divided into four parts. The first part includes the information about the materials used and the preparation of CMC and Carbopol solutions. The second includes the information concerning the high vacuum system which was used for preparing the partially metallized glass slides. The third describes the experimental procedure, and the fourth deals with the computation technique used.

The experimental apparatus is essentially the same as that used by Dalal (5) in a previous study. In general, only the modifications in technique or equipment which were developed in this work are described here. The reader is referred to the work of Dalal (5) for all other details of the apparatus.

A. Preparation of Solutions

1. CMC Solutions

The polymeric systems used to conduct the study are shown in Table 1.

Five different concentrations of CMC in distilled water were prepared. (Table 1). Initially, CMC in the form of a powder was slowly added to the distilled water in an agitated tank in order to prevent the formation of lumps of polymer. The initial stirring process continued for about 12 to 15 hours. In order to know the relation between the solute concentration and the refractive index, five to six solutions of different but known solute concentrations were prepared. (See Figure 8 for the relationship between index of refraction and solute concentration.) The solutions were then placed in air-tight glass bottles. The solutions having no solute and the solution having highest solute concentration were used for photographing the interference pattern.

CMC used in this investigation was from the batch:

Sodium Carboxymethylcellulose (CMC - 7 HP)
High Viscosity Premium Grade - Lot Number 44077.
Hercules Powder Company.

TABLE 1. POLYMERIC SYSTEMS USED FOR THE STUDY

System No.	Polymer	Solvent	Polymer Concent. Wt.%	Solute	Initial Solute Conc. gm/100 cc Soln.
1	CMC	Water	2.20%	D-Glucose	10.0
2	CMC	Water	2.00%	D-Glucose	10.0
3	CMC	Water	1.70%	D-Glucose	10.0
4	CMC	Water	1.35%	D-Glucose	10.0
5	CMC	Water	1.20%	D-Glucose	10.0
6	Carbopol	Water	0.28%	D-Glucose	10.0
7	Carbopol	Water	0.25%	D-Glucose	10.0
8	Carbopol	Water	0.22%	D-Glucose	10.0
9	Carbopol	Water	0.20%	D-Glucose	10.0
10	Carbopol	Water	0.18%	D-Glucose	10.0

2. Carbopol Solutions

Five different concentrations of Carboxypolymethylene (Carbopol) in distilled water were prepared. (Table 1). According to a letter of instruction from the B. F. Goodrich Chemical Company, it was necessary to add 0.42 parts of sodium hydroxide per part of Carbopol (by weight). The sodium hydroxide was added in the form of 10% aqueous solutions. Five solutions of different solute concentrations were prepared.

Carbopol used in this investigation was from the batch:

Carboxypolymethylene (Carbopol 934)
Commercial Grade. Lot Number 125.
B. F. Goodrich Company.

Additives for preparing the polymer-solute solutions:

1. D-Glucose: Reagent Grade. Molecular weight 198.18 Eastman Organic Chemicals; Distillation products industries. Rochester, New York.
2. Distilled Water: Distilled water was obtained from the Materials Research Center, University of Missouri at Rolla.

B. High Vacuum System for Metallizing the Glass Slides

One of the key items in the experimental apparatus is the ordinary glass microscope slides which were partially metallized on one side. The equipment used to vaporize the metal which coats the glass slides is described here.

The Ultek Model TNB is a compact high vacuum system capable of a wide variety of tasks in the laboratory, plant or classroom. The complete operating procedure for creating the high vacuum by this Ultek Model TNB is given in reference (32). Only the main points of interest are discussed here.

1. Rough Pumping

Some three or four pieces of either aluminum or platinum foil of size 1 mm. x 8 mm. were allowed to hang on the tungsten wire of the vaporizer and the whole assembly was then covered with a bell jar. The tungsten wire of about 1 mm. to 1.5 mm. diameter was used for aluminum vaporization while about 2.5 mm. to 3.0 mm. diameter was used for platinum vaporization. The complete assembly under the bell jar with other accessories is shown in Figure 2.

In order to start the "ion-getter" pump it was necessary to reduce the system pressure to less than 10 microns (10^{-2} Torr*) This was accomplished with a roughing system which connects to the Ultek Model 40-141 one inch below the sealed roughing valve. This generally took one to two hours depending upon the cleanliness of the system. The whole system was kept at this pressure for at least three to four hours before the high vacuum pumping was started.

2. High Vacuum Pumping

An "ion getter" pump was used for pumping the work volume to a pressure below 5×10^{-9} Torr. The nominal 50 litres per second ion pump was used to pump the noble gases in the system, and the titanium sublimation or "gettering" pump was used for the "getterable" gases. In long-term operations after initial wall "out-gassing", the ion pump above was

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* 1 Torr = 760 mm. of Hg.

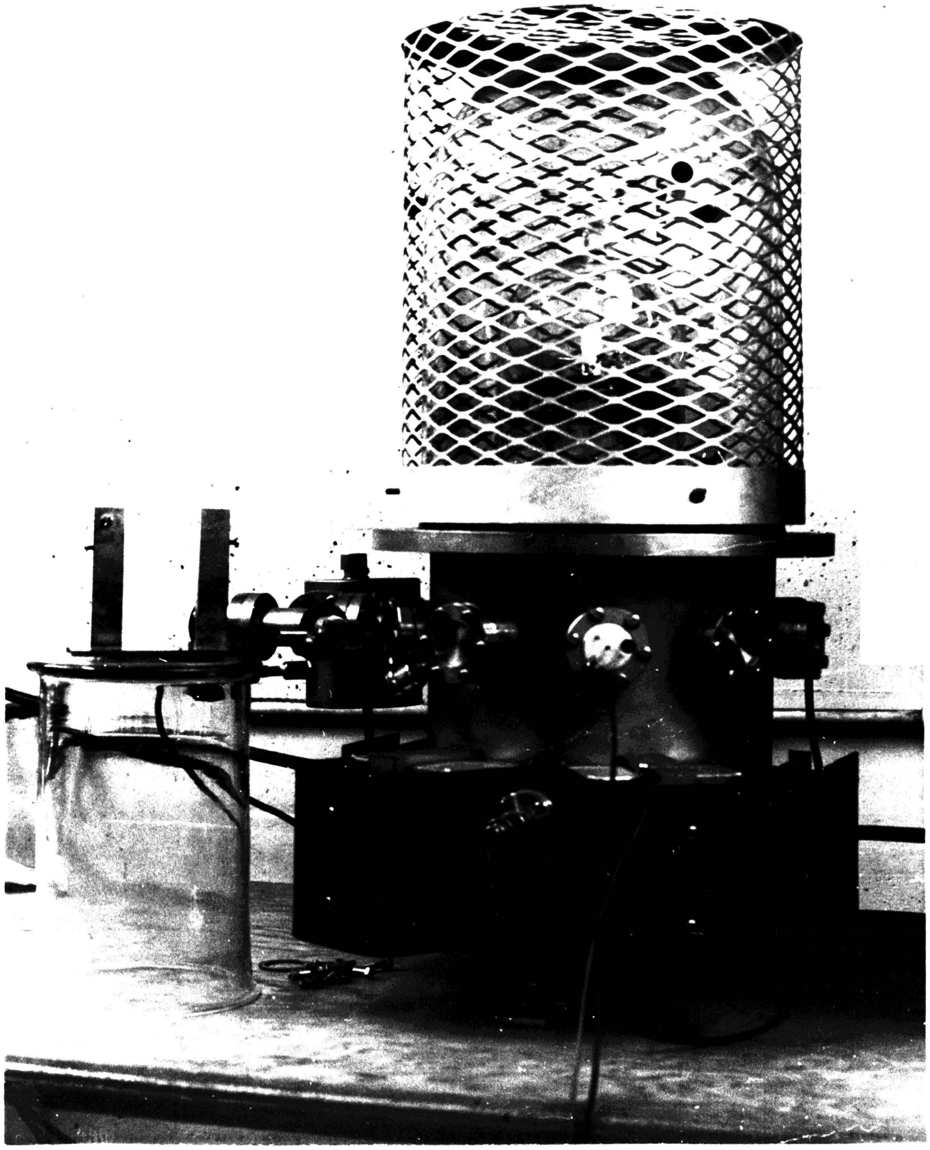


Figure 2. Ultek Model TNB High Vacuum System

satisfactory for maintaining a test pressure condition.

Generally a vacuum of 5×10^{-7} Torr is sufficient for metallizing the glass slides with aluminum, but a higher vacuum of 10^{-8} to -10^{-9} Torr is required for metallizing the glass slides with platinum. This will be discussed later in this work.

3. System Power Unit

An Ultek power unit, model 60-655 was used to power the ion pump and sublimator. This power unit provides both high current at low voltage and high voltage at low current for operation. The sublimator portion of the power supply has a filament current meter and variable transformer for accurate power settings. After creating the high vacuum for evaporating aluminum, generally 30 to 35 amperes evaporator power supply was used. For evaporating platinum, a higher evaporator power supply of 80 to 85 amperes was used. This choice of current depends entirely upon the type of metallic coating required and vacuum created inside the system.

The tungsten wire on which the foil of platinum or aluminum rests is very brittle. After every two platinum coating runs, this tungsten wire was necessarily replaced, as the higher power supply of about 80-85 amperes was used for platinum coating. The purity of platinum foil used in this work was high. For aluminum foil, ordinary available "Reynolds Wrap" was used.

C. Experimental Procedure

Diffusion coefficients for the polymeric systems under consideration were determined at constant temperature by the microinterferometric method. As mentioned earlier, the operating details of the apparatus are given in reference (5).

Here the diffusion cell consists of a wedge formed by two partially metallized glass microscope slides separated by a spacer at one end. The solutions with and without solute are brought into contact in this wedge. Light rays passing through the liquid in this wedge, in a direction perpendicular to the slides, produce interference fringes. These fringes were parallel to each other if there was only one liquid of uniform solute concentration in the wedge. Whenever there were two liquids brought into contact in the wedge, and if a concentration gradient existed between them, the fringes are distorted. (See for example, Figure 5.) Measurement of the distortion of the fringes provided a means for calculating the diffusion coefficient 'D' and for determining its dependence upon the concentration 'C_A' of the solute.

1. The Photograph of Interference Fringes

Method: A polymer solution of known concentration and refractive index was placed on the lower slide in the form of an elongated strip, approximately parallel to the long dimension of the slide. Two cover glasses were placed as a spacer on one end of the slide. The upper slide of the wedge was then lowered to obtain contact with the polymer solutions so that the metallized surfaces of both the slides

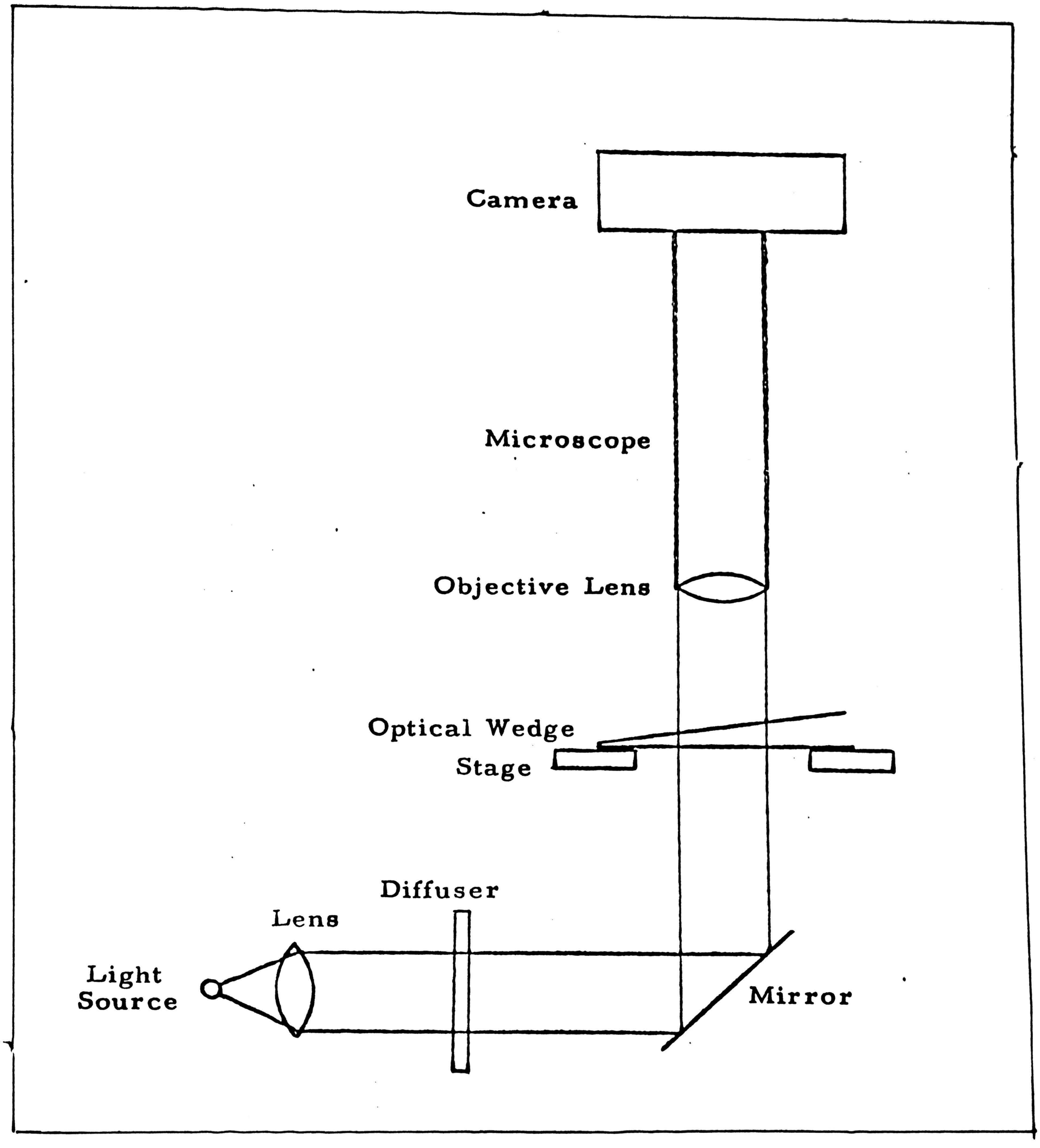


Figure 3. Schematic Drawing of Experimental Apparatus

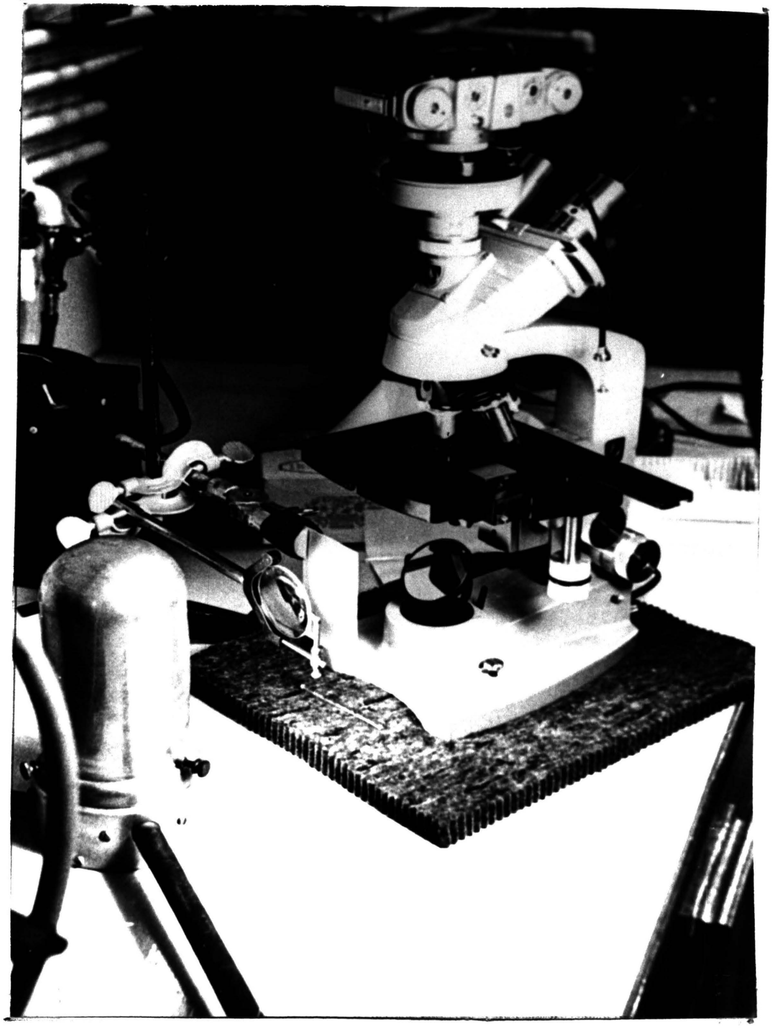


Figure 4. Experimental Apparatus Assembly

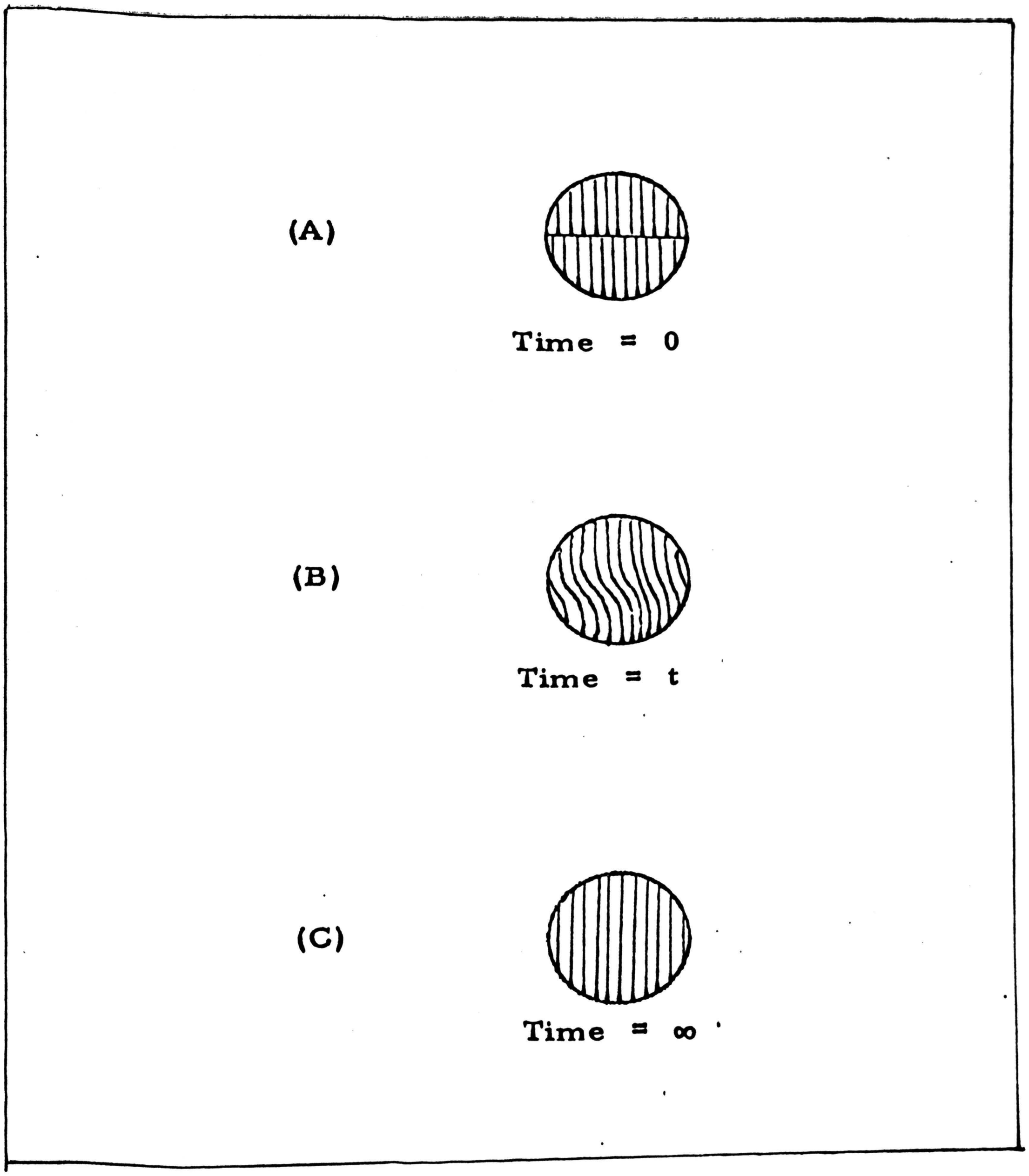


Figure 5. Light Interference Patterns Observed During a Diffusion Experiment

Figure 6. Experimental Interference Pattern at t=20 Seconds for System 3, 1.7 wt.% CMC in Water

Figure 7. Experimental Interference Pattern at t=20 Seconds for System 9, 0.20 wt.% Carbopol in Water

were then in contact with the solute-polymer solution. A set of parallel vertical interference fringes were observed through the microscope. The interface between the polymer solution and the surrounding air was then scanned through the microscope to find a region where the interface was perpendicular to the interference fringes. In case such a region could not be found a new set of slides was prepared and the whole procedure repeated.

After a suitable interface was obtained and brought into focus, a drop of solute-free polymer solution was placed in contact with the side of the wedge. The drop of the solution was immediately drawn in by surface tension forces and as it came into contact with the solute-polymer solution the diffusion began. At this point, the stopwatch was actuated, thereby measuring the elapsed time from the beginning of the diffusion process. By photographing the interference pattern at some known time, 't', after "sufficient" diffusion had occurred, it was possible to obtain the concentration-distance profile. (See Figure 9.) The time and temperature at which the diffusion process occurred were noted very accurately for each system. The precision of the stopwatch having a Fisher Watch Guard is 1/10 of a second. A ruled microscale slide was also photographed through the microscope at the same magnification in order to provide a distance scale for measuring the actual distances between the fringes on the interference pattern. The overall dimension of the microscale was 2.0 mm. This scale was divided into 20 equal parts, each part being further subdivided into 10 equal parts, thus providing an accuracy of 0.01 mm. on the interference pattern. Typical photographs of interference patterns are shown in Figures 6 and 7 for the systems 3 and 9.

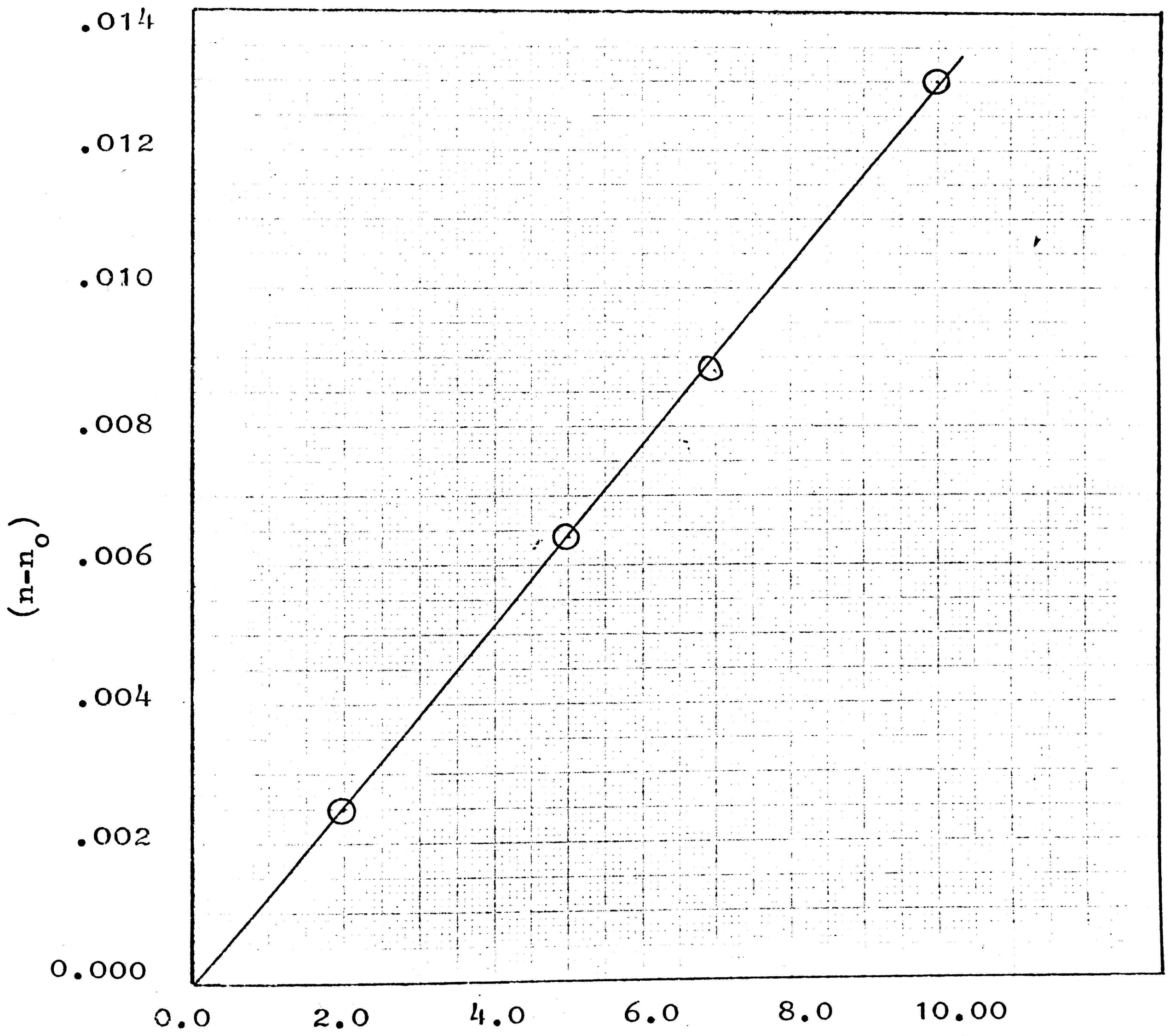
2. Measurement of Solute Concentration

The refractive index-concentration relationship was obtained by making measurements of a series of polymer solutions with known solute concentration using an Abbe Spencer refractometer. The index of refraction using an Abbe Spencer refractometer could be determined to ±.0001, whereas with the Precision Abbe refractometer it could be determined to within ±.00003. The Precision Abbe refractometer was not available, however, until after all the measurements were made with the Abbe Spencer refractometer. However, the difference in the readings obtained by Abbe Spencer refractometer and Precision Abbe refractometer was determined. It was found that the difference in the readings obtained for a polymer solution by Abbe Spencer refractometer and Precision Abbe refractometer was .001445. In this study, one was mainly concerned with the difference of index of refraction between the solute-free polymer solution and solute-polymer solution, and this difference is the same regardless of which refractometer was used. Therefore, the measurements were not repeated with the Precision Abbe refractometer.

3. Procedure for Measuring the Experimental Interference

In the previous study (5), all the photographs of interference patterns were taken using a magnification power of 10X. For measuring the distances between the points of intersection where the straight line cuts the interference fringes, a microscale (magnified by the same amount as the interference pattern) was used. A straight line was drawn in such a way that it was parallel to the fringes at one end and perpendicular to the interface. The procedure for drawing such straight line on the photograph of interference pattern has been fully described in (5). In this previously used technique it is difficult to locate the point where the straight line cuts the interference fringes because the fringes obtained are not very distinct. Therefore, in this work a magnification of 3.5X was used in order to get sharp interference fringes. At this magnfication the distance between the points of intersection where the straight line cuts the interference fringes is very small (as compared with 10X magnification) and can not be measured accurately by the use of a microscale magnified by the same amount as the interference pattern. In order to avoid this difficulty, a Cathetometer which mangifies the distance between the points of intersection of fringes was used.

The Cathetometer is levelled by means of the three large knurled head screws in the base, using a centering level placed in the base for this purpose. The photograph of the interference pattern is then fixed on a drawing-board and kept perpendicular to the plane of the table. The telescope can be focused by loosening the set screws



Concentration, gm. D-Glucose/100 cc. Solution

Figure 8. Refractive Index (Sodium D-line) of Solutions of 0.28 wt.% Carbopol in Water with D-Glucose as a Solute, at 73°F

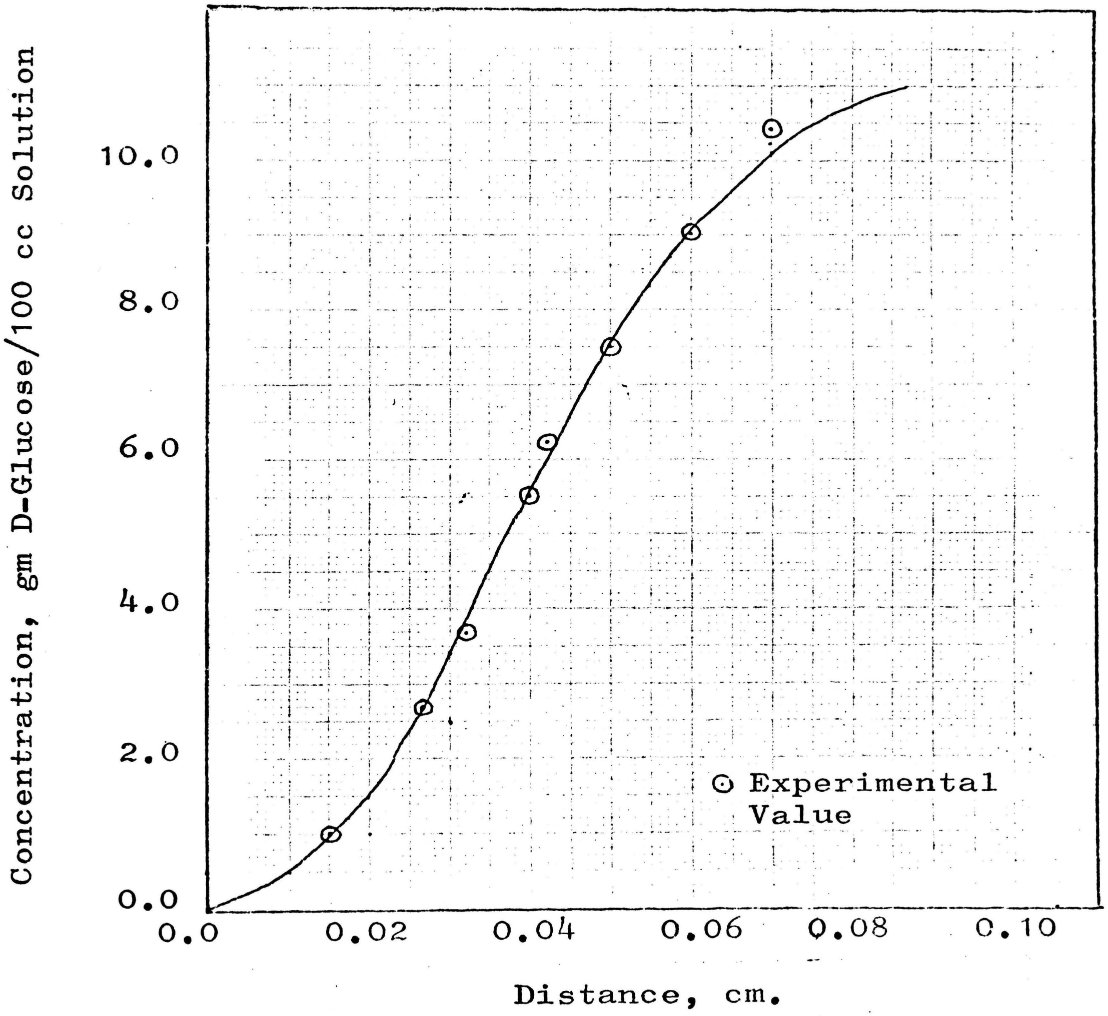


Figure 9. Experimental Concentration Profile for 0.20 wt.% Carbopol System

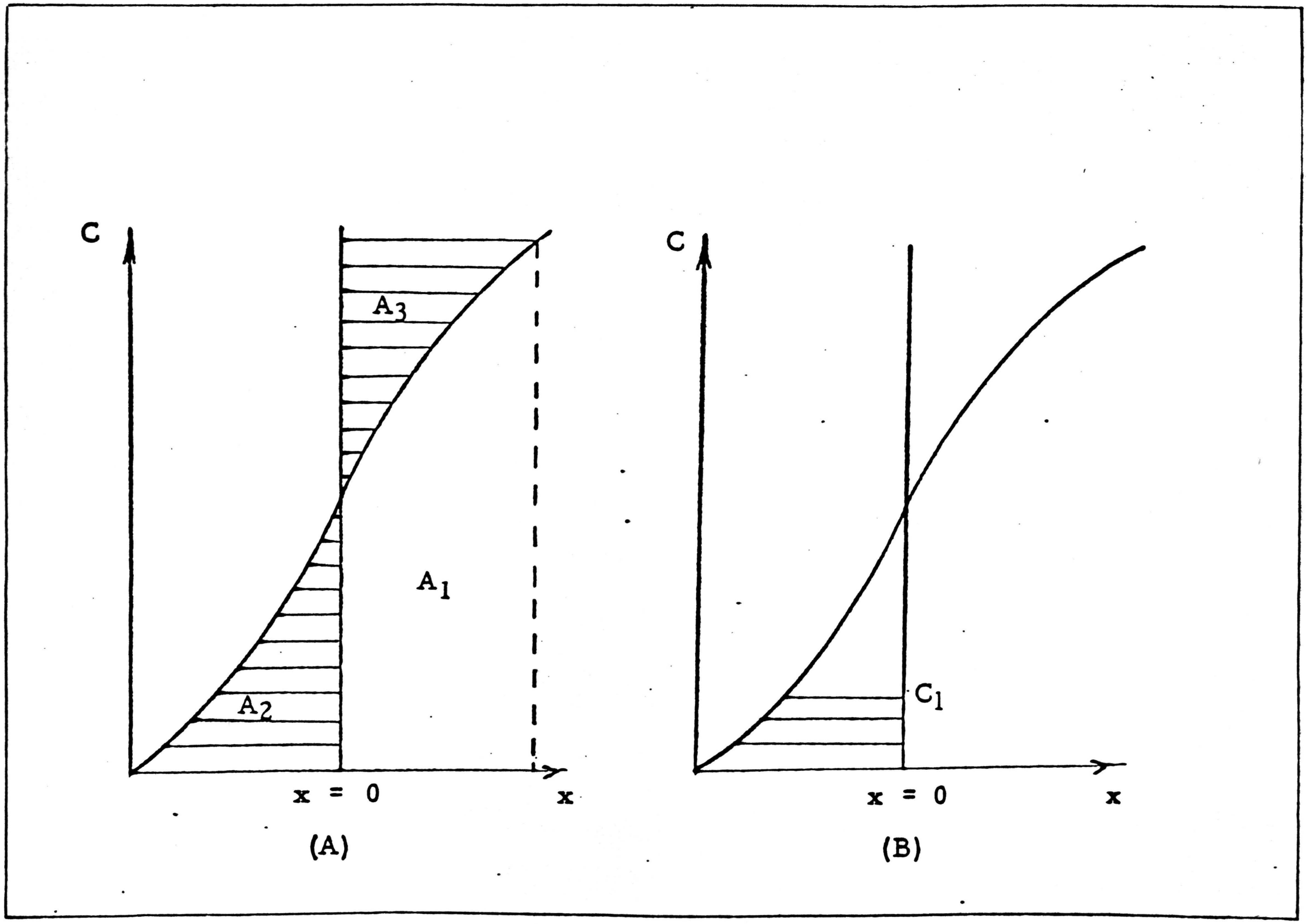


Figure 10. Evaluation of $\int_0^C x \, dc$

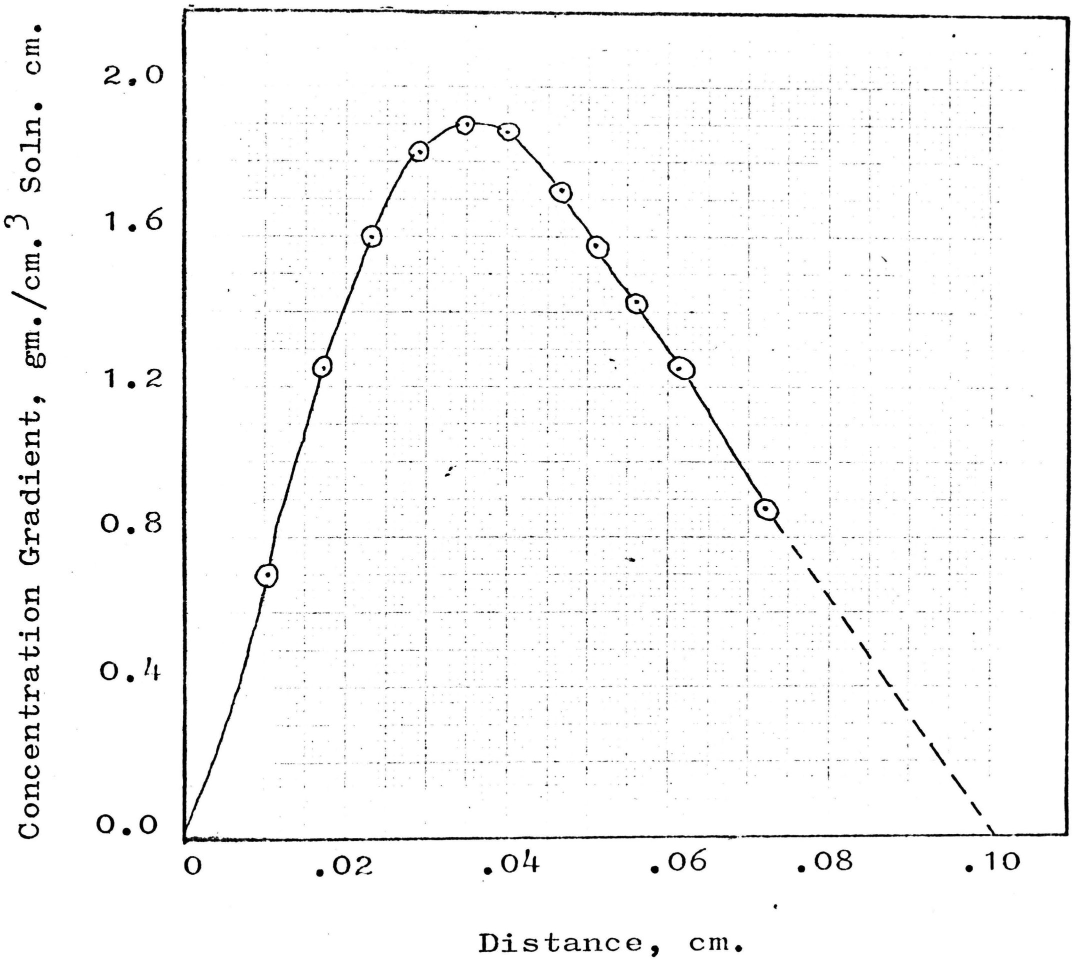


Figure 11. Experimental Concentration Gradient as a Function of Distance for System 6, 0.28 wt.% Carbopol.

on the eye piece, moving the eye piece in or out as required and resetting the set screw until the parallax between the point on the photograph and cross-wise of the eye-piece is removed. For each point of intersection where the straight line cuts the interference fringes, the scale reading with its vernier adjustment was recorded. Similarly for the photograph of the microscale, the scale reading with its vernier adjustment was recorded. With the help of these readings, the actual distance between the successive fringes was calculated. These distances were then used to draw the curve of concentration vs. distance.

D. Computation Techniques

The following equation was used to evaluate the molecular diffusivity of the polymeric system under consideration:

$$D_c = \frac{-\int_o^c x\,dc}{2t\left[\frac{dc}{dx}\right]_c} \qquad (3.1)$$

where D_c is the molecular diffusivity at a solute concentration c. The detailed derivation of the above equation is given in Appendix A.

1. The Modified Gompertz Equation

The nature of concentration vs. distance curve is sigmoid. (Figure 9). The curve is characterized by a very small initial slope followed by a period of rapidly increasing slope, which then gives way to an interval of nearly constant slope, followed by a rapidly decreasing slope as it approaches zero. The modified Gompertz Equation

$$y = \alpha + ab^{c^{x}} \tag{3.2}$$

has been found to be satisfactory in representing such data (6). One method for determining the constants in the above equation requires that the independent variable be selected at equal intervals. In the previous study by Dalal (5), an equal interval of independent variable x = 0.010 cm. was used. In order to have more points for drawing the graph of concentration vs. distance, an equal interval of the independent variable x = 0.005 cm. was used in this work. The distance between the two successive fringes was found to be between .013 cm. to .017 cm. The complete derivation for evaluating the constants of the modified Gompertz Equation is given in reference (6). Some of the details are given here.

The data were divided into three parts of n entries each. S_1, S_2 and S_3 are the sums of the three groups of values of log y, starting with the lowest values. The ceiling value of y is $(a + \alpha)$ for the modified Gompertz Equation, constants a, b, and c can be evaluated from the following equations:

$$c = \left[\frac{S_2 - S_3}{S_1 - S_2}\right]^{\frac{1}{n}} \tag{3.3}$$

$$\log a = \frac{1}{n}\left[S_1 - \frac{S_1 - S_2}{1 - c^n}\right] \tag{3.4}$$

$$\log b = \frac{(S_1 - S_2)(1 - c)}{(1 - c^n)^2} \tag{3.5}$$

When x is zero and y is neither zero nor small relative to its ceiling value the modified Gompertz equation, with α being the value of y corresponding to x=0, should be used. One then works with log $(y-\alpha)$ in place of log y and the constants are determined as before. The computer program for evaluating the constants of the modified Gompertz Equation is given in Appendix B.

2. Evaluation of Integral

After the Gompertz Equation was obtained, the location of the original interface, i.e., a locus of x=0, was obtained. Simpson's numerical method was used to evaluate the areas A_1 and A_2 at a distance x=x' as shown in Figure 10. Area A_3 was then evaluated and compared with A_2. If these were unequal, then another value of x' was specified, $(x'_i = x'_{i-1} + \Delta x)$ depending on which area is large or small. This trial and error procedure was followed until the percentage deviation obtained was less than 0.8, where the percentage deviation is defined as follows:

$$\text{Percentage Deviation} = \frac{A_2 - A_3}{A_2} \times 100$$

In other words, the absolute value of $\frac{A_2 - A_3}{A_2}$ should be less than 8×10^{-3} for all the systems at a final value of x'. This very closely satisfied the requirement that

$$-\int_0^{c'} x\,dc = \int_{c'}^{c_0} x\,dc \qquad (3.6)$$

and the line of original interface was obtained (4).

The integral in the equation (3.1) can not be determined analytically because of the complicated nature of the modified Gompertz equation (6). It was therefore evaluated by numerical integration of the concentration-distance relation given by the Gompertz equation fit of the experimental data. Simpson's numerical method was used for this purpose.

3. Evaluation of Concentration Gradient

The derivative $\frac{dc}{dx}$ was obtained by simply differentiating the Gompertz Equation (3.2).

$$y = \alpha + a_1 a_2^{a_3^x} .$$

$$\frac{dy}{dx} = (a_1 a_2^{a_3^x}) \; (\ln a_2) \; a_3^x \; (\ln a_3) \qquad (3.7)$$

In this work, the concentration gradients for all the systems were evaluated using equation (3.7).

In the previous study by Dalal (5), the modified Gompertz Equation was used to evaluate the value of the integral. For evaluating the concentration gradient, the "Davis method" was followed. Details of this Davis method are fully described in reference (6). Some of the details are given here. Sigmoid curves, both normal and skewed can also be fitted by the equation

$$\phi = \frac{x-x_1}{a+bx} \qquad (3.8)$$

where

$$\phi = \log \frac{20y}{\log(100-y)} \qquad (3.9)$$

x_1 corresponds to $y = 0.1$, and a and b are the intercept and slope respectively, of the straight line that results when $\frac{x-x_1}{\phi}$ is plotted against x. On differentiation of the above equation (3.8),

$$\frac{dy}{dx} = \frac{a+bx_1}{(a+bx)^2 s} \tag{3.10}$$

is obtained where,

$$s = 0.4343 \frac{1}{y} + \frac{0.4343}{(100-y) \log(100-y)} \tag{3.11}$$

For evaluating the concentration gradient the modified Gompertz Equation (equation no. 3.7) was used. The reason for using equation (3.7) rather than equation (3.10) is fully described in Chapter IV.

A comparison of the concentration gradients obtained by the above two methods is given in Table 14 for a typical system number (2), for CMC .

After the above calculations for the concentration gradient were performed, the diffusion coefficient D_c was obtained as a function of solute concentration, c, by appropriate substitution in equation (3.1).

4. Data and Results

The data taken and the results obtained by performing the calculations shown above are presented in Appendix C.

The differences in the index of refraction of solute-polymer solution and solute-free polymer solution were initially observed as a function of solute concentration. A curve of difference of the refractive index of the solute-free polymer solution and the solute polymer solution as a function of solute concentration was obtained for each system. The form of the curves for all the systems studied is an essentially straight line. For each system under consideration, the slopes of the lines were determined in order to obtain the value of refractive index corresponding to the value of concentration obtained from the modified Gompertz Equation. The constants of the modified Gompertz Equation were determined for each system and subsequently used to evaluate the solute concentration corresponding to the observed distances on the photograph. The procedure was similar to that followed in the previous study by Dalal (5).

IV. DISCUSSION

A microinterferometric method of determining the molecular diffusivity was used to determine the effect of solute concentration on the molecular diffusivity in polymer solutions and also to determine the effect of polymer concentration on the molecular diffusivity. For this purpose Carboxymethylcellulose (CMC) and Carboxypolymethylene (Carbopol), water soluble, non-ionic polymers were used. D-Glucose was used as a solute for both the systems. In the previous study by Dalal (5), the water soluble, non-ionic polymer hydroxyethylcellulose (Natrosol) was used and Urea and D-Glucose were used as solutes.

A. Effect of Solute Concentration

The plots of differential diffusion coefficient versus solute concentration are shown in Figures 12 to 23. It was found that as the concentration of solute was increased there was a marked increase in the diffusivity of that system. This increase in molecular diffusivity is particularly significant for the higher solute concentration.

1. Viscosity

In order to measure the viscosity of these solutions, an Ostwald type capillary flow viscometer was used. It has been observed that for these low polymer concentrations and flow rates the rate of shear is very low. It is assumed that these polymer solutions behave as Newtonian fluids under these conditions. The viscosity of the solute-free, 1.2 wt.% CMC polymer solution at 23°C. was found to be 635 centipoise, and the viscosity of the solute-free 0.18 wt.% Carbopol polymer solution at 23°C. was found to be 819 centipoise. These were the least viscous solutions of the two different polymer systems. The viscosities of the most highly viscous polymer solutions of 2.2 wt.% CMC and 0.28 wt.% Carbopol were also measured. It was found that at 23°C. the viscosity of the solute-free 2.2 wt.% CMC solution was about 9840 centipoise and the viscosity of the solute-free 0.18 wt.% Carbopol solution was about 17980 centipoise. In this study the range of viscosity available for the CMC system was from 635 centipoise to 9840 centipoise, and the range of viscosity available for the Carbopol system was from 819 centipoise to 17980 centipoise. For systems with viscosities significantly outside these ranges, the micro-interferometric method could not be used.

2. Prediction of the Differential Diffusion Coefficient from the Wilke-Chang Correlation

For predicting the differential diffusivity of a solute at very low solute concentration using the Wilke-Chang correlation, the viscosity of the solvent (pure water) rather than that of the solution at that temperature was used. The value of the differential diffusion coefficient of D-Glucose in water at 23°C. using Wilke-Change equation is 0.71×10^{-5} cm.^{2}/sec., and at 21°C. it is 0.67×10^{-5} cm.^{2}/sec. as calculated in Appendix E. If the viscosity of low concentration solute-free 1.2 wt.% CMC solution and 0.18 wt.% Carbopol solutions (635 and 819 centipoise) were used in predicting the differential diffusion coefficient of a solute in polymer solutions using the Wilke-Chang equation, the value obtained might be about 650-800 times less than the values obtained above.

In the previous study by Dalal (5), for very low solute (D-Glucose) concentrations in aqueous Natrosol solution the differential diffusion coefficient was found experimentally to be in the range of 0.50×10^{-5} cm.^{2}/sec. to 0.85×10^{-5} cm.^{2}/sec. The Wilke-Chang value was 0.67×10^{-5} cm.^{2}/sec.

It can be said that for the systems studied in this work the Wilke-Chang correlation may approximately predict the differential diffusivity of the solute at very low solute concentrations in the polymer solutions using the viscosity of the solvent rather than that of the solution. This observation can not be extended to the situations in which diffusion occurs simultaneously with fluid flow, since all of the experiments in this work were performed under conditions of zero fluid shear rate.

3. Results

For 2.0 wt.% CMC system, the curve of differential diffusion coefficient vs. solute concentration is flat between the solute concentration of 2 gm/100 cc to 7 gm/100 cc. The flattening of the curve is also observed for the 1.2 wt.% CMC system, between the solute concentration of 3.5 gm/100 cc to 5.5 gm/100 cc. There is a marked increase in differential diffusion coefficient for solute concentrations greater than 5.5 gm/100 cc.

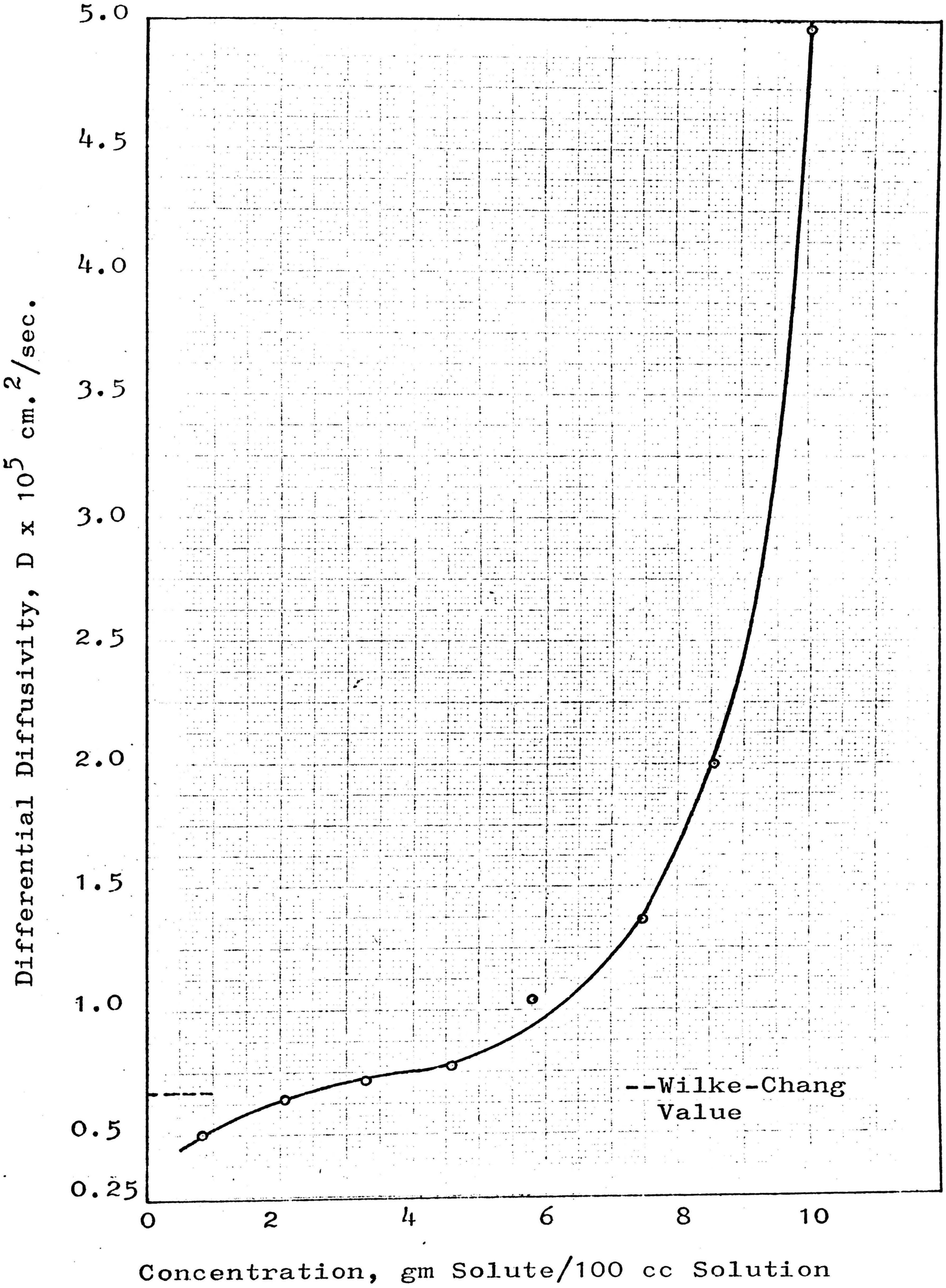


Figure 12. Differential Diffusivity Versus Concentration for 2.2 wt.% CMC in Water with D-Glucose as Solute, at 73°F, with t=12 Seconds

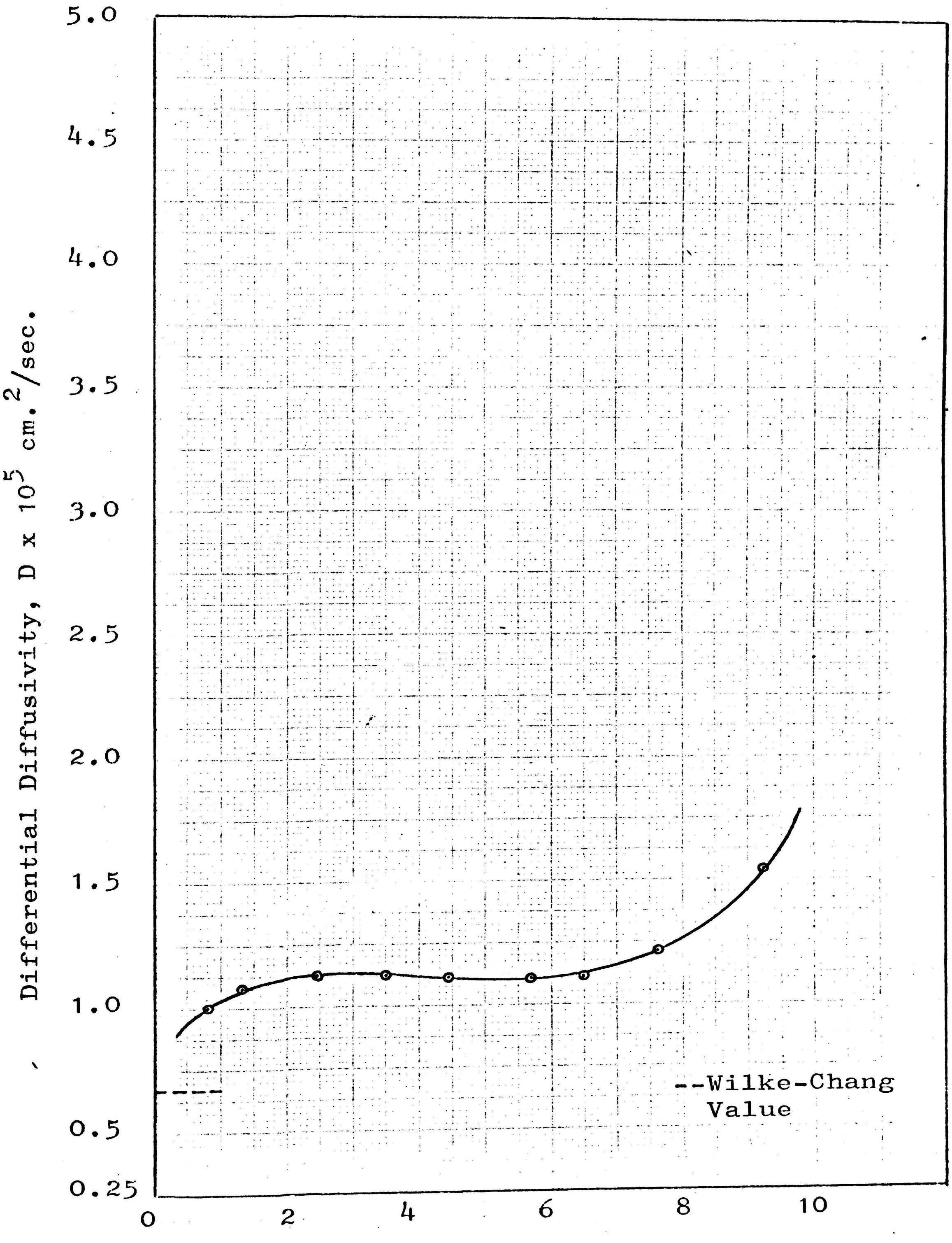


Figure 13. Differential Diffusivity Versus Concentration for 2.0 wt.% CMC in Water with D-Glucose as Solute, at 73°F with t=50 Seconds.

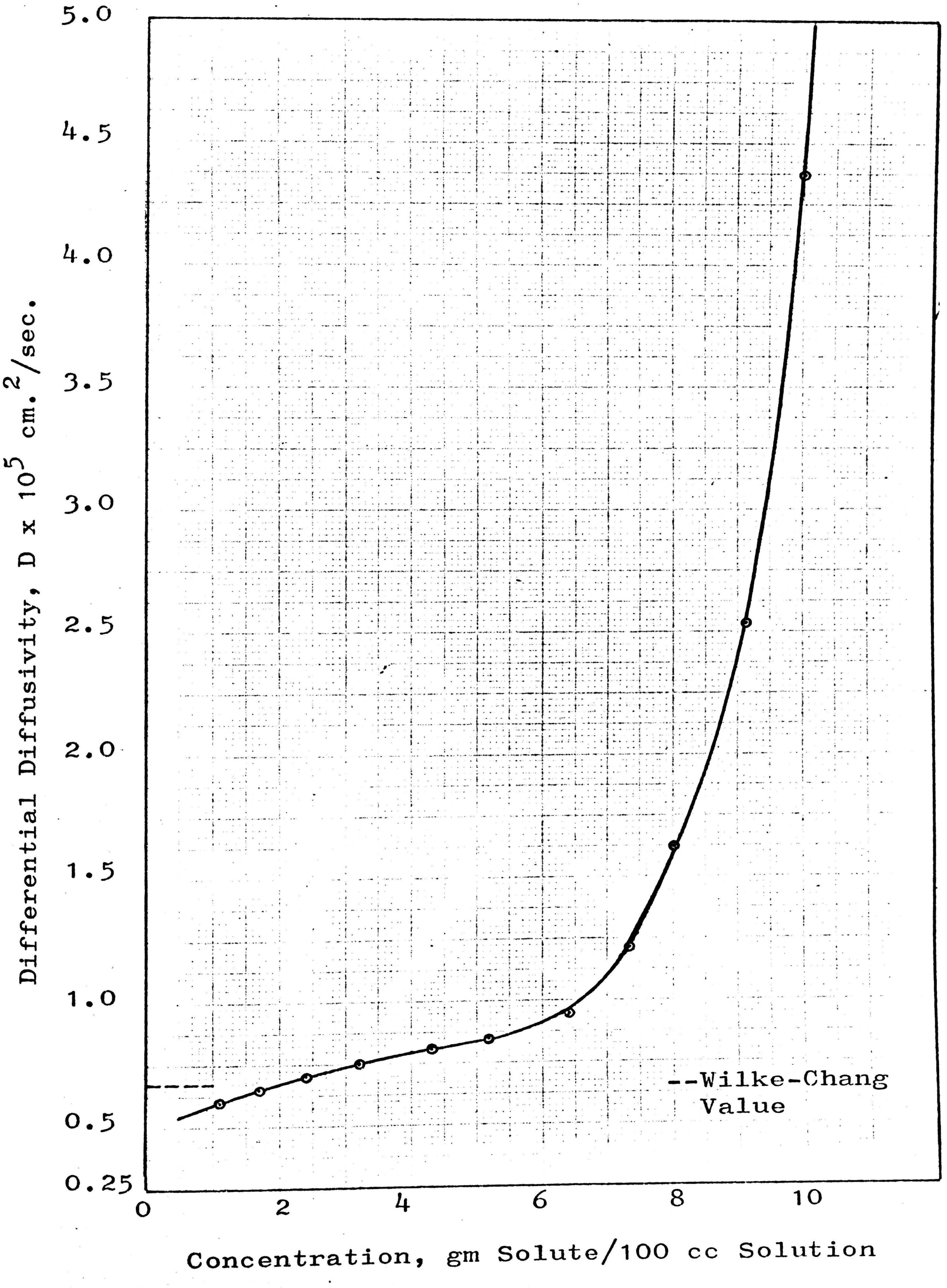


Figure 14. Differential Diffusivity Versus Concentration for 1.7 wt.% CMC in Water with D-Glucose as Solute, at 73°F, with t=20 Seconds

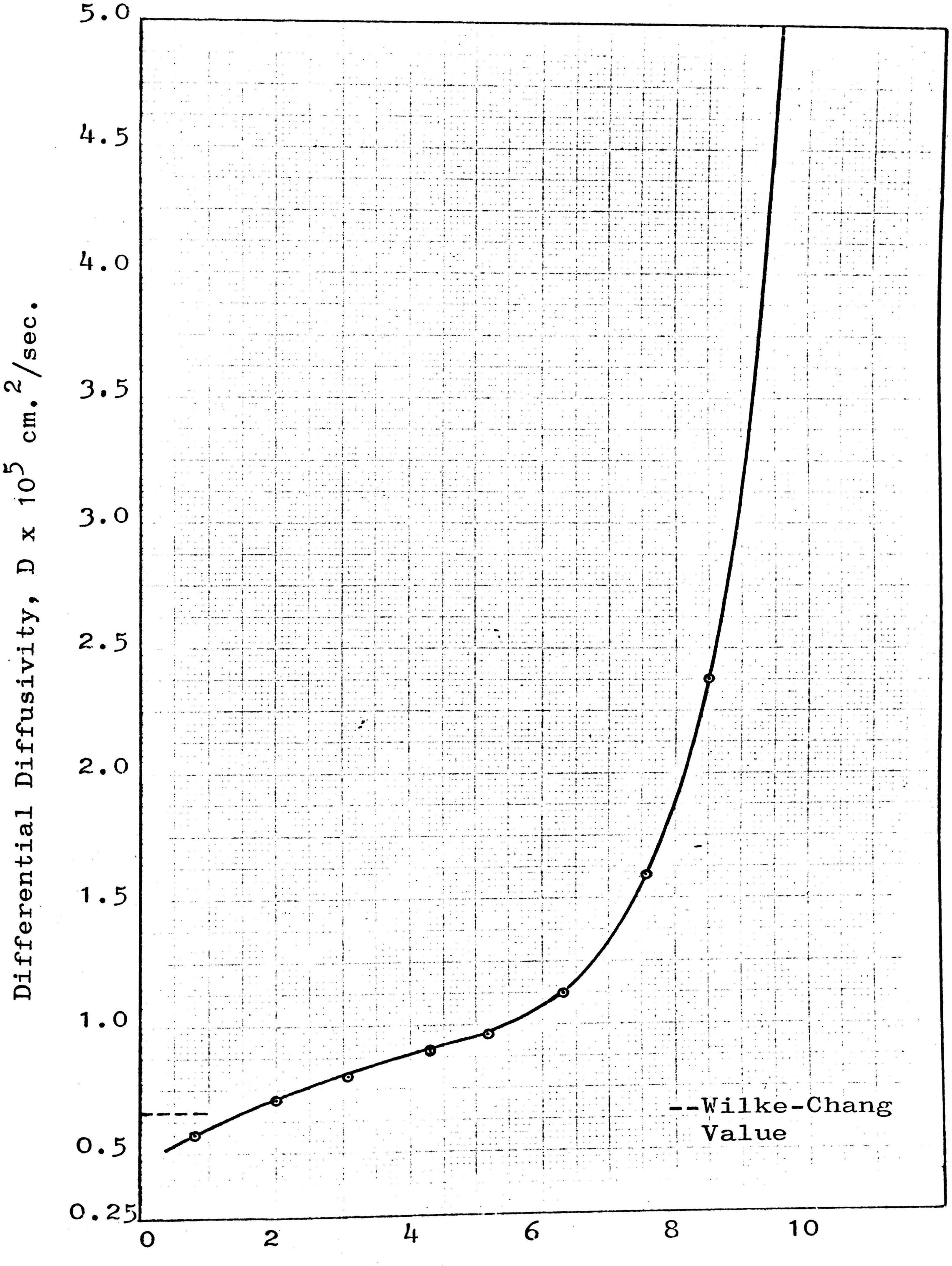


Figure 15. Differential Diffusivity Versus Concentration for 1.35 wt.% CMC in Water with D-Glucose as Solute at 73°F, with t=18 Seconds

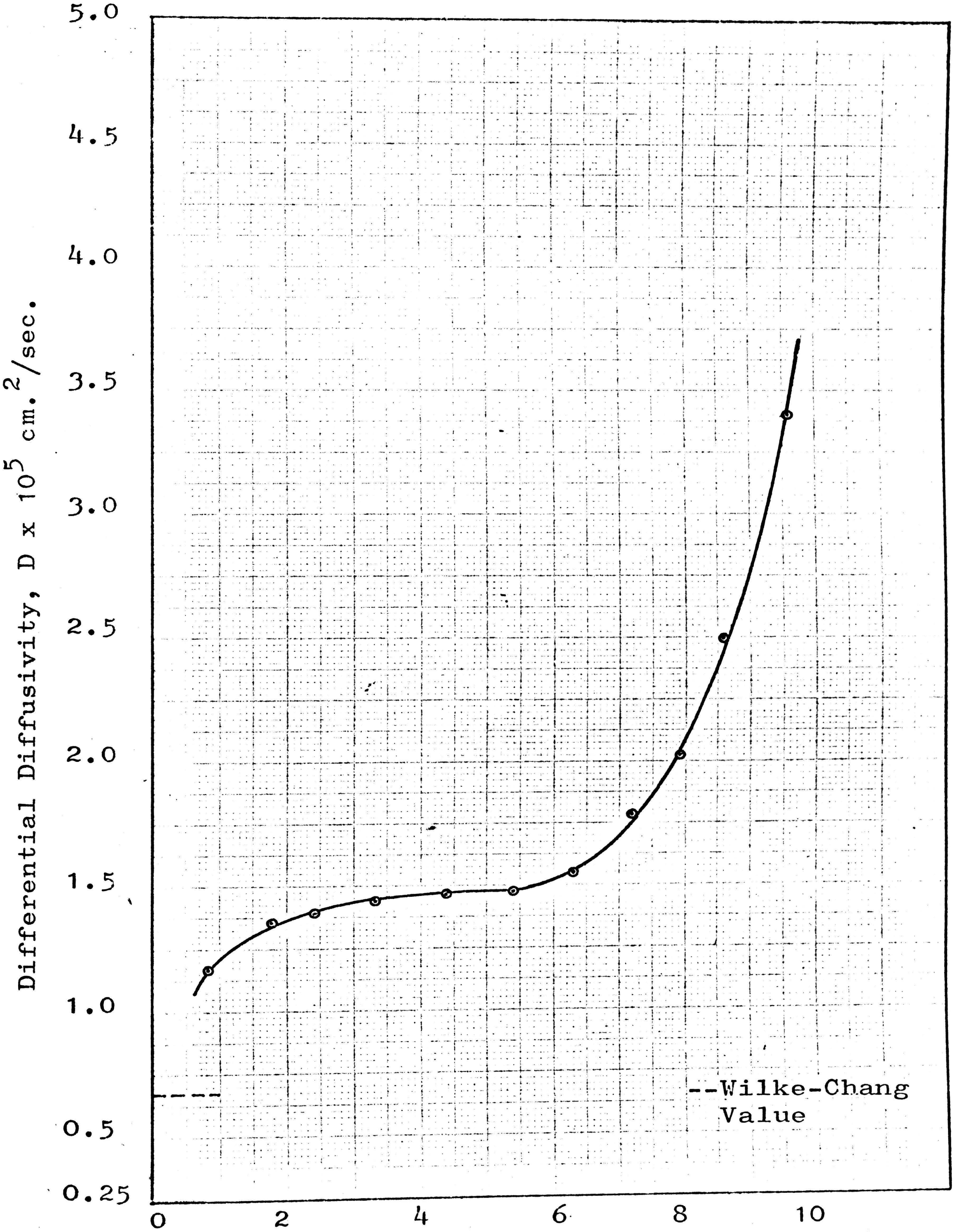


Figure 16. Differential Diffusivity Versus Concentration for 1.20 wt.% CMC in Water with D-Glucose as Solute at 73°F, with t=20 Seconds

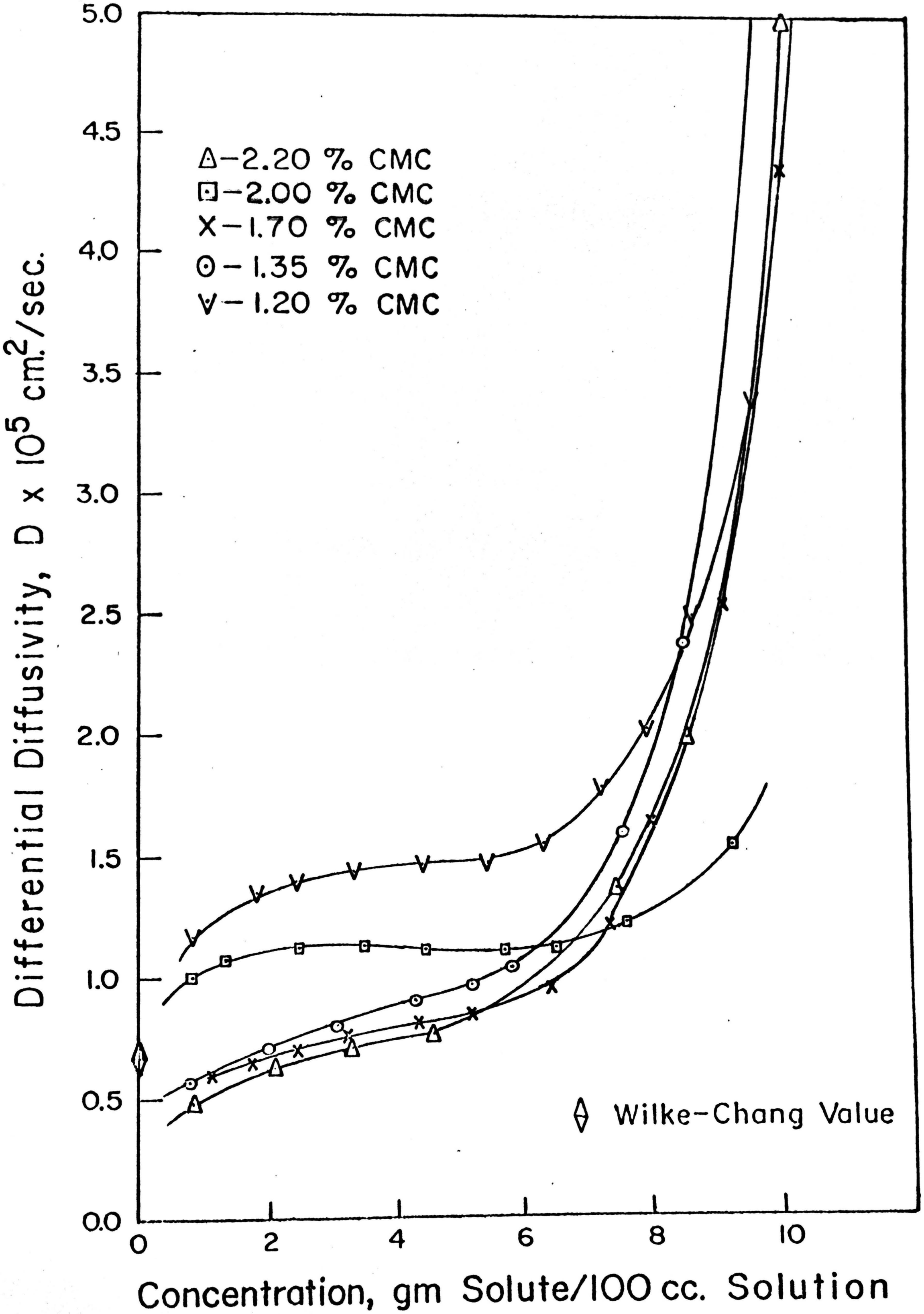


Figure 17. Differential Diffusivity vs. Solute Concentration for CMC-Water System

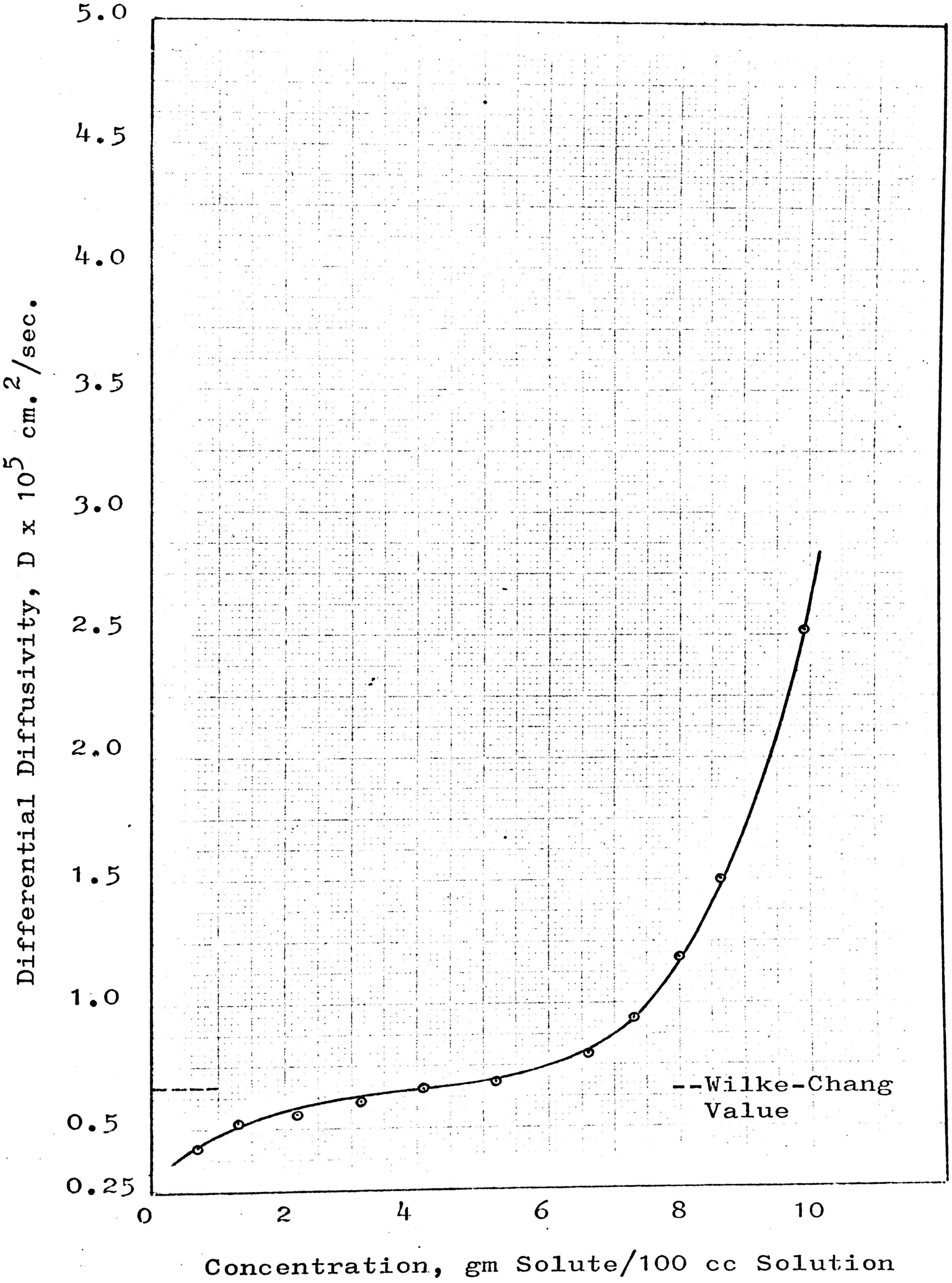


Figure 18. Differential Diffusivity Versus Concentration for 0.28 wt.% Carbopol in Water with D-Glucose as Solute, at 73°F, with t=30 Seconds

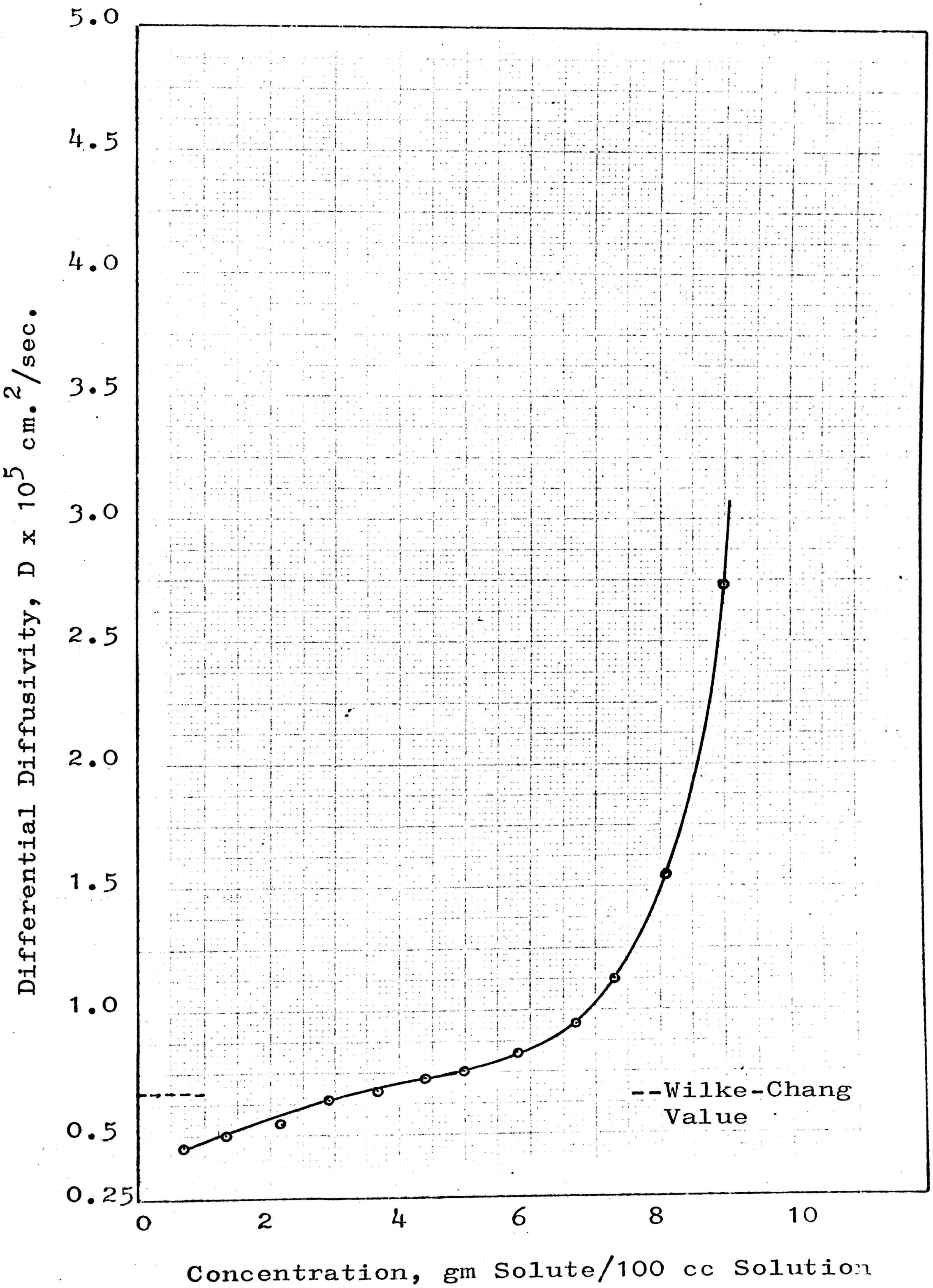


Figure 19. Differential Diffusivity Versus Concentration for 0.25 wt.% Carbopol in Water with D-Glucose as Solute at 70°F, with t=24 Seconds

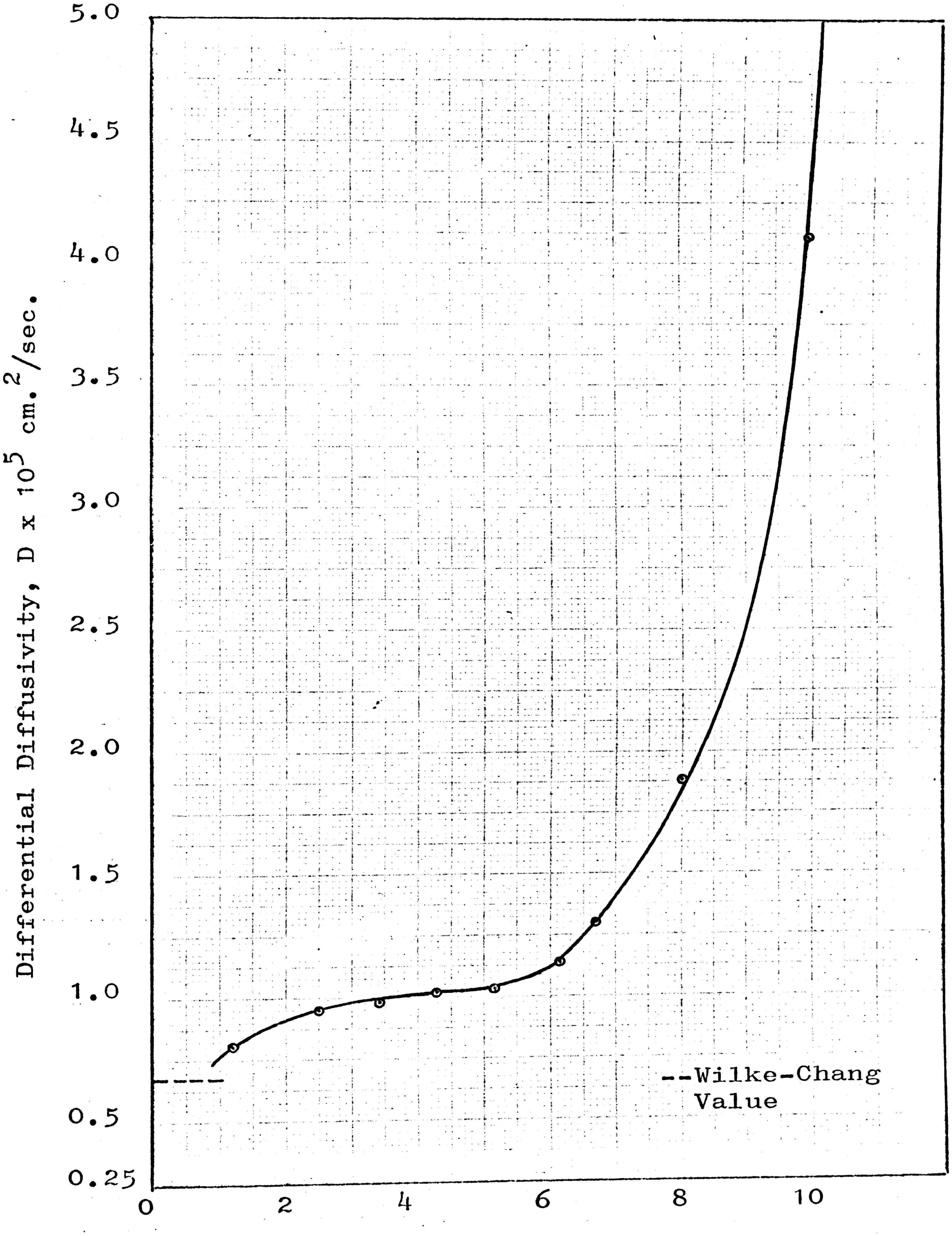


Figure 20. Differential Diffusivity Versus Concentration for 0.22 wt.% Carbopol in Water with D-Glucose as Solute at 70°F, with t=6 Seconds

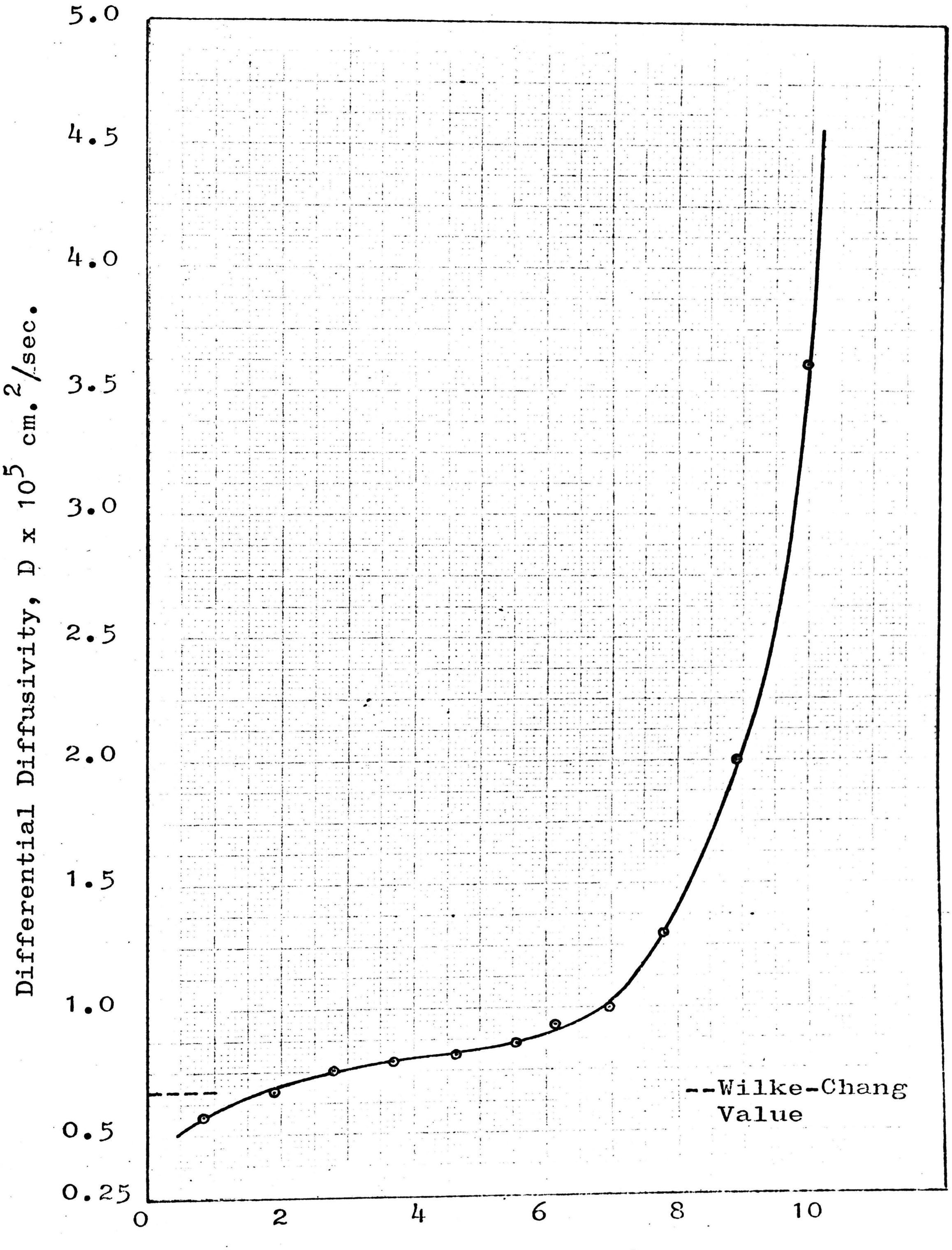


Figure 21. Differential Diffusivity Versus Concentration for 0.20 wt.% Carbopol in Water with D-Glucose as Solute at 73°F, with t=20 Seconds

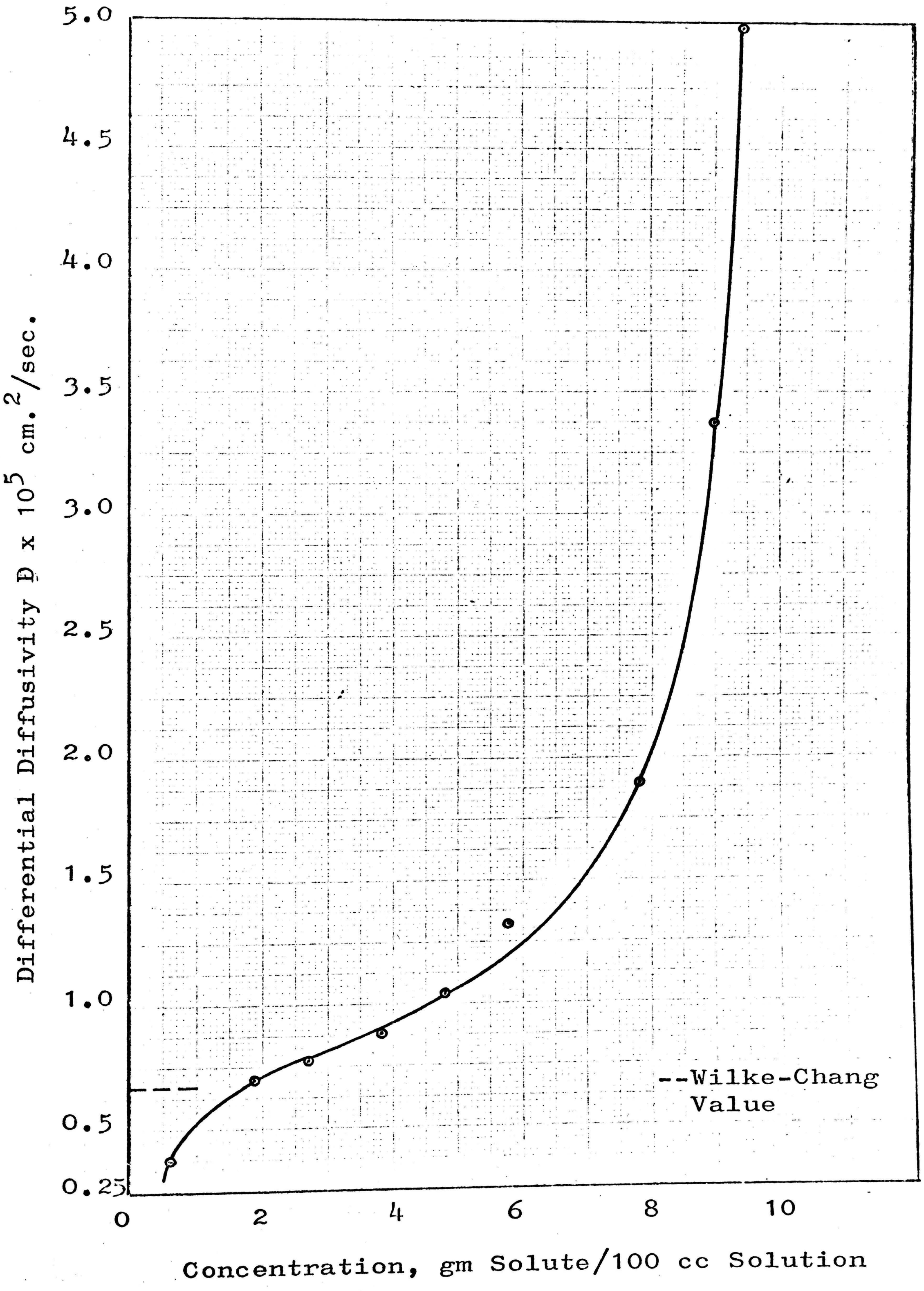


Figure 22. Differential Diffusivity Versus Concentration for 0.18 wt.% Carbopol in Water with D-Glucose at 73°F, with t=20 Seconds

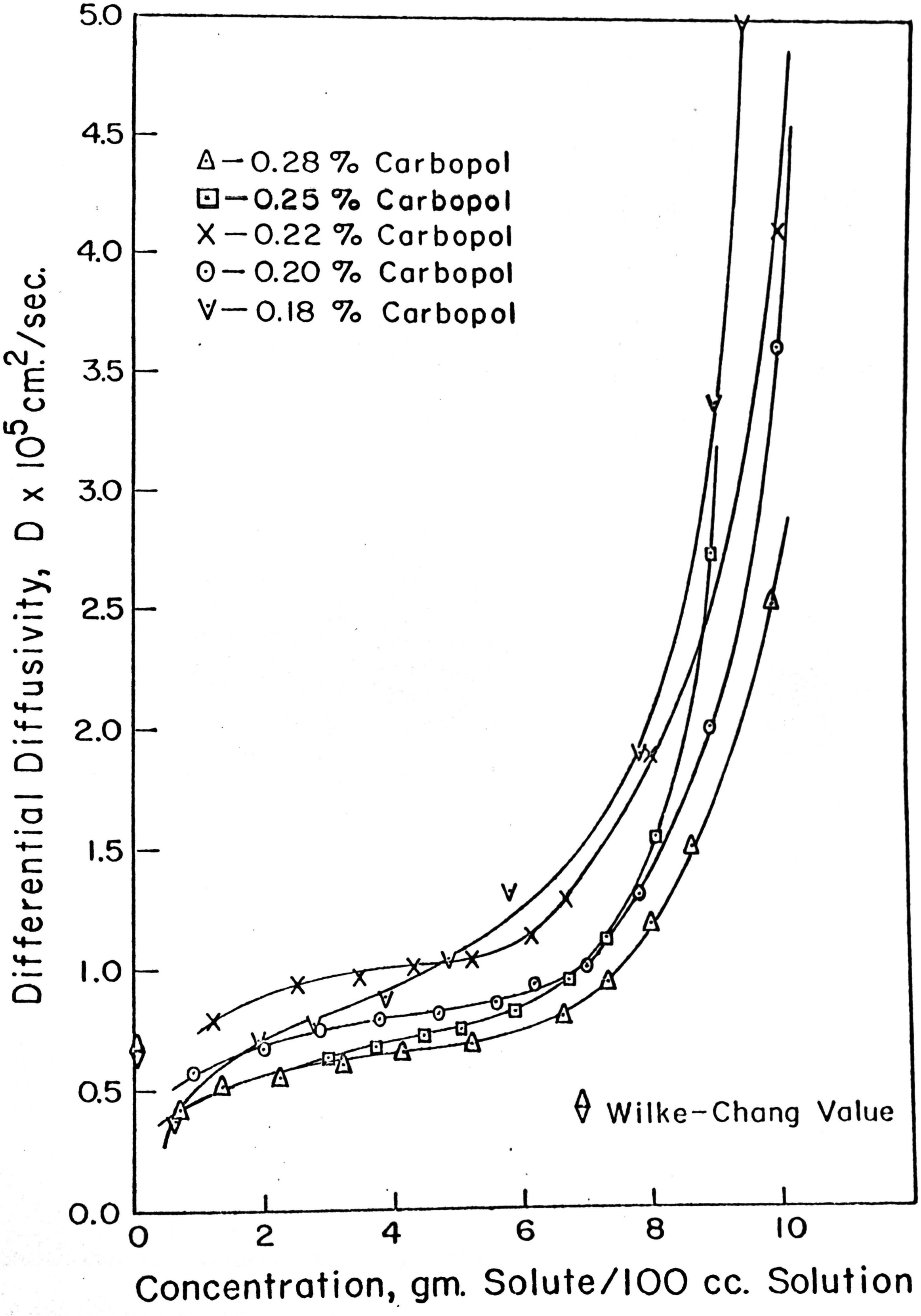


Figure 23. Differential Diffusivity vs. Solute Concentration for Carbopol-Water System

Similar flat regions are also noted for 0.22 wt.% Carbopol system and 0.20 wt.% Carbopol system. For the 0.18 wt.% Carbopol system such a flat region is not obtained. The increase in differential diffusion coefficient is significant after a certain critical concentration has been reached.

In the previous study by Dalal (5), a similar behavior was found. The differential diffusion coefficient was found to increase with the increase in solute concentration. However, the differential diffusion coefficient vs. solute concentration curve for the Urea system used by Dalal is relatively steeper than the one for the D-Glucose system. Considering the Wilke-Chang correlation, this can be explained as follows:

The differential diffusion coefficient is an inverse function of six-tenth power of the solute molal volume. Since the molal volume of D-Glucose is larger than that of Urea, (177.6 cu.cm./g. mole vs. 48 cu.cm./g. mole) diffusion coefficients for Urea were found to be higher than the corresponding diffusion coefficient for D-Glucose in the particular Natrosol concentration solutions used.

4. Choice of the Initial Solute Concentration

The solute-polymer solution which was used for photographing the interference pattern had a solute concentration of 10 gm/100 cc solution for all the systems under consideration. This solute concentration was chosen so that the distortion of the fringes could be observed after some convenient period of time (15 to 20 seconds). If a lower solute concentration was selected then such a fringe distortion could not be observed after a short period of time. This was due to the fact that the concentration became uniform in a very short time for lower solute concentration polymer solutions. In the previous study (5), the solute concentration selected for both Urea and D-Glucose systems was also 10 gm/100 cc solution. The maximum difference in indices of refraction for the CMC systems was 0.0127 and for the Carbopol systems was 0.0130.

B. Effect of Polymer Concentration on the Integral Diffusion Coefficient

From the plots of the differential diffusion coefficient vs. solute concentration, mean integral diffusion coefficients for the solute concentration range of 1 gm/100 cc to 10 gm/100 cc were calculated. For this purpose, the following equation was used to evaluate the integral diffusion coefficient.

$$\overline{D} = \frac{\int_{c_1}^{c_2} D_c \cdot dc}{\int_{c_1}^{c_2} dc} \qquad (4.1)$$

where c_1 = 1 gm/100 cc soln.

c_2 = 10 gm/100 cc soln.

Simpson's numerical method was used for the above integration. Plots of the integral diffusivity vs. polymer concentration for both CMC and Carbopol systems were made.

It was found that the integral diffusion coefficient is comparatively high for lower polymer concentrations of

TABLE 2. VALUES OF THE INTEGRATED DIFFUSIVITY, $\overline{D}$, FOR THE SYSTEMS STUDIED

System No.	Polymer	Solvent	Solute 10 gm/100 cc Soln.	$\overline{D} \times 10^{-5}$ sq.cm./sec.
1	CMC 2.20%	Water	D-Glucose	1.244
2	CMC 2.00%	Water	D-Glucose	1.227
3	CMC 1.70%	Water	D-Glucose	1.233
4	CMC 1.35%	Water	D-Glucose	1.373
5	CMC 1.20%	Water	D-Glucose	1.602
6	Carbopol 0.28%	Water	D-Glucose	0.949
7	Carbopol 0.25%	Water	D-Glucose	1.228
8.	Carbopol 0.22%	Water	D-Glucose	1.576
9	Carbopol 0.20%	Water	D-Glucose	1.158
10.	Carbopol 0.18%	Water	D-Glucose	1.601

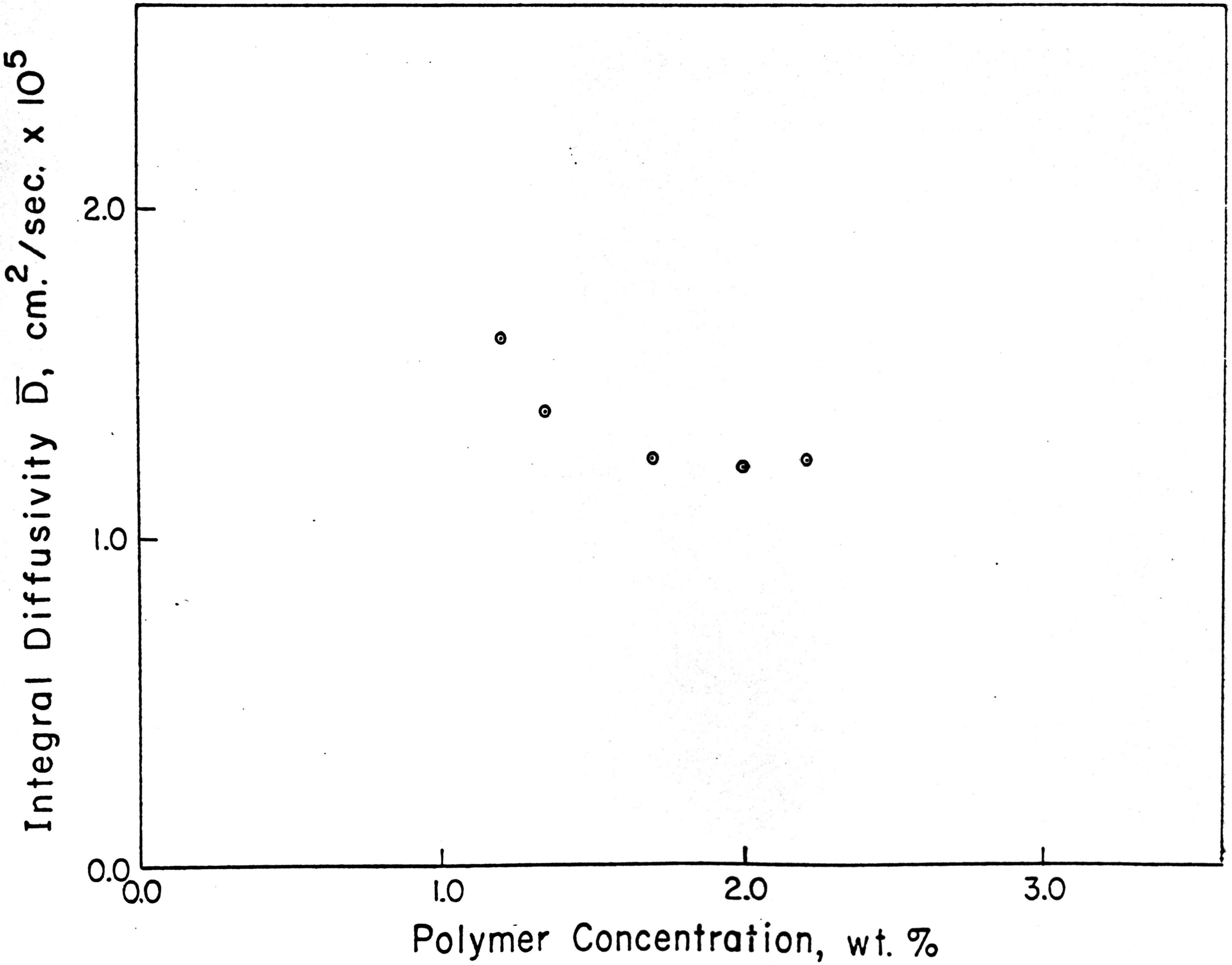


Figure 24. Integral Diffusivity as a Function of Polymer Concentration (CMC-Water)

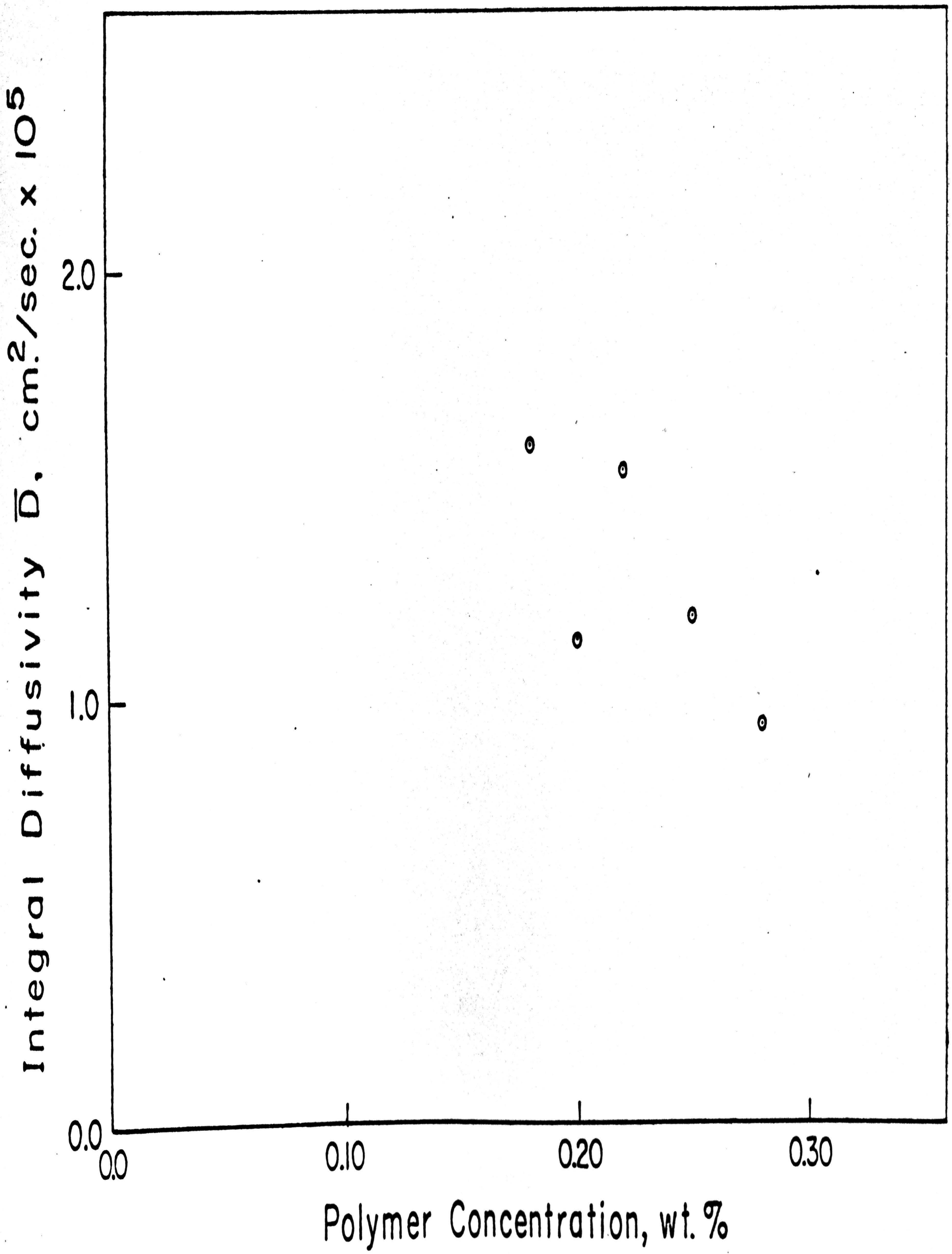


Figure 25. Integral Diffusivity as a Function of Polymer Concentration (Carbopol-Water)

CMC in water. (See Figure 24.) As the polymer concentration was increased there was a marked decrease in the integral diffusion coefficient. The value of the integral diffusion coefficient levels off after a certain polymer concentration has been reached.

For low polymer concentrations of Carbopol (0.18 wt.%), the integral diffusion coefficient was found to be high. (See Figure 25.) There is a large deviation in the values of integral diffusion coefficient for 0.20 wt.% Carbopol. From the plots of the integral diffusion coefficient vs. polymer concentration of Carbopol it can be said that the integral diffusion coefficient decreases continuously with the increase in polymer concentration, although the data are somewhat scattered. This may be due to the fact that all the measurements were not taken at one constant temperature. The difference in the temperatures at which all the measurements were taken was ±2°C. The photographs of the interference pattern for systems no. 6, 9 and 10 were taken at 23°C. and those for systems no. 7 and 8, for Carbopol, were taken at 21°C.

This behavior in the value of the integral diffusion coefficient for both CMC and Carbopol may be explained by the following qualitative hypothesis:

In very low concentration (solute-free) polymer solutions, the polymer molecules are independent and D-Glucose molecules diffuse through the solvent practically unimpeded by the presence of polymer molecules. Hence, a relatively high value of the integral diffusion coefficient is obtained. Above a certain critical polymer concentration, the polymer molecules overlap and the local environment in which D-Glucose molecules move is of a much higher viscosity than that of the solvent. As the concentration of polymer molecules increases, the D-Glucose molecules become more entangled until finally they lose their identity and the solution becomes a large network (17). Thus, a relatively lower value of the integral diffusion coefficient is obtained.

In the previous study by Dalal (5), no effect of polymer concentration on the integral diffusion coefficient could be deduced from the experimental data for the Natrosol systems using Urea and D-Glucose as solute, because of the large fluctuations obtained in the value of the integral diffusion coefficient for various polymer concentrations.

A relatively small range of Carbopol polymer concentration from 0.18 wt.% Carbopol to 0.28 wt.% Carbopol was studied in this work. The reason why such a small range was used in the work will be discussed here. It has been found that at certain polymer concentrations, the "local" viscosity of a polymer solution rises rapidly and then levels off to a fairly constant value (17). The concentration at which the rise commences (known as the critical concentration) is smaller the higher the molecular weight of the polymer and, in fact, is roughly inversely proportional to the three-fourth power of the molecular weight of the polymer molecules. For Carbopol, a higher molecular weight polymer, such a rise in local viscosity occurs at a very low critical concentration. Therefore, only a very small range of polymer concentration of Carbopol was available and useful for this study since very high viscosity solutions can not be studied using the microinterferometric method.

C. Experimental Equipment

As was pointed out earlier, both the polymers used in this work are water soluble. In the case of Carbopol, it was necessary to add 0.42 parts (by weight) of sodium hydroxide per part of Carbopol. The glass slides which were partially coated with aluminum for the CMC system could not be used for a corrosive system like Carbopol with the sodium hydroxide. Hence, for the Carbopol system the glass slides were partially coated with platinum.

Considerable difficulty was experienced in metallizing the glass slides. As platinum has a boiling point of about 4300°C (compared with 2056°C for aluminum), a high vacuum of 10^{-8} to 10^{-9} Torr is required for platinum as compared with 10^{-6} to 10^{-7} Torr for aluminum. For the same reason, the tungsten wire on which the foil of platinum rests must have a diameter of 2.5 mm.-3.0 mm. as compared with 1 mm.-1.5 mm. for aluminum vaporization.

If the metallic coating on the slide were too thin, the percent transmittance would be too great and it would not be possible to get bright fringes. On the other hand, a thicker coating tends to make the slides opaque. Four to five attempts were made for partially coating the glass slides with platinum, and two to three attempts were made for partially coating the glass slides with aluminum before such slides were successfully prepared.

To obtain a monochromatic light source, an external sodium lamp was used. The light passes through a diffuser, and is then reflected upwards into the diffusion cell by an optically flat mirror at the base of the microscope. The lens used has a focal length of 10 cm. The photographs were taken with a Kodak Tri-X Pan (ASA speed 400), fast, black and white film. An exposure time of 1/20 to 1/30 second was found to be satisfactory. This depends entirely upon the type of the slides prepared. For the development of prints from the negatives, Kodak Polycontrast paper (F Single Weight of Size 5" x 7") was used.

In this work, a magnification of 3.5X was mainly used for taking the photographs of interference pattern. This is fully described in the experimental section. However, the photograph of the interference pattern using 3.5X as magnification power, for the system no. 8 (0.22 wt.% Carbopol) was spoiled. So for this system the photograph using a 10X magnification power was used for drawing the graph of concentration vs. distance.

D. Computer Program

Data that led to Sigmoid curves can be fitted either by a modified Gompertz Equation or the equation suggested by Davis (6). The comparison of the average absolute percentage deviation of observed concentrations with those predicted by the modified Gompertz Equation and Davis method is shown in the Appendix D, page 107. The modified Gompertz Equation was used to evaluate the value of the integral, and was also used to evaluate the concentration gradient. In the previous work by Dalal (5), the modified Gompertz Equation was used to evaluate the value of the integral, and the Davis method was used for evaluating the concentration gradient.

It has been mentioned (5) that the Davis method for the evaluation of concentration gradient is applicable even for the cases where the Gompertz method is not found to be satisfactory. In this work, in order to maintain the "validity" of equation (3.1) for evaluating the differential diffusion coefficient, only the modified Gompertz Equation was used for both evaluations. The "validity" means that the same equation should be used for evaluating the integral and also for evaluating the concentration gradient in equation (3.1).

The comparison of concentration gradients, evaluated at those values of concentration which were predicted by the modified Gompertz Equation or the Davis Equation with the observed values of concentration are also given in the Appendix D.

In order to locate the line of the original interface, different increments in the value of x were chosen for the different systems. Initially, an increment of 0.0002 cm. in the value of x was used for all the systems; but system nos. 7, 8, 9 and 10 did not seem to converge (i.e., $A_2 \neq A_3$). For these non-converging systems, an increment of 0.00001 cm. in the value of x was used in order to obtain the required convergence. In the previous study by Dalal (5), an increment of 0.0001 cm. in the value of x was successfully used for all the systems.

Most of the references in this work are taken from the previous study by Dalal (5). This is due to the fact that to the author's knowledge no new references are available since the previous study by Dalal (5) was conducted.

E. Limitations of the Microinterferometric Method

This technique is dependent on the existence of a relatively large difference in the refractive index between the solution and the solvent initially contacted. If the difference in refractive index were small, little or no distortion of the fringes would be observed. The minimum required difference in refractive index depends on several factors. In general, a minimum difference of 0.01 is usually adequate (25). The minimum difference in the index of refraction was 0.0117 for CMC and .0118 for Carbopol.

The viscosity of the solution initially contacted should also be considered. If the viscosity of both the solutions were low, considerable convection or turbulence may be observed when the drops come in contact with each other in the wedge. In these systems, the concentration becomes uniform in a very short time and hence no distortion of the fringes could be easily observed. Even if the fringes were observed, the diffusion could have been obtained by turbulent diffusion rather than by molecular diffusion. In this event the equation used would not be applicable. As might be expected, this type of behavior was not noted with the drops of higher viscosity. However, it is very difficult to handle extremely high viscosity solutions while taking the photographs of the interference pattern because these solutions have very high resistance to flow due to friction and two drops of such high viscosity solutions may not come into contact with each other. This factor limits the range of polymer concentrations which one can use with the microinterferometric method.

The volatility of the solvent must also be considered, as it would create a problem due to its evaporation on the glass slide.

V. CONCLUSIONS

The following conclusions concerning the molecular diffusion coefficient have been drawn from the data and the results obtained for Carboxymethylcellulose (CMC) and Carboxypolymethylene (Carbopol) systems using D-Glucose as solute. The solute concentration range is from 0 gm/100 cc solution to 10 gm/100 cc solution.

(1) The microinterferometric method is a very rapid technique for determining the molecular diffusivity in moderately viscous solutions.

(2) The qualitative effect of solute concentration on the differential diffusion coefficient is similar for various polymer concentrations of CMC and Carbopol solutions. The differential diffusion coefficient increases with increase in solute concentration in all cases. There is an increase in the value of differential diffusion coefficient by a factor of 2.5 to 3.0 for the higher solute concentration range of 8 gm/100 cc solution to 10 gm/100 cc solution as compared with the low concentration range.

(3) The Wilke-Chang correlation may be used to approximately predict the molecular diffusivity of a solute at its very low solute concentration in polymer solutions using the viscosity of the solvent rather than that of the solution. This conclusion is based on studies with zero fluid velocity. The approximate percentage deviation in the value of the differential diffusion coefficient of a solute at the lowest

solute concentration from that predicted by Wilke-Chang correlation is ±10%. A similar conclusion was found by Dalal (5) for the Natrosol system with D-Glucose and urea as solutes.

(4) For the CMC systems, the integral diffusion coefficient decreases with increase in polymer concentration. After a certain polymer concentration has been reached, the integral diffusion coefficient levels off and reamain constant.

(5) For the Carbopol systems, the integral diffusion coefficient appears to decrease with increase in polymer concentration, although the data are somewhat scattered.

(6) The integral diffusivity of D-Glucose in both the CMC and Carbopol aqueous polymer systems for its lowest concentration of 1.2 wt.% and 0.18 wt.% respectively is found to be similar and of the order of 1.600×10^{-5} $cm.^2$/second.

(7) In a previous study by Dalal (5) for aqueous Natrosol systems, the differential diffusion coefficient increased with an increase in solute concentration in all cases. However, no effect of polymer concentration on the integral diffusion coefficient could be deduced from the experimental data because the data obtained were scattered.

(8) The microinterferometric method can not be used to determine the diffusion coefficient for very low viscosity solutions, as it may not give satisfactory fringe distortion. However, the range of viscosity in which this technique may be applicable, can be determined by trial

and error rather quickly.

(9) In the design of chemical process equipment, particularly in the field of extraction, absorption and reactor design, an understanding of the diffusion process is very important. It has been found in this work that the differential diffusion coefficient increases with increase in solute concentration for all cases. For the higher ranges of solute concentration, the predicted value of the differential diffusion coefficient using the Wilke-Chang correlation may be very inaccurate. The potential application of this work is to add to knowledge of the solute concentration dependent molecular diffusion coefficients of a solute in polymer solutions. It may be ultimately possible to obtain general prediction relations for polymer solutions which consider the effect of solute and polymer concentrations.

(10) From the results of previous studies (5) and (25), and from the results obtained in this study, it may be concluded that the differential diffusion coefficient of the solute increases with the increase in solute concentration. A more positive generalization for all non-ionic, aqueous polymer systems awaits the results of further experimental work. However, it is believed that it may be more profitable to explore the possibility of this generalization being extended to <u>non-aqueous</u> systems. No such generalization regarding the integral diffusivity in non-ionic, aqueous polymer systems can be drawn from the results of previous study (5) and this work.

VI. RECOMMENDATIONS

(1) It has been found that there is a marked increase in differential diffusion coefficient of a solute for higher solute concentrations. The range of the solute concentration in which this behavior is observed is very small. In order to study this typical range of solute concentrations more effectively, a higher solute concentration of about 15 to 16 gm/100 cc of solution is recommended.

(2) Some kind of arrangement must be made by which the molecular diffusivity in polymer solutions at different temperatures can be studied.

(3) The use of a continuous gas laser as a more powerful source of light is recommended. Its main advantages are the power, parallelism and monochromaticity of light (31). The laser surpasses, in power and parallelism, other conventional sources of light. Sharper fringes would be obtained with the use of a laser.

(4) Non-aqueous polymeric systems should also be studied.

(5) In this work the range of polymer concentration for both aqueous systems of CMC and Carbopol, in which the microinterferometric method can be effectively used, was small. It was also difficult to prepare more polymer solutions of different concentrations without the viscosity becoming too great so only five different concentrations of CMC and Carbopol were studied. If it is possible to study

the molecular diffusivity of a solute in polymer solutions at higher temperature, a greater range of concentrations of polymer solutions could be used in an effort to determine more positively the effect of varying polymer concentration on the diffusion coefficient.

(6) In this work one photograph of interference pattern for each system was analyzed. In order to take into account the possibility of experimental error in each system, it is suggested that in future work of this nature at least two to three photographs of the interference pattern for each system should be taken and the integral diffusivity data should be averaged for each polymer concentration.

VII. APPENDICES

APPENDIX A

Derivation of equation for evaluation of the diffusion coefficient, D, as a function of concentration, C, is shown in this section.

Fick's first law for molecular diffusion neglecting bulk flow obeys the relation

$$N = (-D \nabla C) \qquad (A.1)$$

where

N = flux of the solute,

D = the molecular diffusion coefficient,

∇C = the vector gradient of solute concentration.

Fick's second law, in vector notation is,

$$\frac{\partial C}{\partial t} + \nabla \vec{N} = 0 \qquad (A.2)$$

$$\begin{aligned} \frac{\partial C}{\partial t} &= - \nabla \vec{N} \\ &= - \nabla (-D \nabla C) \\ &= \nabla (D \nabla C) \qquad (A.2\text{-a}) \end{aligned}$$

$$\begin{aligned} \frac{\partial C}{\partial t} &= \frac{\partial}{\partial x} (D \partial C/\partial x) + \frac{\partial}{\partial y} (D \partial C/\partial y) \\ &\quad + \frac{\partial}{\partial z} (D \partial C/\partial z) \qquad (A.2\text{-b}) \end{aligned}$$

The following assumptions are made:

1. Equation (A.1) is valid only for an isotropic medium.

2. The structure and diffusion properties of the medium in the neighborhood of any point are the same relative

to all directions.

3. Assumption (2) implies that the flow of the diffusing substance at any point is along the line of constant concentration through the point and normal to the surface contacting the diffusing substance.

If the diffusion is in the x direction only, then equation (A.2-b) reduces to

$$\frac{\partial C}{\partial t} = \frac{\partial}{\partial x}\left[D \frac{\partial C}{\partial x}\right] \tag{A.3}$$

The following initial and boundary conditions apply:

$$C = 0, \qquad t = 0, \qquad x < 0 \tag{A.4}$$

$$C = C_o, \qquad t = 0, \qquad x > 0 \tag{A.5}$$

$$C = 0, \qquad t = t, \qquad x \rightarrow -\infty \tag{A.6}$$

$$C = C_o, \qquad t = t, \qquad x \rightarrow \infty \tag{A.7}$$

$$C = \frac{C_o V_{co}}{V_o + V_{co}} \qquad t \rightarrow \infty \qquad \text{all } x\text{'s} \tag{A.8}$$

It is also assumed that D is a function of C only.

Therefore equation (A.3) can be reduced to an ordinary differential equation by the introduction of a new variable, r, (Boltzmann's variable) where

$$r = \frac{1}{2} \frac{x}{\sqrt{t}} \tag{A.9}$$

$$\frac{\partial C}{\partial x} = \frac{1}{2\sqrt{t}} \frac{dC}{dr} \tag{A.10}$$

and

$$\frac{\partial C}{\partial t} = -\frac{x}{4\ t^{3/2}} \frac{dC}{dr} \tag{A.11}$$

Substituting equations (A.10) and (A.11) in equation (A.3) we get

$$- \frac{x}{4\ t^{3/2}} \quad \frac{dC}{dr} = \frac{\partial}{\partial x} \left[\frac{D}{2\sqrt{t}} \quad \frac{dC}{dr} \right]$$

$$= \frac{\partial}{\partial r} \left[\frac{D}{2\ t^{1/2}} \quad \frac{dC}{dr} \right] \frac{\partial r}{\partial x} \qquad (A.12)$$

From equation (A.9):

$$\frac{\partial r}{\partial x} = \frac{1}{2\sqrt{t}} \qquad (A.13)$$

$$2r = \frac{x}{t^{1/2}} \qquad (A.13a)$$

$$- \frac{x}{4t^{3/2}} \quad \frac{dC}{dr} = \frac{d}{dr} \left[\frac{D}{2\sqrt{t}} \quad \frac{dC}{dr} \right] \frac{1}{2\sqrt{t}} \qquad (A.14)$$

$$- \frac{x}{\sqrt{t}} \quad \frac{dC}{dr} = \frac{d}{dr} \left[D \frac{dC}{dr} \right] \qquad (A.15)$$

Therefore, we get:

$$- 2r \quad \frac{dC}{dr} = \frac{d}{dr} \left[D \frac{dC}{dr} \right] \qquad (A.16)$$

On integrating equation (A.16) with respect to r, we get

$$-2 \int_0^C r\ dC = \int_0^C \frac{d}{dr} \left[D \frac{dC}{dr} \right] dr$$

$$= \left[D \frac{dC}{dr} \right]_0^C \qquad (A.17)$$

$$-2 \int_0^C r\ dC = \left[D \frac{dC}{dr} \right]_{C=C} - \left[D \frac{dC}{dr} \right]_{C=0}$$

since (D dC/dr) = 0 when C = 0, we get

$$-2 \int_0^C r\ dC = \left[D \frac{dC}{dr} \right]_{C=C} \qquad (A.18)$$

substituting for r, we get

$$-2 \int_{0}^{C} \frac{x}{2\sqrt{t}}\, dC = 2\sqrt{t}\, D_c \left[\frac{dC}{dx}\right]_C \qquad (A.19)$$

where D_c indicates that D is a function of concentration.

Therefore,

$$D_c = \frac{-\int_{0}^{C} x\, dC}{2t\left[\frac{dC}{dx}\right]_C} \qquad (A.20)$$

APPENDIX B

COMPUTER PROGRAMS

The programs used for the computations described in this thesis are given in this appendix. The programs were written in the Fortran IV language. The programs were run on an IBM 360 Model 40.

Program No. 1

```
C     NON-LINEAR CURVE FITTING BY MODIFIED GOMPERTZ EQUATIONS, FOR EQUAL
C     INTERVALS OF THE INDEPENDANT VARIABLE.
      DIMENSION X(30),Y(30),S(3),G(30)
      READ(1,905)KK
      DO 900 IJK=1,KK
      WRITE(3,901)
      WRITE(3,902)IJK
      WRITE(3,903)
      WRITE(3,904)
      READ(1,100)(S(J),J=1,3)
      READ(1,101)N,A
      READ(1,109)(G(I),Y(I),I=1,N)
      DO 1 I=1,N
    1 X(I)=(G(I)/0.05-1.0)
      SUM=0.0
      K=N/3
      L=1
      K1=K
      DO 10 J=1,3
      DO 11 I=L,K
   11 S(J)=S(J)+ALOG(Y(I)-A)
      L=K+1
   10 K=K+K1
      P=N/3
      P=1./P
      CN=(S(2)-S(3))/(S(1)-S(2))
      C=CN**P
      AL=(S(1)-((S(1)-S(2))/(1.-CN)))*P
      AL=EXP(AL)
      BL=(S(1)-S(2))*(1.-C)/((1.-CN)**2)
      BL=EXP(BL)
      SR=0.0
      WRITE(3,103)A,AL,BL,C
      WRITE(2,102)A,AL,BL,C
```

continued

```
      WRITE(3,105)
      WRITE(3,104)
      DO 12 I=1,N
      YC=A+AL*(BL**(C**X(I)))
      D=YC-Y(I)
      DV=(D/Y(I))*100.0
      SUM=SUM+(ABS(DV))
      SR=SR+(D**2)
      WRITE(3,107)X(I),Y(I),YC,D,DV
   12 CONTINUE
      WRITE(3,105)
      WRITE(3,106)SR
      E=N
      DEV=SUM/E
      WRITE(3,105)
      WRITE(3,108)DEV
  900 CONTINUE
      CALL EXIT
  100 FORMAT(3E18.8)
  101 FORMAT(I5,E18.8)
  102 FORMAT(4E18.8)
  103 FORMAT(7H ALPHA=,E18.8,4X,2HA=,E18.8,4X2HB=,E18.8,4X2HC=,E18.8)
  104 FORMAT(9X4HX(I),14X4HY(I),12X8HY(I)CALC,12X4HDIFF,12X8HPER DEVI)
  105 FORMAT(///)
  106 FORMAT(25H SUM OF RESIDUAL SQUARE =,E18.8)
  107 FORMAT(5E18.8)
  108 FORMAT(25H ABS. AVE. PERCENT DEVI.=,E18.8)
  109 FORMAT(2E18.8)
  901 FORMAT(1H1)
  902 FORMAT(1X10HSYSTEM NO.,I3)
  903 FORMAT(//)
  904 FORMAT(/)
  905 FORMAT(I5)
      END
```

G(I) = Distance, cm.

Y(I) = Concentration, gm./100 cc. soln.

N = Total number of data points.

A = Alpha (Intercept)

AL, BL, CL = Constants for theGompertz Equation.

Program No. 2-A

```
C     EXPERIMENTAL CONCENTRATION GRADIENT AS A FUNCTION OF DISTANCE
      DIMENSION X(15),DV(15),Y(15),G(15)
      READ(1,905)KK
      DO 900 IJK=1,KK
      WRITE(3,901)
      WRITE(3,902)IJK
      WRITE(3,903)
      WRITE(3,904)
      READ(1,102)K
      READ(1,101)ALP,AL,BL,CL
      READ(1,109)(G(I),Y(I),I=1,K)
      DO 10 I=1,K
      X(I)=(G(I)/0.005)-1.0
      DV(I)=(AL*(BL)**(CL**X(I)))*ALOG(BL)*((CL**X(I))*ALOG(CL))
      WRITE(3,200)G(I),DV(I)
   10 CONTINUE
  900 CONTINUE
      CALL EXIT
  101 FORMAT(4E18.8)
  102 FORMAT(I5)
  109 FORMAT(2E18.8)
  901 FORMAT(1H1)
  902 FORMAT(1X10HSYSTEM NO.,I3)
  903 FORMAT(//)
  904 FORMAT(/)
  905 FORMAT(I5)
  200 FORMAT(2E18.8)
      END
```

Program No. 2-B

```
C     CALCULATION OF THE DERIVATIVES OF SIGMOID CURVES
      DIMENSION YT(400),PT(400),Y(20),X(20),F(20),P(20),PC(20),S(15,16)
      DIMENSION YC(20)
      READ(1,100)(YT(I),PT(I),I=1,389)
      READ(1,905)KK
      DO 900 IJK=1,KK
      WRITE(3,901)
      WRITE(3,902)IJK
      WRITE(2,905)IJK
      WRITE(3,903)
      WRITE(3,904)
      READ(1,101)S1,S2,S3,S4,S5
      READ(1,102)K
      READ(1,109)(X(I),Y(I),I=1,K)
      DO 1 I=2,K
      P(I)=ALOG(20.0*Y(I)/(ALOG(100.0-Y(I))/2.303))/2.303
      F(I)=(X(I)-X(1))/P(I)
      S1=S1+X(I)
      S2=S2+X(I)*X(I)
      S3=S3+F(I)
    1 S4=S4+X(I)*F(I)
      S(1,1)=K-1
      S(1,2)=S1
      S(1,3)=S3
      S(2,1)=S1
      S(2,2)=S2
      S(2,3)=S4
      WRITE(3,100)(S(1,I),I=1,3)
      WRITE(3,100)(S(2,I),I=1,3)
      B=(S(1,2)*S(1,3)-S(1,1)*S(2,3))/(S(1,2)*S(2,1)-S(1,1)*S(2,2))
      A=(S(1,3)-B*S(2,1))/S(1,1)
      WRITE(3,106)A,B
      DO 2 I=2,K
```

continued

```
      PC(I)=(X(I)-X(1))/(A+B*X(I))
      J=1
    3 J=J+1
      PS2=PT(J)-PC(I)
      IF(PS2)4,4,5
    4 PS1=PT(J)
      GO TO 3
    5 PS2=PT(J)
      YC(I)=(PC(I)-PS1)*(YT(J)-YT(J-1))/(PS2-PS1)+YT(J-1)
      D=Y(I)-YC(I)
      DEV=(D/Y(I))*100.0
      S5=S5+ABS(DEV)
      G=0.4343*(1./YC(I)+0.4343/((100.0-YC(I))*ALOG(100.0-YC(I))/2.303))
      DV=(A+B*X(1))/(((A+B*X(I))**2)*G)
      WRITE(3,103)Y(I),P(I),PC(I),D,DV
      WRITE(3,104)X(I),F(I),YC(I),G
      WRITE(2,108)DV
    2 CONTINUE
      WRITE(3,105)
      PP=K
      APD=S5/(PP-1.0)
      WRITE(3,105)
      WRITE(3,107)APD
  900 CONTINUE
      CALL EXIT
  100 FORMAT(4E18.8)
  101 FORMAT(5F10.5)
  102 FORMAT(I5)
  103 FORMAT(5F20.5)
  104 FORMAT(10X,4F20.5)
  105 FORMAT(////)
  106 FORMAT(3H A=,F18.8,4X,2HB=,F18.8)
  107 FORMAT(40H AVERAGE ABSOLUTE PERCENT DEVIATION IS =,F18.8)
  108 FORMAT(E18.8)
```

continued

```
  109 FORMAT(2E18.8)
  901 FORMAT(1H1)
  902 FORMAT(1X10HSYSTEM NO.,I3)
  903 FORMAT(//)
  904 FORMAT(/)
  905 FORMAT(I5)
      END
```

X = Distance, cm.

Y = Concentration, gm./100 cc. soln.

DV = Concentration gradient, gm./100 cc. soln./cm.

Program No. 3

```
C     LOCATING THE LINE OF ORIGINAL INTERFACE
      DIMENSION YA(25),YB(25)
      READ(1,905)KK
      DO 900 IJK=1,KK
      WRITE(3,901)
      WRITE(3,902)IJK
      WRITE(3,903)
      WRITE(3,904)
      READ(1,100)A,B,P,N
      READ(1,101)ALP,AL,BL,CL
      WRITE(3,102)
      DP=0.0002
      F=N-1
      M=F/2.0+1.0
      DA=(B-A)/F
      X=A
      DO 10 I=1,N
      YA(I)=ALP+AL*(BL**(CL**(X/0.005-1.0)))
      X=X+DA
   10 CONTINUE
      S1=0.0
      S2=0.0
      MA=N-1
      DO 20 I=2,MA,2
      S1=S1+YA(I)
   20 CONTINUE
      MB=N-2
      DO 21 I=3,MB,2
      S2=S2+YA(I)
   21 CONTINUE
      SIM=(YA(1)+YA(N)+4.0*S1+2.0*S2)*DA/3.0
      A1=SIM
   15 DB=(P-A)/(F/2.0)
```

continued

```
      X=A
      DO 11 I=1,M
      YB(I)=ALP+AL*(BL**(CL**(X/0.005-1.0)))
      X=X+DB
   11 CONTINUE
      S1=0.0
      S2=0.0
      MA=M-1
      DO 22 I=2,MA,2
      S1=S1+YB(I)
   22 CONTINUE
      MB=M-2
      DO 23 I=3,MB,2
      S2=S2+YB(I)
   23 CONTINUE
      SIM=(YB(1)+YB(M)+4.0*S1+2.0*S2)*DB/3.0
      A2=SIM
      A3=(B-P)*YA(N)-(A1-A2)
      D=A2-A3
      DV=(A2-A3)/A2
      PD=DV*100.0
      WRITE(3,103)A1,A2,A3,D,PD,P
      IF (ABS(DV)-8.0E-03)6,6,7
    7 IF(A2-A3)12,6,14
   12 P=P+DP
      WRITE(3,105)P
      GO TO 15
   14 P=P-DP
      WRITE(3,105)P
      GO TO 15
    6 WRITE(3,104)
      WRITE(3,102)
```

continued

```
      WRITE(3,103)A1,A2,A3,D,PD,P
      WRITE(2,101)ALP,AL,BL,CL
      WRITE(2,101)A,B,P
  900 CONTINUE
      CALL EXIT
  100 FORMAT(3E18.8,I18)
  101 FORMAT(4E18.8)
  102 FORMAT(11X,2HA1,15X,2HA2,15X,2HA3,13X,5HA2-A3,11X,5HP.DEV,16X,1HP)
  103 FORMAT(6E17.8)
  104 FORMAT(///)
  105 FORMAT(5X,2HP=,F18.8)
  901 FORMAT(1H1)
  902 FORMAT(1X10HSYSTEM NO.,I3)
  903 FORMAT(//)
  904 FORMAT(/)
  905 FORMAT(I5)
      END
```

A = Lower limit for Distance, cm.

B = Upper limit for Distance, cm.

P = Position of the line of original interface.

ALP, AL, BL, CL = Constants for Gompertz equation.

A_1, A_2, A_3 = Areas as shown in Figure 10 , page 34.

Program No. 4

```
C     EVALUATION OF INTEGRAL
      DIMENSION X(70),C(70),XD(70),YD(70)
      READ(1,905)KK
      DO 900 IJK=1,KK
      WRITE(3,901)
      WRITE(3,902)IJK
      WRITE(3,903)
      WRITE(3,904)
      READ(1,100)ALP,AL,BL,CL
      READ(1,101)A,B,P
      READ(1,103)N,K,L,NT
      F=N
      READ(1,104)(XD(I),YD(I),I=1,NT)
      JJ=1
      DO 10 I=1,K
      GO TO (30,31),JJ
   30 M=I*N
      GO TO 32
   31 M=(I*N)+1
      JJ=JJ-2
      GO TO 32
   32 X(1)=A
      C(1)=ALP+AL*(BL**(CL**(X(1)/0.005-1.0)))
      MA=M-1
      MB=M-2
      AM=MA
      X(M)=XD(I)
      DX=(X(M)-X(1))/(AM)
      S1=0.0
      S2=0.0
      DO 11 J=1,MA
      X(J+1)=X(J)+DX
      C(J+1)=ALP+AL*(BL**(CL**(X(J+1)/0.005-1.0)))
```

continued

```
   11 CONTINUE
      DO 12 J=2,MA,2
      S1=S1+C(J)
   12 CONTINUE
      DO 13 J=3,MB,2
      S2=S2+C(J)
   13 CONTINUE
      SIM=(C(1)+C(M)+4.0*S1+2.0*S2)*DX/3.0
      SIM=SIM+(C(M)*(P-X(M)))
      WRITE(3,102)X(M),C(M),SIM,I
      WRITE(2,100)SIM
      JJ=JJ+1
   10 CONTINUE
      A2=SIM
      JJ=1
      DO 20 I=1,L
      GO TO (40,41),JJ
   40 M=I*N
      GO TO 42
   41 M=(I*N)+1
      JJ=JJ-2
      GO TO 42
   42 X(1)=P
      C(1)=ALP+AL*(BL**(CL**(X(1)/0.005-1.0)))
      MA=M-1
      MB=M-2
      AM=MA
      KJ=K+I
      IF (KJ-NT)24,24,900
   24 X(M)=XD(KJ)
      DX=(X(M)-X(1))/(AM)
      S1=0.0
```

continued

```
      S2=0.0
      DO 21 J=1,MA
      X(J+1)=X(J)+DX
      C(J+1)=ALP+AL*(BL**(CL**(X(J+1)/0.005-1.0)))
   21 CONTINUE
      DO 22 J=2,MA,2
      S1=S1+C(J)
   22 CONTINUE
      DO 23 J=3,MB,2
      S2=S2+C(J)
   23 CONTINUE
      SIM=(C(1)+C(M)+4.0*S1+2.0*S2)*DX/3.0
      SIM=C(M)*(X(M)-P)-SIM
      SIM=SIM+A2
      WRITE(3,102)X(M),C(M),SIM,I
      WRITE(2,100)SIM
      JJ=JJ+1
   20 CONTINUE
  900 CONTINUE
      CALL EXIT
  100 FORMAT(4E18.8)
  101 FORMAT(3E18.8)
  102 FORMAT(3F18.8,I18)
  103 FORMAT(4I10)
  104 FORMAT(2E18.8)
  901 FORMAT(1H1)
C     CONTINUED
  902 FORMAT(1X10HSYSTEM NO.,I3)
  903 FORMAT(//)
  904 FORMAT(/)
  905 FORMAT(I5)
      END
```

$$\text{Sim} = \int_0^C x \, dc$$

Program No. 5

```
C     CALCULATION OF THE DIFFUSIVITY AS A FUNCTION OF CONCENTRATION IN
C     POLYMERIC SYSTEMS
      DIMENSION X(30),C(30),EN(30),ED(30),DC(30),S(30),R(30)
      READ(1,905)KK
      DO 900 IJK=1,KK
      WRITE(3,901)
      WRITE(3,902)IJK
      WRITE(3,903)
      READ(1,100)N,T
      WRITE(3,200)T
      WRITE(3,903)
      WRITE(3,904)
      READ(1,102)S(IJK)
      READ(1,101)(X(I),C(I),I=1,N)
      READ(1,102)(EN(I),I=1,N)
      READ(1,102)(ED(I),I=1,N)
      DO 10 I=1,N
      R(I)=S(IJK)*C(I)
      DC(I)=(EN(I)/(2.0*T*ED(I)))
      ED(I)=ED(I)/100.0
      DC(I)=DC(I)*(10.0**5)
      WRITE(3,203)X(I),R(I),C(I),EN(I),ED(I),DC(I)
      WRITE(3,904)
   10 CONTINUE
  900 CONTINUE
      CALL EXIT
  100 FORMAT(I5,F10.1)
  101 FORMAT(2F18.8)
  102 FORMAT(E18.8)
  200 FORMAT(5X8HTIME T =,F5.1)
  203 FORMAT(5X,F10.3,F10.4,F11.3,F9.3,2F10.3)
```

continued

```
  901 FORMAT(1H1)
  902 FORMAT(1X10HSYSTEM NO.,I3)
  903 FORMAT(//)
  904 FORMAT(/)
  905 FORMAT(I5)
      END
```

X(I) = Distance, cm.

R(I) = Refractive Index.

C(I) = Concentration, gm./100 cc.soln.

EN(I) = Value of $\int_{0}^{C} x \, dc$.

ED(I) = Value of concentration gradient.

DC(I) = Differential Diffusivity, sq.cm./sec.

T = Time, sec.

APPENDIX C

DATA AND RESULTS

TABLE 3. POLYMERIC SYSTEMS USED FOR THE STUDY

System No.	Polymer	Solvent	Polymer Concent. Wt.%	Solute	Initial Solute Conc. gm/100 cc Soln.
1	CMC	Water	2.20%	D-Glucose	10.0
2	CMC	Water	2.00%	D-Glucose	10.0
3	CMC	Water	1.70%	D-Glucose	10.0
4	CMC	Water	1.35%	D-Glucose	10.0
5	CMC	Water	1.20%	D-Glucose	10.0
6	Carbopol	Water	0.28%	D-Glucose	10.0
7	Carbopol	Water	0.25%	D-Glucose	10.0
8	Carbopol	Water	0.22%	D-Glucose	10.0
9	Carbopol	Water	0.20%	D-Glucose	10.0
10	Carbopol	Water	0.18%	D-Glucose	10.0

Table 4 Data and Results for System No. 1

Distance cm	Refractive Index $(n - n_o)$	Concentration gm. solute per 100 cc.sol.	$\int_0^C x \, dc \times 10^2$ gm/sq.cm.	$\frac{dC}{dx}$ gm/cc/cm	$D \times 10^5$ cm^2/sec.
0.008	0.0011	0.947	0.020	1.596	0.518
0.014	0.0025	2.067	0.036	2.386	0.621
0.019	0.0042	3.482	0.048	2.784	0.715
0.023	0.0056	4.664	0.052	2.802	0.779
0.028	0.0070	5.861	0.054	2.610	0.857
0.035	0.0092	7.674	0.065	2.008	1.353
0.041	0.0103	8.606	0.077	1.582	2.034
0.052	0.0119	9.923	0.104	0.863	5.036

Time t = 12.0 seconds; n_o = 1.3385; T = 23°C

Table 5 Data and Results for System No. 2

Distance cm	Refractive Index $(n - n_o)$	Concentration gm. solute per 100 cc.sol.	$\int_0^C x\,dc \times 10^2$ gm/sq.cm.	$\frac{dC}{dx}$ gm/cc/cm	$D \times 10^5$ cm^2/sec.
0.026	0.0010	0.775	0.047	0.452	1.032
0.035	0.0016	1.233	0.066	0.616	1.079
0.050	0.0031	2.415	0.103	0.914	1.127
0.061	0.0045	3.524	0.123	1.095	1.125
0.069	0.0056	4.395	0.131	1.191	1.100
0.074	0.0064	5.028	0.133	1.241	1.069
0.080	0.0073	5.760	0.135	1.281	1.052
0.087	0.0085	6.667	0.143	1.308	1.095
0.094	0.0097	7.638	0.159	1.311	1.214
0.109	0.0121	9.522	0.211	1.258	1.677

Time $t = 50.0$ seconds; $n_o = 1.3380$; $T = 23^\circ C$

Table 6 Data and Results for System No. 3

Distance cm	Refractive Index $(n - n_o)$	Concentration gm. solute per 100 cc.sol.	$\int_0^C x \, dc \times 10^2$ gm/sq.cm.	$\frac{dC}{dx}$ gm/cc/cm	D x 10^5 cm^2/sec.
0.017	0.0012	1.018	0.029	1.210	0.590
0.022	0.0020	1.726	0.042	1.611	0.653
0.026	0.0029	2.423	0.052	1.865	0.702
0.030	0.0038	3.207	0.061	2.035	0.748
0.036	0.0052	4.378	0.068	2.120	0.800
0.040	0.0062	5.271	0.069	2.080	0.830
0.046	0.0076	6.428	0.074	1.921	0.957
0.051	0.0087	7.410	0.083	1.706	1.213
0.055	0.0095	8.026	0.091	1.438	1.590
0.064	0.0109	9.255	0.117	1.138	2.560

Time t = 20.0 seconds; n_o = 1.3380; T = 23°C

Table 7 Data and Results for System No. 4

Distance cm	Refractive Index $(n - n_o)$	Concentration gm. solute per 100 cc.sol.	$\int_0^C x\,dc \times 10^2$ gm/sq.cm.	$\frac{dC}{dx}$ gm/cc/cm	$D \times 10^5$ $cm^2/sec.$
0.008	0.0010	0.825	0.023	1.126	0.575
0.017	0.0024	2.085	0.047	1.829	0.719
0.022	0.0036	3.107	0.060	2.074	0.806
0.028	0.0051	4.381	0.069	2.132	0.900
0.032	0.0062	5.263	0.071	2.054	0.957
0.038	0.0075	6.396	0.074	1.839	1.121
0.045	0.0089	7.599	0.086	1.496	1.590
0.052	0.0100	8.528	0.101	1.161	2.416
0.065	0.0113	9.667	0.131	0.678	5.346

Time t = 18.0 seconds; n_o = 1.3378; T = 23°C

Table 8 Data and Results for System No. 5

Distance cm	Refractive Index $(n - n_o)$	Concentration gm. solute per 100 cc.sol.	$\int_0^C x \, dc \times 10^2$ gm/sq.cm.	$\frac{dC}{dx}$ gm/cc/cm	$D \times 10^5$ cm^2/sec.
0.016	0.0010	0.840	0.034	0.699	1.221
0.026	0.0021	1.730	0.058	1.077	1.350
0.032	0.0030	2.438	0.072	1.277	1.407
0.039	0.0041	3.340	0.084	1.445	1.446
0.045	0.0054	4.363	0.090	1.551	1.452
0.052	0.0066	5.339	0.092	1.581	1.449
0.058	0.0078	6.352	0.098	1.570	1.563
0.063	0.0088	7.187	0.108	1.518	1.785
0.068	0.0098	7.931	0.121	1.451	2.091
0.073	0.0106	8.636	0.137	1.368	2.508
0.081	0.0119	9.647	0.166	1.220	3.409

Time t = 20.0 seconds; n_o = 1.3370; T = 23°C

Table 9 Data and Results for System No. 6

Distance cm	Refractive Index $(n - n_o)$	Concentration gm. solute per 100 cc. sol.	$\int_0^C x \, dc \times 10^2$ gm/sq.cm.	$\frac{dC}{dx}$ gm/cc/cm	D x 10^5 cm^2/sec.
0.011	0.0009	0.715	0.023	0.858	0.454
0.017	0.0017	1.335	0.038	1.251	0.510
0.023	0.0029	2.198	0.054	1.597	0.562
0.029	0.0043	3.282	0.067	1.831	0.608
0.034	0.0054	4.125	0.072	1.903	0.634
0.040	0.0068	5.268	0.075	1.887	0.658
0.047	0.0086	6.580	0.081	1.739	0.779
0.051	0.0096	7.365	0.090	1.597	0.939
0.056	0.0105	8.092	0.102	1.433	1.181
0.061	0.0114	8.740	0.115	1.264	1.515
0.072	0.0130	9.962	0.150	0.891	2.801

Time t = 30.0 seconds; n_o = 1.3360; T = 23°C

Table 10 Data and Results for System No. 7

Distance cm	Refractive Index $(n - n_o)$	Concentration gm. solute per 100 cc. sol.	$\int_0^C x\, dc \times 10^2$ gm/sq.cm.	$\frac{dC}{dx}$ gm/cc/cm	$D \times 10^5$ cm^2/sec.
0.010	0.0009	0.734	0.022	1.043	0.437
0.015	0.0017	1.355	0.036	1.487	0.500
0.020	0.0026	2.140	0.049	1.832	0.562
0.024	0.0037	2.994	0.061	2.033	0.621
0.028	0.0046	3.741	0.067	2.100	0.668
0.031	0.0054	4.455	0.071	2.090	0.711
0.034	0.0062	5.111	0.073	2.027	0.748
0.038	0.0072	5.882	0.074	1.897	0.811
0.043	0.0082	6.727	0.079	1.693	0.966
0.047	0.0090	7.367	0.085	1.501	1.178
0.052	0.0098	8.070	0.095	1.257	1.575
0.061	0.0110	9.013	0.115	0.877	2.731
0.076	0.0122	9.970	0.146	0.440	6.926

Time t = 24.0 seconds; n_o = 1.3360; T = 21°C

Table 11 Data and Results for System No. 8

Distance cm	Refractive Index $(n - n_o)$	Concentration gm. solute per 100 cc.sol.	$\int_0^C x\,dc \times 10^2$ gm/sq.cm.	$\frac{dC}{dx}$ gm/cc/cm	$D \times 10^5$ cm^2/sec.
0.012	0.0015	1.217	0.021	2.096	0.820
0.017	0.0031	2.501	0.034	2.982	0.937
0.020	0.0042	3.382	0.039	3.282	0.991
0.022	0.0053	4.290	0.042	3.412	1.031
0.025	0.0063	5.144	0.043	3.404	1.054
0.028	0.0076	6.148	0.045	3.262	1.146
0.030	0.0083	6.786	0.048	3.108	1.277
0.034	0.0098	8.007	0.057	2.692	1.753

Time t = 6.0 seconds; n_o = 1.3360; T = 21°C

Table 12 Data and Results for System No. 9

Distance cm	Refractive Index $(n - n_o)$	Concentration gm. solute per 100 cc.sol.	$\int_0^C x\,dc \times 10^2$ gm/sq.cm.	$\frac{dC}{dx}$ gm/cc/cm	$D \times 10^5$ cm^2/sec.
0.014	0.0011	0.870	0.026	1.077	0.594
0.022	0.0024	1.855	0.045	1.640	0.685
0.027	0.0037	2.809	0.058	1.939	0.746
0.031	0.0048	3.717	0.066	2.079	0.790
0.036	0.0060	4.622	0.070	2.115	0.823
0.041	0.0073	5.627	0.071	2.057	0.861
0.044	0.0082	6.273	0.074	1.975	0.931
0.047	0.0091	6.982	0.079	1.849	1.068
0.052	0.0102	7.840	0.089	1.652	1.351
0.059	0.0116	8.905	0.108	1.346	2.010

Time t = 20.0 seconds; n_o = 1.3360; T = 23°C

Table 13 Data and Results for System No. 10

Distance cm	Refractive Index $(n - n_o)$	Concentration gm. solute per 100 cc.sol.	$\int_0^C x\,dc \times 10^2$ gm/sq.cm.	$\frac{dC}{dx}$ gm/cc/cm	$D \times 10^5$ cm^2/sec.
0.013	0.0011	0.970	0.029	1.966	0.363
0.019	0.0023	1.940	0.048	1.704	0.708
0.024	0.0032	2.727	0.060	1.920	0.781
0.029	0.0046	3.883	0.071	2.032	0.878
0.034	0.0057	4.812	0.076	1.990	0.952
0.039	0.0069	5.816	0.077	1.842	1.047
0.045	0.0081	6.863	0.083	1.592	1.306
0.052	0.0093	7.892	0.096	1.266	1.892
0.062	0.0106	8.948	0.118	0.861	3.421
0.078	0.0117	9.931	0.150	0.428	8.772

Time t = 20.0 seconds; n_o = 1.3362; T = 23°C

APPENDIX D

TABLE 14. COMPARISON OF CONCENTRATION GRADIENTS OBTAINED BY TWO DIFFERENT METHODS

DAVIS METHOD		GOMPERTZ EQUATION	
Predicted Conc. gm/100 cc Soln.	Conc. Gradient gm/cc cm.	Predicted Conc. gm/100 cc Soln.	Conc. Gradient gm/cc cm.
1.001	0.5724	0.77	0.4518
1.557	0.7154	1.23	0.6160
2.827	0.9238	2.41	0.9144
3.905	1.0310	3.52	1.0950
4.711	1.0861	4.39	1.1912
5.284	1.1157	5.02	1.2412
5.939	1.1416	5.76	1.2812
6.746	1.1641	6.66	1.3076
7.614	1.1788	7.63	1.3114
9.343	1.1855	9.52	1.2576

TABLE 15. AVERAGE ABSOLUTE PERCENTAGE DEVIATION OF OBSERVED CONCENTRATIONS FROM THOSE PREDICTED BY GOMPERTZ EQUATION AND DAVIS METHOD

System No.		Average Absolute % Deviation* Using Gompertz Method	Average Absolute % Deviation* Using Davis Method
1	2.2% CMC	1.06	2.11
2	2.0% CMC	8.80	6.75
3	1.7% CMC	3.46	11.01
4	1.35% CMC	6.33	4.98
5	1.20% CMC	2.99	2.04
6	0.28% Carbopol	4.89	3.93
7	0.25% Carbopol	2.22	7.80
8	0.22% Carbopol	8.80	12.71
9	0.20% Carbopol	3.02	6.46
10	0.18% Carbopol	8.52	7.61

$$* \text{ A.A.P.D} = \frac{100}{N} \sum_{i=1}^{N} \left| \frac{C_{A_{io}} - C_{A_i}}{C_{A_i}} \right|$$

APPENDIX E

CALCULATION OF DIFFERENTIAL DIFFUSION COEFFICIENT OF D-GLUCOSE USING WILKE-CHANG CORRELATION

The form suggested by Wilke and Chang is

$$D_{AB} = \frac{7.4 \times 10^{-8} (\psi_B M_B)^{1/2} T}{\mu (V_A)^{0.6}}$$

where D_{AB} = diffusivity of solute A in dilute solutions in solvent B, sq. cm./sec.

M_B = mol. wt. of solvent;

T = temp. °K.

μ = viscosity of solution,centipoise.

V_A = solute molal volume of the normal boiling point, cc /gm mole.

ψ_B = an association factor for the solvent, 2.6 for water as solvent.

The differential diffusion coefficient of D-Glucose in water at 21°C is calculated as follows:

M_B = 18

T = 294 °K

μ = 0.9810

ψ_B = 2.6

V_A = 177.6

$$D_{AB} = \frac{7.4 \times 10^{-8} (2.6 \times 18)^{0.5}\ 294}{(177.6)^{0.6} \times 0.9810}$$

$$= 0.67 \times 10^{-5} \text{ cm.}^2\text{/sec.}$$

In a similar way the differential diffusion coefficient of D-Glucose in water at 23°C is calculated to be 0.71 x 10^{-5} $cm.^2/sec$.

APPENDIX F

LIST OF EQUIPMENT AND APPARATUS USED

1. Ultek TNB High Vacuum System: M.O. 7-7225; Serial No. 7161, designed and manufactured for University of Missouri, Rolla, Missouri.

2. Microscope: American Optical, Microstar Series 4 microscope; Serial No. 392668, ALOE Scientific Co., St. Louis, Missouri.

3. Abbe Spencer Refractometer: No. 1182; A. S. ALOE Co., St. Louis, Missouri.

4. Precision Abbe Refractometer: Cat. No. 33-45-01-01; Bausch and Lomb; Rochester, New York.

5. Cathetometer: Nos. 5100 and 5150 Cathetometer; Eberbach Corporation, Ann Arbor, Michigan.

6. Sodium Lamp: SLA-5c for use on 110-120 volts-A.C. 60 cycle; George W. Gates and Co., Franklin Square, L. I., New York.

7. Ostwald Type Capillary Flow Viscometer: Cat. No. 13-617; Cannon-Fenske Routein; Fisher Scientific Co., Pittsburgh, Pennsylvania.

8. Fisher Watch Guard: Catalog No. 14-651-5; Instrument Division; Fisher Scientific, Pittsburgh, Pennsylvania.

APPENDIX G

NOMENCLATURE

A = area under the curve of concentration versus distance, (gm/100 cc soln.) cm.

a = intercept of straight line that results when $(x - x_1)/\oint$ is plotted against x.

a_1, a_2, a_3 = constants in Gompertz Equation.

b = slope of straight line that results when $(x - x_1)/\oint$ is plotted against x.

C = concentration of solute, gm/cc.

C_o = initial concentration of solute, gm/cc.

C' = concentration of solute at original interface, gm/cc.

c = concentration of solute, gm/100 cc.

D = molecular diffusion coefficient of a solute, sq. cm./sec.

$\overline{D}$ = integral (average) diffusion coefficient of a solute, sq. cm./sec.

d = distance between adjacent bright fringes, cm.

J_i = diffusion flux of 'i' relative to mass average velocity, gm/sq.cm. sec.

M = molecular weight.

N = diffusion flux, gm/sq. cm. sec.

N_i = diffusion flux of 'i' relative to stationary coordinates, gm/sq. cm. sec.

n = refractive index of solution.

n_o = refractive index of solvent.

r = $x/2\sqrt{t}$, Boltzmann's variable, cm./(sec.)$^{1/2}$

T = absolute temperature, ^{o}K.

t = time, seconds.

V = volume, cu. cm.

w = weight fraction of solute.

X = fractional area occupied, sq. cm.

x = coordinate, corresponds to distance, cm.

y = coordinate, corresponds to concentration of solute, gm/cc.

Subscripts

A = solute A

B = solvent B.

C = at some concentration C.

C_o = at initial concentration C_o.

i = i th solute.

t = at time t.

x = direction x.

y = direction y.

Greek Letters and Other Symbols

α = intercept, Gompertz Equation.

θ = wedge angle, minutes or rad.

λ = wave length, m or cm.

μ = viscosity of fluid, cps.

∇ = vector notation.

Ψ = an association factor for solvent.

$\oint$ = symbol used for sigmoid function.

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IX. VITA

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