MEASUREMENT OF LIQUID PHASE DIFFUSIVITIES[41] OF SODIUM POLYSTYRENE SULFONATE, DEXTRAN T40, AND DEXTRAN T80 AT 25°C

by 45

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TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

LIST OF FIGURES -- Continued

CHAPTER I

INTRODUCTION

For over a century interest has been maintained in both theoretical and practical aspects of liquid phase diffusion phenomena. As a controlling factor governing molecular diffusion, the knowledge of diffusivity is essential in chemical engineering designs involving distillation, absorption, extraction, mixing, catalytic reactions and other processes. A summary of experimental methods for measuring diffusivity has been reported (1). Unfortunately experimental data for high molecular weight chemicals are seldom available in the literature.

The main reason for the lack of experimental results is the excessive time required for measuring the diffusivity. Furthermore, most of the methods employed involve tedious and difficult measurements of concentration patterns in liquid phase diffusion.

One of the recent developments in this field has been reported by Nishijima and Oster (2,3), in which a microinterferometric method was employed in evaluating the concentration gradient in the liquid phase diffusion for systems whose refractive index-concentration relationship is linear. Simple and powerful as it is, this technique reduces the time required for measurement from hours or days to minutes.

This study was conducted to find the range of applicability of this method and its application in determining the diffusivities of some high molecular weight polymers in aqueous systems. Sodium polystyrene sulfonate (SPSS) with an average molecular weight of 525,000 and two dextrans, T40 and

T80, with average molecular weights of 39,500 and 85,800 respectively were selected for measurement because of their increasing importance in medical research (4,5,6).

The SPSS system was measured with an average concentration of 5 % to 30 % SPSS by weight, and the two dextran systems were both measured at 15 % to 45 % dextran by weight. All were at ambient pressure and at a temperature of 25°C.

As a minor part of this undertaking, a revised Chauvenet's criterion for discarding invalid measurements was developed for analyzing the experimental data.

CHAPTER II

THEORETICAL ASPECTS

(1) Theory of diffusion

In a binary system of two miscible liquids the existence of a concentration gradient will give rise to a driving force which tends to make the system homogeneous. This phenomenon is called ordinary diffusion. The theoretical foundation of the quantitative study done by Fick (7) and Graham (8) established the experimental basis of this study. The diffusivity is expressed by Fick's first law. For diffusion in a one-dimensional binary system Fick's first law may be written as (9)

$$J = - D \frac{\partial C}{\partial x} \tag{1}$$

where J is the flux of mass transfer through a unit area in a reference plane perpendicular to the x direction in a unit of time; $\frac{\partial C}{\partial x}$ is the concentration gradient in the direction of flux; the proportionality factor D is called the binary diffusion coefficient, or binary diffusivity; and the negative sigh indicates that the flow is in the opposite direction to the direction of the concentration gradient.

For mathematical analysis of diffusion experiments, it is convenient to transform Fick's first law into a form known as Fick's second law. By combining equation (1) with the requirements of continuity of mass over a differential volume element of unit cross-section, Fick's second law may be written as (10)

$$\frac{\partial C}{\partial t} = \frac{\partial}{\partial x} \left(D \frac{\partial C}{\partial x} \right) \tag{2}$$

If the diffusivity, D, is a constant, equation (2) becomes

$$\frac{\partial C}{\partial t} = D \frac{\partial^2 C}{\partial x^2} \tag{3}$$

Consider the case of free diffusion in which two solutions of different concentrations fill a column of effectively infinite length under no external forces. The diffusion begins from the sharp interface of the two solutions and does not reach the ends of the column during the period of observation. Equation (1) is now subject to the following initial conditions

$$C = C_o' \qquad \text{at} \quad t = 0 \qquad x > 0 \tag{4}$$

$$C = C_o'' \qquad \text{at} \quad t = 0 \qquad x < 0 \tag{5}$$

and these boundary conditions.

$$C = C_o' \qquad \text{at} \quad t > 0 \qquad x = +\infty \tag{6}$$

$$C = C_o'' \qquad \text{at} \quad t > 0 \qquad x = -\infty \tag{7}$$

By defining the dimensionless concentration gradient

$$\overline{C} = \frac{C - C_o''}{C_o' - C_o''}$$

and introducing the dimensionless parameter

$$\eta = \frac{x}{\sqrt{4Dt}}$$

equation (3) can be transformed into the following ordinary differential equation

$$\frac{d^2\overline{C}}{d\eta^2} = -2\eta \frac{d\overline{C}}{d\eta} \tag{8}$$

The initial and boundary conditions, equations (4) through (7) become

$$\overline{C} = 1 \qquad \text{at} \qquad \eta = +\infty \tag{9}$$

$$\overline{C} = 0 \qquad \text{at} \qquad \eta = -\infty \tag{10}$$

Equation (8) is a second order ordinary differential equation. Its analytical solution is

$$\overline{C} = \int_o^{\eta} K_1 e^{-z^2} dz + K_2 \tag{11}$$

where K_1 and K_2 are integration constants. Substitution of equation (9) and (10) into equation (11) yields

$$1 = \int_o^{\infty} K_1 e^{-z^2} dz + K_2 \tag{12}$$

$$0 = \int_o^{-\infty} K_1 e^{-z^2} dz + K_2 \tag{13}$$

By solving equations (12) and (13) simultaneously the two constants, K_1 and K_2, are found to be

$$K_1 = \frac{1}{\sqrt{\pi}}$$

$$K_2 = \tfrac{1}{2}$$

The analytical solution of equation (8) subject to equations (9) and (10) can thus be written as

$$\overline{C} = \tfrac{1}{2} \left(1 + \frac{2}{\sqrt{\pi}} \int_o^{\eta} e^{-z^2} dz \right)$$

$$= \tfrac{1}{2} \left[1 + \operatorname{erf} (\eta) \right] \tag{14}$$

or

$$\frac{C - C_o''}{C_o' - C_o''} = \tfrac{1}{2} \left[1 + \operatorname{erf} \left(\frac{x}{\sqrt{4Dt}} \right) \right] \tag{15}$$

If the relationship between the concentration gradient and the coordinate x is measurable experimentally, D can then be determined from equation (15).

(2) Microinterferometric method

The most important feature of this study is the use of a microinterferometric method which permits the concentration profiles to be determined easily, rapidly and without disturbing the materials under study. This method, developed by Nishijima and Oster (2,3) and employed by F. S. Jerome (11), is based on the determination of the refractive index gradient by interferometric measurements observed under a microscope.

According to the theory concerning the Brownian movement (12), the average of the square of the displacement of a particle is proportional to the time during which it was traveling. Thus, by observing the diffusion process under a microscope, the time required for the observation is reduced by the square of the magnification factor. Diffusion measurements normally requiring hours or days to carry out in a conventional apparatus may be finished in minutes by use of the micro-method.

The basic feature of the present interferometric method is the use of a diffusion cell which forms an optical wedge. When a parallel beam of monochromatic light passes through a wedge of air or liquid between two partially reflecting glass plates, multiple reflections occur within the wedge and the Fabry-Perot type interference fringes are produced from the alternative constructive and destructive interference of the transmitted and the reflected light beams. When the optical distance, which is defined as the product of the geometric distance and the refractive index of the medium in the wedge, is some odd integer of half the wavelength of the incident light then cancellation occurs, as shown in Figure 1 (a).

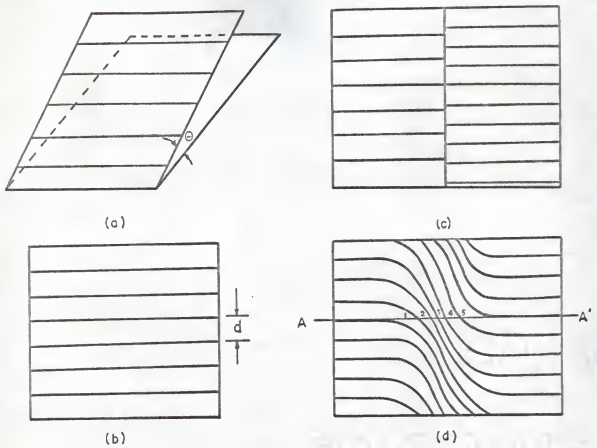


Fig. 1. The various interference patterns obtained by an optical wedge diffusion cell.

(a) The optical wedge.

(b) The interference pattern obtained when the medium in the cell is homogeneous.

(c) The interference pattern for two non-diffusing liquids.

d The interference pattern for two diffusing liquids at $t > 0$.

If the refractive index of the medium in the wedge is constant throughout the wedge, then the optical distance between two successive beams varies linearly along the length of the wedge. In this case equally spaced interference fringes are formed as shown in Figure 1 (b). The distance d between two adjacent fringes is given by (13)

$$d = \frac{\lambda}{2n\theta} \tag{16}$$

where λ is the wavelength of the incident light, n is the refractive index of the medium in the wedge, and θ is the wedge angle.

When two non-diffusing liquids are placed in the wedge, the distance d is shorter at the side occupied by the liquid with the greater refractive index. The fringes are discontinuous at the interface where they contact each other, as shown in Figure 1 (a).

If two diffusing liquids are placed in the wedge, a sharp interface similar to that in Figure 1 (c) is formed at the moment when the two liquids make contact. After diffusion occurs between the two liquids, the refractive index across the interface varies continuously so that curved interference fringes are obtained as shown in Figure 1 (d). This interference pattern has three significant properties upon which the experiment in this study is based:

(1) Along any fringe the optical distance is constant, that is, the fringes represent contour lines of constant optical distance.

(2) Along any line parallel to the original interface, the distance between adjacent fringes is constant. From equation (16) it is seen that the refractive index is constnat along this line.

(3) Any line, e. g. AA' in Figure 1 (d), perpendicular to the original interface represents a line of constant wedge thickness. It is evident the

change of optical distance along this reference line AA' depends on the change of the refractive index along this line. A plot of the fringe density against the position of the intersections of the fringes and the reference line is a refractive index gradient curve.

If there exists a linear relationship between the refractive index n and the concentration of the liquid, C, i.e. if

$$n = n_o + KC$$

where n_o and K are constants, then equation (15) can be written as

$$\frac{n - n_o''}{n_o' - n_o''} = \frac{1}{2}\left[1 + \text{erf}\left(\frac{x}{\sqrt{4Dt}}\right)\right] \qquad (17)$$

in which n_o' and n_o'' are the refractive indices of the liquids with concentration C_o' and C_o'' respectively.

The diffusivity can now be evaluated from equation (17) once the relationship between n and x is determined along a line perpendicular to the original interface in the diffusion wedge.

(3) Evaluation of diffusivity

For the experimental runs of diffusivity measurements (the procedures are presented in Chapter III), pictures of the interference pattern are taken at successive time intervals. A reference line perpendicular to the original interface in the diffusion wedge is drawn on the diffusion picture. If the reference line is suitably selected, it is possible that each end of the reference line will coincide with a fringe at both sides of the diffusion picture as shown in Figure 1 (d). The intersections are numbered from the left side of the diffusion picture. In this case the intersections divide the dif-

ference $n_o'-n_o''$, and thus $C_o'-C_o''$, exactly into equal parts numbering one plus the total number of intersections. The dimensionless refractive index, $\frac{n - n_o''}{n_o'-n_o''}$, and thus the dimensionless concentration, $\frac{C - C_o''}{C_o'-C_o''}$, can therefore be expressed as

$$\frac{\text{intersection number at a certain intersection}}{1 + \text{total number of intersections}}$$

i.e.

$$\frac{j}{1 + \text{total number of intersections}}$$

where j is equal to 1, 2, 3, • • • •, total number of intersections.

From equation (17), which is reproduced below

$$\frac{n - n_o''}{n_o'-n_o''} = \tfrac{1}{2}\left(1 + \operatorname{erf}\left(\frac{x}{\sqrt{4Dt}}\right)\right) \tag{17}$$

or

$$\bar{n} = \tfrac{1}{2}\left[1 + \operatorname{erf}(\eta)\right] \tag{18}$$

one can see that a plot of the position of the intersections, x, versus the dimensionless refractive index, $\bar{n}$, on probability graph paper will yield a straight line. The slopes of these lines are equal $(4Dt)^{\frac{1}{2}}$ if the $\bar{n}$ is converted to η according to Figure 2, e.g.

$$\eta = \frac{x}{\sqrt{4Dt}} = 0.90622 \qquad \text{at } \bar{n} = 0.90$$

$$= -0.90622 \qquad \text{at } \bar{n} = 0.10$$

The diffusivity can therefore be determined according to the following equa-

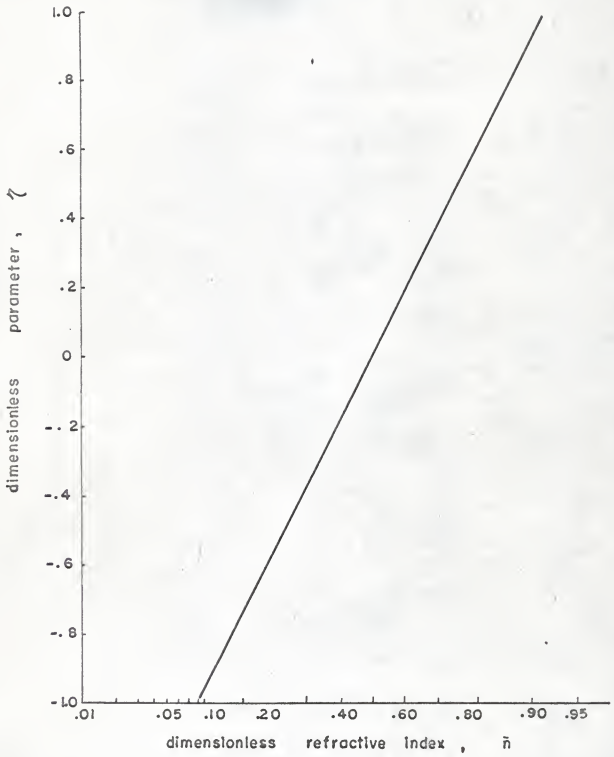


Fig. 2. Relationship of γ & $\bar{n}$ in equation (18).

tion:

$$D = \frac{(\text{Slope})^2}{4t} \tag{19}$$

where t is the time at which the diffusion picture is taken.

(4) Zero time correction

When the two liquids are brought into physical contact by lowering the upper slide of the optical wedge diffusion cell, there will be some bulk mixing of the two liquids. This initial mixing causes the concentration distribution at any time to appear as though the boundary had been formed before it actually took place. The time between the apparent and actual boundary formation must be calculated and added to the observation time.

Let the time difference between the apparent and the observed time be t_o, i.e.

$$t = t' + t_o \tag{20}$$

where t is the apparent time and t' is the observed time. Equation (19) can then be written as

$$Dt = \frac{(\text{Slope})^2}{4} \tag{21}$$

Substituting equation (20) into equation (21) gives

$$D(t' + t_o) = \frac{(\text{Slope})^2}{4} \tag{22}$$

Dividing equation (22) through by t' yields

$$D(1 + \frac{t_o}{t'}) = \frac{(\text{Slope})^2}{4t'} \tag{23}$$

The $\frac{(\text{Slope})^2}{4t'}$ in equation (23) is defined as observed diffusivity. From equation (23) it can be seen that the plot of the observed diffusivity against the reciprocal of the observed time will yield a straight line. The intercept is the actual diffusivity.

CHAPTER III

EXPERIMENTAL APPARATUS AND PROCEDURES

The experimental apparatus used in this study consisted of the diffusion apparatus (optical wedge diffusion cell, microscope, camera and laser), the coordinate measuring apparatus, a refractometer and viscometers. A brief description of the apparatus is given as follows:

(1) Diffusion apparatus (11)

A diagrammatic sketch of the diffusion apparatus is shown in Figure 3. The narrow cone of coherent monochromatic light from laser L is directed onto the flat reflecting mirror R. This mirror reflects the light beam upward through the optical wedge diffusion cell W which is mounted on a temperature controlled microscope stage S. The image of interference fringes is focused and magnified through the microscope M onto the photographic film F in camera C for taking pictures. Further description of particular elements follows:

(i) Optical wedge diffusion cell

The optical wedge diffusion cell consists of two 1.5" x 1" microscope slides. These slides were prepared by the Tokyo Electronics Corp., Tokyo, Japan. Each slide was partially metal coated on one side in order to give about 85 % reflectivity and 15 % transmission of the incident light. The slides were separated by spacers to form the optical wedge diffusion cell. Figure 4 shows a close view of the diffusion cell assembled in position on the temperature controlled stage.

(ii) Microscope and camera

A Bausch & Lomb student series microscope was used in this study. The

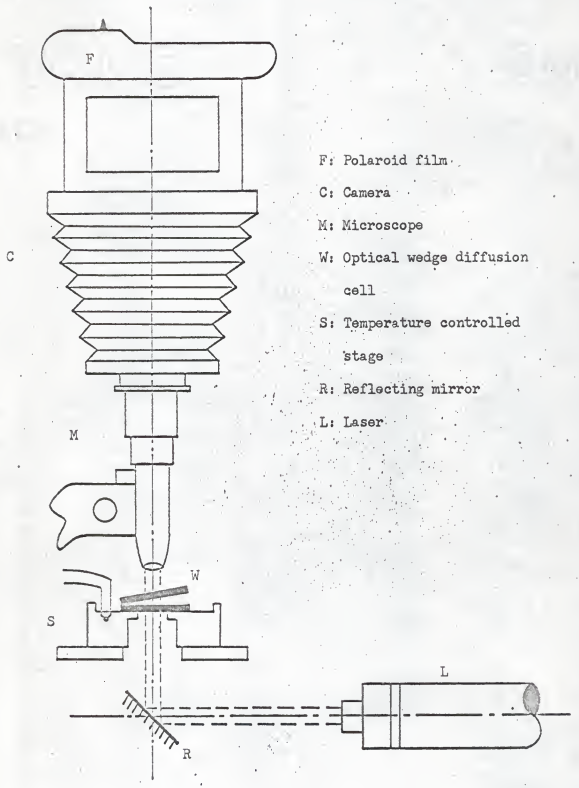


Fig.3. The diagram of the diffusion apparatus.

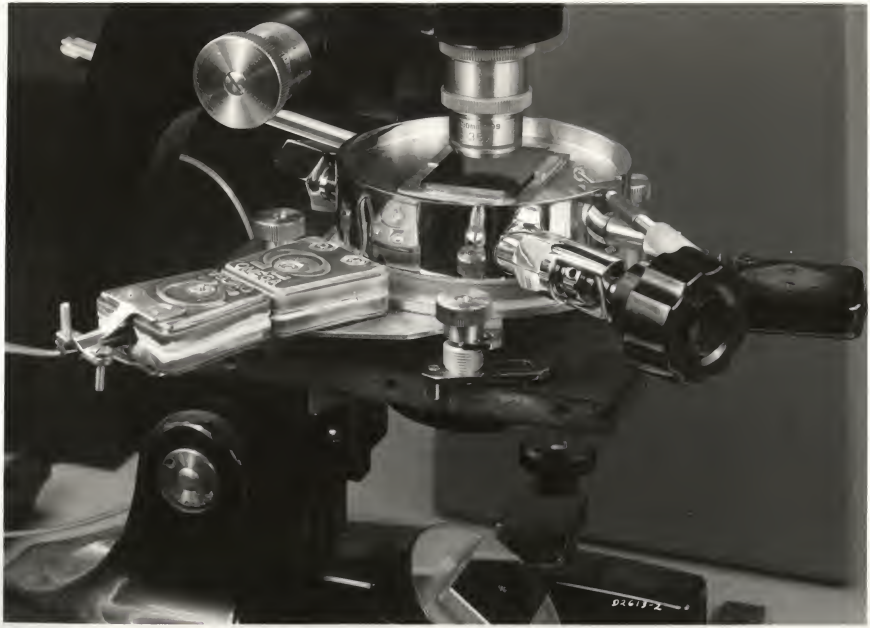


Fig. 4. The optical wedge diffusion cell on the temperature controlled stage.

objective lens has a 30 mm focal length, N.A. 0.09 and a magnification factor of 3.5. The ocular is an ultraplane lens with a magnification factor of 7. The ultraplane lens is a combination of high precision negative lenses in order to reduce the distortion of the image caused by the curvature of the field.

The camera was a Bausch & Lomb photomicrographic camera model L. It was mounted with a Bausch & Lomb reflex attachment and a Polaroid Land back camera. A Polaroid black and white transparency film type 46-L was used. The assembly of the Bausch & Lomb microscope and camera is shown in Figure 5.

(iii) Light source -- Laser

The Model 5200 gas laser of the Perkin-Elmer Corp. was used as the source of polarized coherent monochromatic radiation. This produced radiation at 6328 $\mathring{A}$ by means of the Model 5202 dc power supply. Both are shown in Figure 6.

(2) Coordinate measuring apparatus

Figure 7 shows the Leitz-Wetzlar 6 x 6 inch coordinate measuring microscope. Beneath the microscope tube is a micrometer table which can be moved along two horizontal axes at right angles to each other and which may also be rotated in the same horizontal plane. This apparatus was used to measure the positions of the intersections of fringes and the reference line on the diffusion pictures taken during experimental runs.

(3) Refractometer

The Bausch & Lomb type Abbe-3L refractometer was used for the measurements of the refractive indices of liquids of interest in this study. The temperature controller was a Haake, Berlin Circulator Series ED. This unit was mounted in an open water bath.

(4) Viscometers

Fig. 5. The Bausch & Lomb microscope and camera.

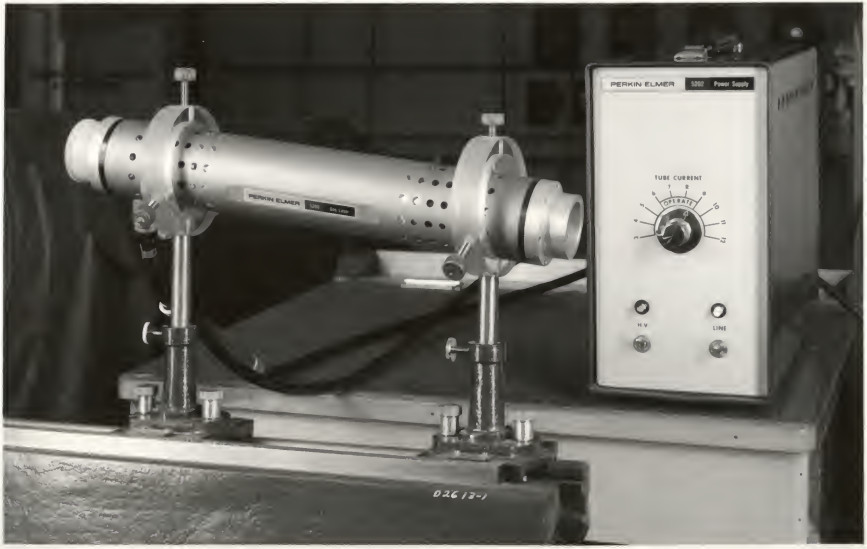


Fig. 6. The Perkin Elmer Model 5200 gas laser and Model 5202 power supply.

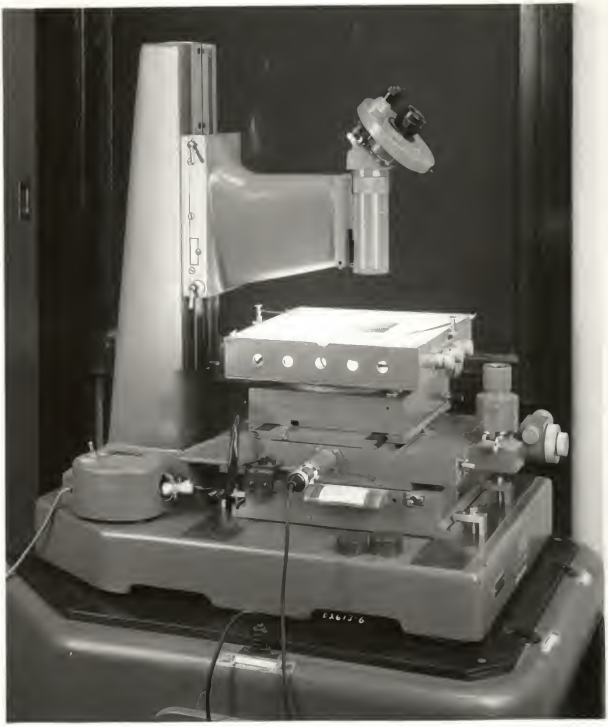


Fig. 7. The coordinate measuring apparatus.

The viscosity of the liquids employed in this study ranged from several centipoises to several hundred poises. For low viscosity range measurements the Cannon-Fenske routine viscometers were used. The Brookfield viscometer was used for measuring viscosity at the high range in which the viscosity usually depends on the shear rate. A description of both viscometers follows:

(i) Cannon-Fenske routine viscometers

Figure 8 shows a Cannon-Fenske routine viscometer immersed in a temperature controlled water bath. The viscometers of size 50, 100, 150, 200, 300 and 350 were used in the present measurements. They were manufactured by Fisher Scientific Co. and calibrated by Cannon Instrument Co. according to Standard Test ASTM D 445.

(ii) Brookfield viscometer

Figure 9 shows the Brookfield model LVF viscometer. It has four spindles to provide various torques and eight speeds, 60, 30, 12, 6, 3, 1.5, 0.6 and 0.3 rpm, to provide a wide range of shear rate. The full scale torque is 673.7 dyne-cm and the relationship between torque and dial reading is linear. This viscometer was manufactured by the Brookfield Engineering Lab. Inc..

(5) Experimental procedures

First of all, the refractive index was measured in order to check the linear relationship between it and the concentration of solution. A diffusion run started with the setting of one of the slides on the microscope stage with the metallized surface up. A drop of each of the two liquids at different concentrations was pipetted onto the slide side by side along the width of the slide. The second slide which was slowly placed over the first with the metallized surface down forced the two drops into physical contact. The stopwatch was started when the wedge was formed. Four observations of

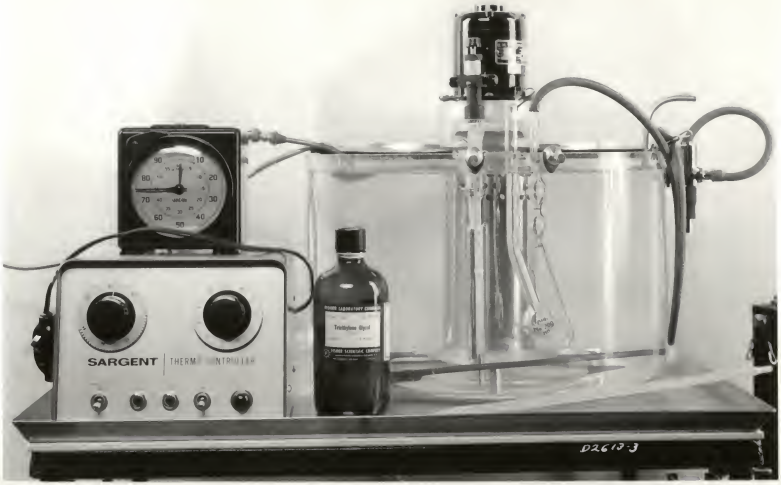


Fig. 8. The Cannon-Fenske routine viscometer immersed in the water bath.

Fig. 9. The Brookfield Model LVF viscometer.

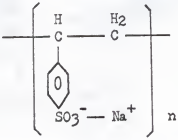
each diffusion run were recorded by taking pictures at successive time intervals. Reference lines were drawn on these diffusion pictures, as was stated in Section II-3, after they were developed by use of Polaroid Dippit # 646. The positions of the intersections of the reference lines and the interference fringes were then measured with the coordinate measuring apparatus. The diffusivity can then be evaluated from a plot of the positions of the intersections versus the dimensionless refractive index on probability graph paper according to the explanations in Sections II-3 and II-4.

CHAPTER IV

MATERIALS

(1) Sodium polystyrene sulfonate

Sodium polystyrene sulfonate, abbreviated as SPSS, is a synthetic, water-soluble, high molecular weight, organic polymer. Its typical structure is



Some of its physical properties are listed in Table 1.

The SPSS employed in this study was produced by The Dow Chemical Company, Midland, Michigan. It was subsequently purified to be 84.04 % active.

(2) Dextrans

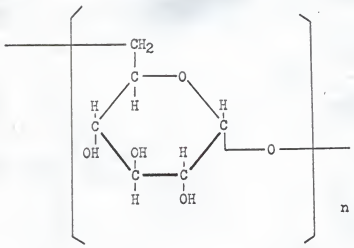
Dextran is an anhydroglucose polymer produced by numerous strains of Leuconostoc and closely related bacteria in sucrose-containing solutions. It has been shown that the bacteria produce an enzyme, termed dextransucrase, which converts sucrose to dextran according to the following equation (4).

$$n\ \text{Sucrose} \longrightarrow \text{Dextran} + n\ \text{Fructose}$$

Thus, it is evident that dextran consists of long chains of glucose units with the following structure (5).

Table 1. Physical properties of SPSS used in this study.

Average molecular weight		525,000
Form		white powder
Bulk density		40 lb/ft^3
Soluble in		water, glycerine, ethylene & propylene glycols
Ionic charge		strongly anionic
Solution PH	1 % solution	11.6
	3 % solution	12.0
Freezing point	1 % solution	30.42° F
	3 % solution	31.06° F
Maximum recommended storage temperature		130° F
Maximum recommended storage time		one year
Maximum recommended storage time, 3 % solution		one month



$(C_6 H_{10} O_5)_n$

Dextrans are found useful in various fields of medical research, especially in the rheology of human blood (5, 6, 14, 15).

The dextrans used in this research were T40 and T80 produced by Pharmacia, Uppsala, Sweden. Some of their properties are listed in Table 2. Figure 10 shows their integral molecular weight distribution.

Table 2. Properties of Pharmacia dextrans.

Molecular weight, $\bar{M}w$*	T40	39,500
	T80	85,800
$\bar{M}n$*	T40	24,000
	T80	43,700
Form		spray-dried white powder
Bulk density		20.6 lb/ft^3
Solution PH		about 7
Ionic charge		neutral
Soluble in		water
Specific rotation		+199°
Hetrogeneity, $\bar{M}w/\bar{M}n$	T40	1.646
	T80	1.963
Intrinsic viscosity,		$2.43 \times 10^{-3} (\bar{M}w)^{0.42}$
	T40	0.196
	T80	0.270

* $\bar{M}w$ = weight average of molecular weight

$$= \frac{\sum n_i M_i^2}{\sum n_i M_i}$$

$\bar{M}n$ = number average of molecular weight

$$= \frac{\sum n_i M_i}{\sum n_i}$$

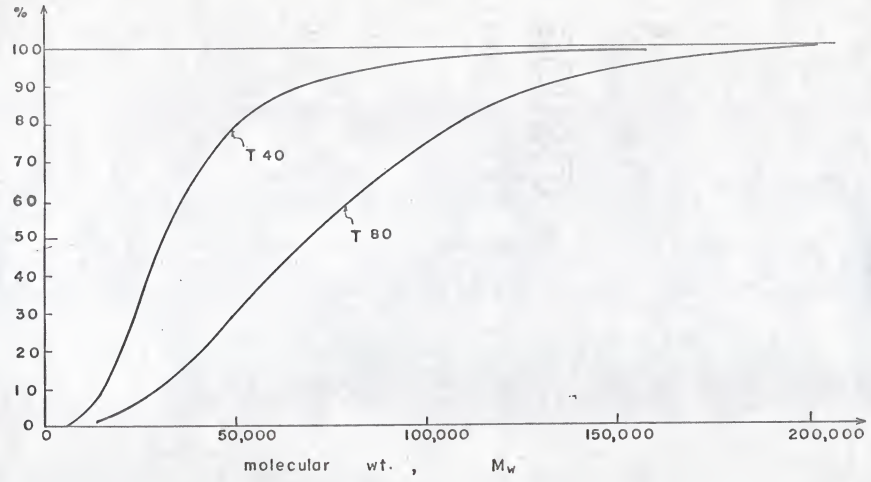


Fig. 10 Integral molecular weight distribution curve of Dextrans.

CHAPTER V

EXPERIMENTAL RESULTS

The diffusivities for the SPSS system with a concentration range of 5 % to 30 % SPSS by weight and for the two dextran systems from 5 % to 45 % dextran by weight at 25°C were measured. Each experimental run was carried out at ambient pressure and with a concentration difference, $C_o'-C_o''$, of 10 % solute by weight. As the optical wedge diffusion cell is not well insulated, the temperature of diffusing liquids in the cell will change drastically if the ambient temperature is quite different. The laboratory temperature was therefore adjusted to a temperature around 25°C. Minor changes of temperature were achieved by employing the temperature controller embedded in the microscope stage. The temperature on the stage can be measured with the thermometer attached to the stage. During the experimental runs of this study, the temperature was 25° ± 0.5°C. Measurements of refractive index, specific gravity and viscosity were also made for each of the above systems at 25°C.

In the first two sections of this chapter the experimentally measured specific gravity, refractive index and viscosity are presented with some pertinent discussion regarding the data. In Section 3 the evaluation of observed diffusivity from the diffusion pictures taken in diffusivity runs and zero time correction in these observed diffusivities are presented.

(1) Specific gravity and refractive index

The observations concerning specific gravity and refractive index measurements are listed in Tables 3 and 4 and are plotted against concentrations of the solution in Figure 11, 12 and 13 for the SPSS and the two dextran systems respectively.

Table 3. Specific gravity and refractive index of SPSS system at 25°C.

Concentration, Wt. fraction of SPSS	Specific gravity	Refractive index
0	0.9971	1.3327
0.050	1.0211	1.3415
0.100	1.0462	1.3505
0.150	1.0685	1.3602
0.200	1.0938	1.3700
0.250	1.1155	1.3801
0.300	1.1425	1.3907
0.350	--	1.4025

Table 4. Specific gravity and refractive index of dextran systems at 25°C.

Concentration, Wt. fraction of dextran	Specific gravity		Refractive index	
	T40	T80	T40	T80
0.050	1.0095	1.0180	1.3393	1.3400
0.100	1.0281	1.0355	1.3466	1.3472
0.150	1.0474	1.0566	1.3527	1.3550
0.200	1.0684	1.0782	1.3610	1.3628
0.250	1.0892	1.0975	1.3712	1.3711
0.300	1.1105	1.1216	1.3790	1.3798
0.350	1.1343	1.1417	1.3881	1.3885
0.400	1.1575	1.1713	1.3981	1.3979
0.450	1.1821	1.1954	1.4087	1.4079
0.500	--	--	1.4185	1.4189

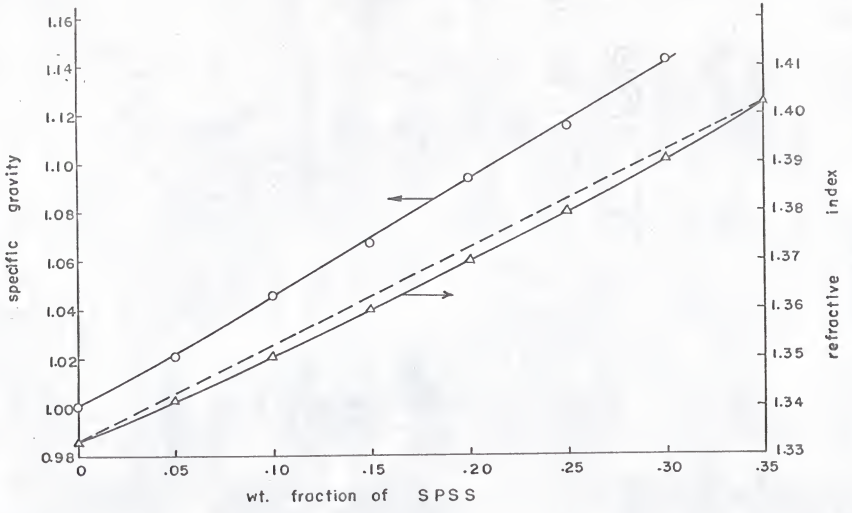


Fig 11. Specific gravity & refractive index vs. concentration for SPSS system at 25° C.

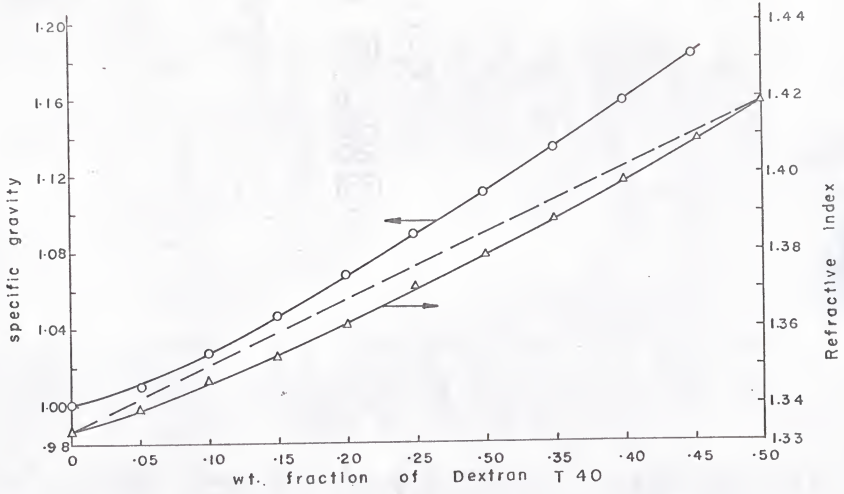


Fig.12. Specific gravity & refractive index vs. concentraction for Dextran T40 system at 25° C.

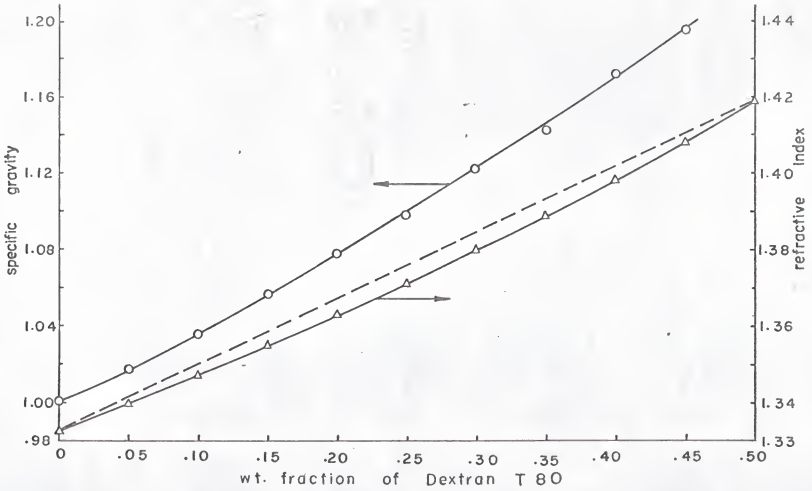


Fig.13. Specific gravity & refractive index vs. concentration for Dextran T 80 system at 25° C.

Data concerning specific gravity are used in the following section for the determination of Newtonian viscosity which is defined as the product of density and kinematic viscosity measured with the Cannon-Fenske viscometers.

As in most cases, the refractive indices of these three systems were found to be not absolutely linear for the whole concentration range, but for a small concentration range such as 0.10 solute by weight, it is satisfactory to consider the refractive index-concentration relationship as linear. That confirmed the assumption made in obtaining equation (17).

(2) Viscosity

For a high molecular weight polymer solution to flow, the polymer segments must move relative to the solvent. Local viscosity is determined by the solvent as altered by the chain entanglement of the polymer segments. The orientation of solvent molecules along the polymer chain increases the effective volume of the segment which must move with respect to the solvent. Since water possesses a hydrogen-bonded polymeric structure, local distortions in the polymer chain tend to be stabilized by association with water. This stabilization gives rise to the high shear rate dependence of viscosity of some polymer solutions (16). The SPSS system was found to be one of them. Figure 14 shows the effects of shear rate on SPSS solution viscosities measured with a Brookfield viscometer.

In the optical wedge diffusion cell the diffusion between two liquids occurs under almost no shear rate. Hence the data in Figure 14 were extrapolated to zero shear rate to obtain the viscosity suitable for this study. A summary of these viscosities is listed in Table 5; they are plotted versus concentration of SPSS solution in Figure 15.

Contrary to the finding for the SPSS system, the viscosities of the two dextran systems were found to be shear rate independent. Table 6 and Figures

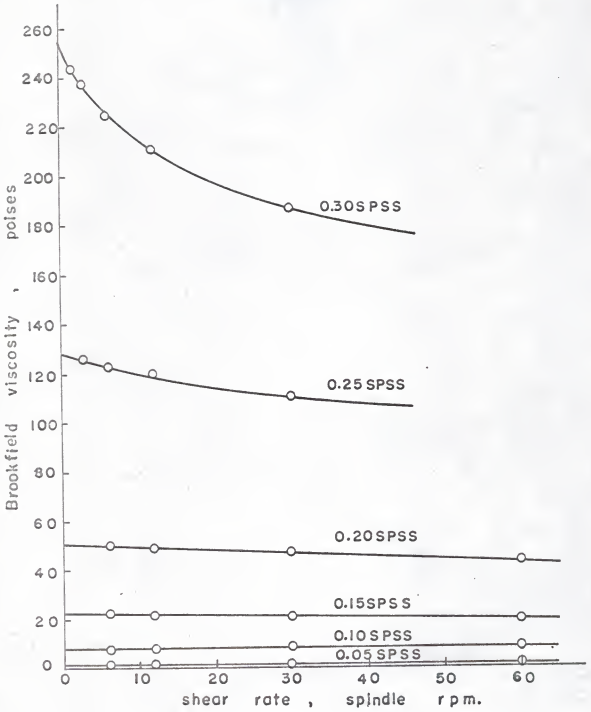


Fig. 14. Brookfield viscosity vs. shear rate for SPSS system at 25° C.

Table 5. Summary of Brookfield viscosity of SPSS system at 25°C.

Concentration, Wt. fraction of SPSS	Spindle no. / Shear rate, Spindle rpm	Brookfield viscosity, poises						
		1.5	3	6	12	30	60	0*
0.050	2	--	--	1.85	1.875	1.91	1.905	1.87
0.100	3	--	--	8.40	8.50	8.56	8.32	8.50
0.150	3	--	--	22.20	22.00	21.28	19.64	22.60
0.200	4	--	--	50.00	48.50	47.00	42.90	50.50
0.250	4	--	126.0	123.0	120.0	110.8	--	128.0
0.300	4	244.0	238.0	225.0	211.0	187.0	--	254.0

* By extrapolation.

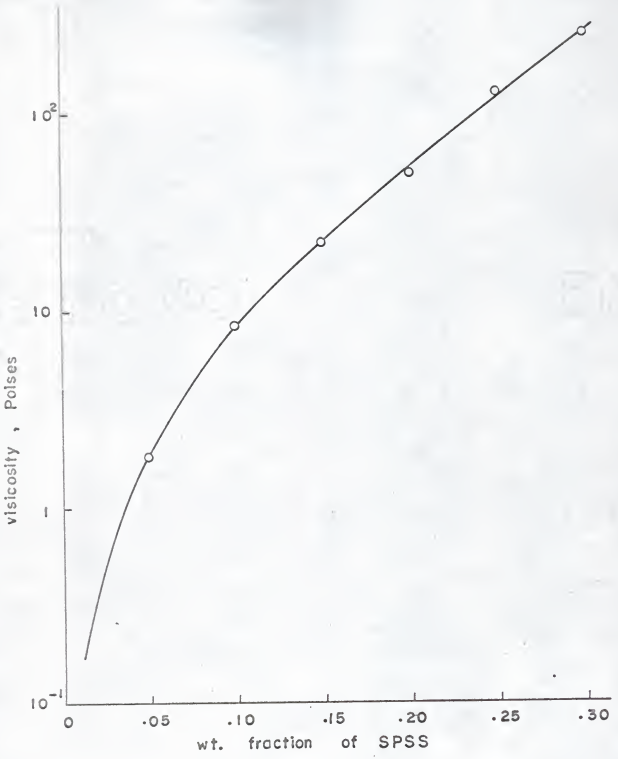


Fig.15. Visicosity vs. concentration for SPSS system at 25° C.

Table 6. Summary of Brookfield viscosity of dextran systems at 25°C.

	Concentration, Wt. fraction of dextran	Spindle no.	Shear rate, Spindle rpm	Viscosity, centipoises 3	6	12	30	60	0*
T40	0.400	2		--	283	288	281	280	286
	0.450	2		600	583	599	600	--	592
T80	0.400	2		683	678	684	703	--	681
	0.450	3		--	1700	1700	1724	1713	1702

* By extrapolation.

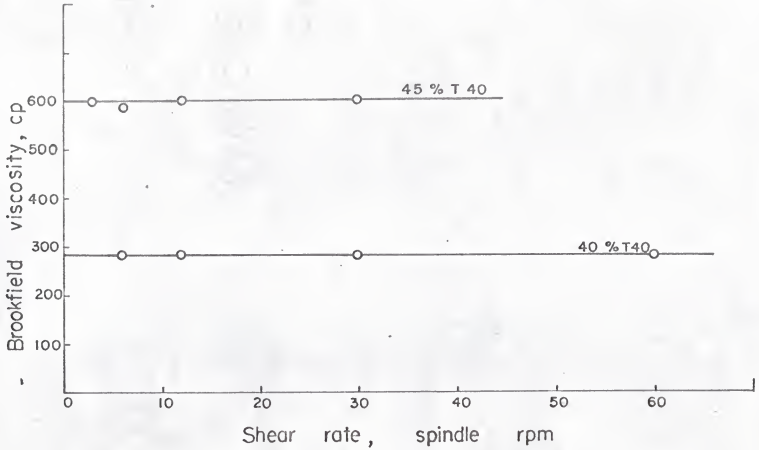


Fig. 16. Brookfield viscosity vs. shear rate for Dextran T 40 system at 25°C.

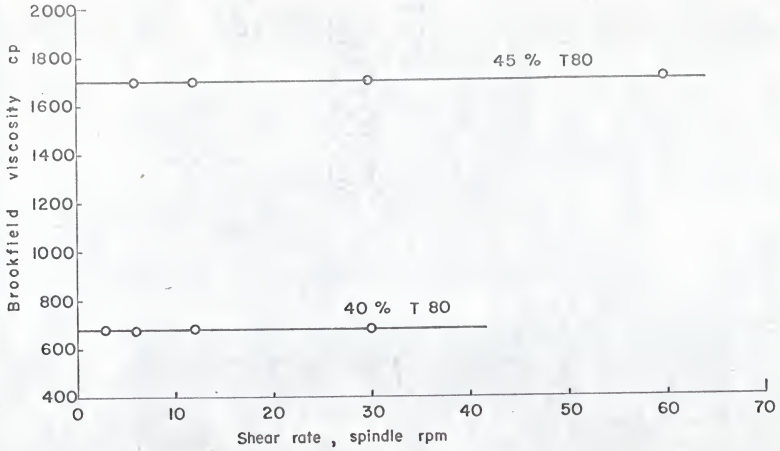


Fig. 17. Brookfield viscosity vs. shear rate for Dextran T 80 system at 25° C.

16 and 17 show the Newtonian behavior of the dextran solutions. A summary of the viscosities of these two systems is presented in Table 7 and Figure 18. Viscosities of the dextran solutions at a lower concentration range were measured with the Cannon-Fenske routine viscometers. These at higher concentration range were measured with the Brookfield viscometer. The continuity in employing these viscometers was checked by measuring the viscosity of a certain dextran solution with both viscometers. Measurement of the solution of 40 % dextran T40 by weight with the Cannon-Fenske viscometer yielded 287.2 cp. and that with the Brookfield viscometer gave 286 cp..

(3) Diffusivity

The data obtained from the diffusion experiments consisted of the positions along the reference line at which each fringe intersected it on a series of diffusion pictures and the time at which these successive pictures were exposed. The positions of intersections, x, were plotted versus the dimensionless refractive index, $\bar{n}$, on probability graph papers according to equation (17). Figure 19 shows x versus $\bar{n}$ for Run 99 for the dextran T80 system. The diffusivity can then be determined by use of equation (19).

The SPSS system and the high concentration range of the two dextran systems were found to agree with the linear relationship existing between x and $\bar{n}$ satisfactorily. For the low concentration range of the two dextran systems, skewness was observed because of the concentration dependence of diffusivity and bulk mixing disturbance of forced diffusion caused by the low viscosities in this range. Thus for these two systems, the diffusion data for the average concentration range between 5 % and 15 % dextran by weight were discarded. Data of diffusivities are presented for only the average concentration range between 15 % and 45 % dextran by weight.

Table 7. Viscosity of dextran systems at 25°C.

Concentration, Wt. fraction of dextran	Viscosity, centipoises T40	T80
0.050	2.177	2.962
0.100	4.623	7.580
0.150	9.713	17.22
0.200	19.30	37.36
0.250	36.22	76.54
0.300	71.28	157.8
0.350	138.3	335.5
0.400	286.0*	681.0*
0.450	592.0*	1702.*

* Brookfield viscosity.

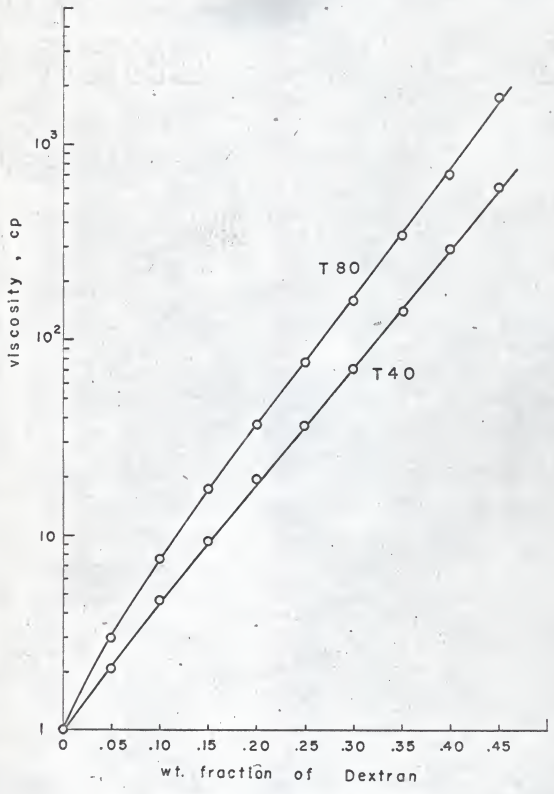


Fig. 18 Viscosity vs. concentration for Dextran systems at 25° C.

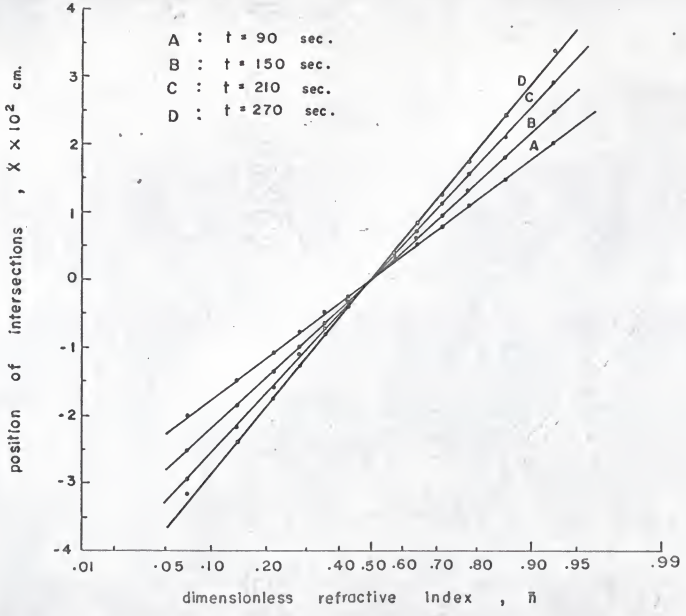


Fig. 19. The plot of x vs. $\bar{n}$ for run 99 for Dextran T 80 system.

The diffusivity obtained from equation (19) was defined as observed diffusivity in Section II-4. A zero time correction for these data should be made. Figure 20 illustrates the zero time correction for observed diffusivity for the dextran T80 system of $C_{average}$ = 35 % dextran T80 by weight. The data for this figure are listed in Table 8.

Summaries of zero time corrected diffusivities of the SPSS system and the two dextran systems are listed in Tables 9, 10 and 11, and are plotted versus concentrations of solutions in Figures 21, 22 and 23. In Chapter VI revised Chauvenet's criterion is employed for discarding the invalid measurements of diffusivity. The remaining diffusivities are discussed for their physical significance in Section VI-3.

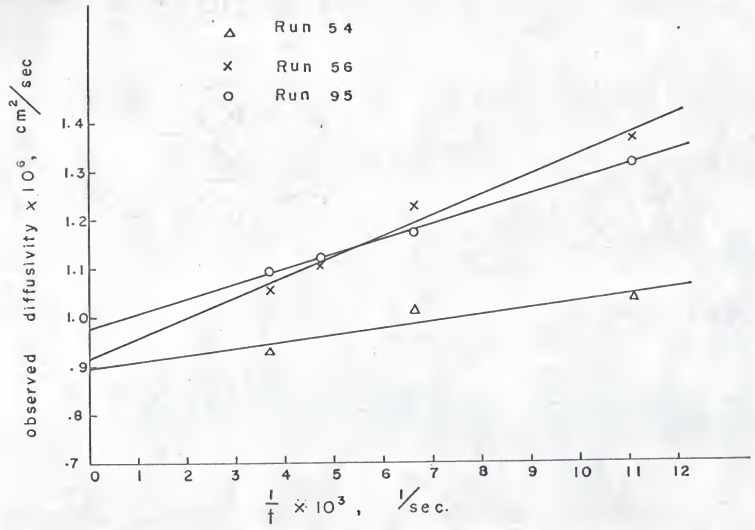


Fig. 20. Zero time correction for Dextran T 80 system at

$C_{avg} = 0.35$ wt. fraction of T 80.

Table 8. Zero time correction for observed diffusivity for dextran T80 system at $C_{average}$ = 35 % dextran T80 by weight.

Run no. \ 1/t, 1/sec.	0.01111 (=1/90)	0.00667 (=1/150)	0.00476 (=1/210)	0.00370 (=1/270)	0*
	Diffusivity, D x10^6 cm^2/sec.				
54	1.036	1.018	--	0.929	0.897
56	1.319	1.174	1.124	1.094	0.978
95	1.367	1.228	1.104	1.056	0.914

* By extrapolation.

Table 9. Diffusivity of SPSS system at 25°C.

$$D = 1.5 \times 10^{-5} \text{ Exp } (-0.904 \times 10^{-1} C + 0.133 \times 10^{-2} C^2)^{**}$$

Concentration, Wt. fraction of SPSS			Diffusivity, D x10^6 cm^2/sec.			
C_o"	C_o'	$C_{average}$	1	2	3	Average***
0.	0.09994	0.04997	11.05	11.78	7.243	9.840
0.05003	0.15015	0.1001	7.188	8.078	5.492	6.914
0.09994	0.19865	0.1493	4.218	8.168	4.800	5.218
0.15015	0.24999	0.2001	4.164	4.182	5.743*	4.176
0.19865	0.29999	0.2493	3.188	8.543*	3.369	3.594
0.24999	0.34997	0.3000	3.440	2.925*	3.418	3.293

* These data are discarded after applying Chauvenet's criterion stated in Chapter VI.

** Empirical equation stated in Section VI-3.

*** Calculated from the empirical equation.

Table 10. Diffusivity of dextran T40 at 25°C.

$D = 0.671 \times 10^{-3} \exp(-0.297C + 0.344 \times 10^{-2} C^2)$**

Concentration, Wt. fraction of dextran			Diffusivity, D x10^6 cm^2/sec.							
C_o"	C_o'	$C_{average}$	1	2	3	4	5	6	7	Average***
0.100	0.200	0.150	17.326	18.604	16.711					16.83
0.150	0.250	0.200	5.079	6.822	5.299					6.961
0.200	0.300	0.250	3.410	3.306	2.882*					3.407
0.250	0.350	0.300	2.468	1.404	2.610	1.688				1.990
0.300	0.400	0.350	1.272	1.673*	1.340					1.372
0.350	0.450	0.400	1.181	0.9022	0.8243	1.335	0.8940	0.9588		1.128
0.400	0.500	0.450	0.7195	1.276	1.386	1.132	0.8415	0.6803	1.217	1.099

* These data are discarded after applying Chauvenet's criterion stated in Chapter VI.

** Empirical equation stated in Section VI-3.

*** Calculated from the empirical equation.

Table 11. Diffusivity of dextran T80 at 25°C.

$D = 0.198 \times 10^{-3} \text{ Exp } (-0.279C + 0.356 \times 10^{-2} C^2)$ for $C_{avg.} = 0.15$ to 0.35 **

$D = 0.110 \times 10^{-5} \text{ Exp } (-0.521 \times 10^{-2} C)$ for $C_{avg.} = 0.35$ to 0.45 **

Concentration, Wt. fraction of dextran			Diffusivity, $D \times 10^6$ cm^2/sec.					
C_o"	C_o'	$C_{average}$	1	2	3	4	5	Average***
0.100	0.200	0.150	6.048	7.212	7.861			6.683
0.150	0.250	0.200	3.268	2.790	3.307			3.084
0.200	0.300	0.250	1.430	1.664	1.212			1.700
0.250	0.350	0.300	1.026	1.037	0.7136*	1.354	1.211	1.120
0.300	0.400	0.350	0.8968	0.8540	0.9779	0.9452	0.9136	0.9185
0.350	0.450	0.400	0.8653	0.9623	1.105*	0.8893		0.8949
0.400	0.500	0.450	0.8206	0.6284*	0.8581	0.9324	0.8706	0.8719

* These data are discarded after applying Chauvenet's criterion stated in Chapter VI.

** Empirical equation stated in Section VI-3.

*** Calculated from the empirical equation.

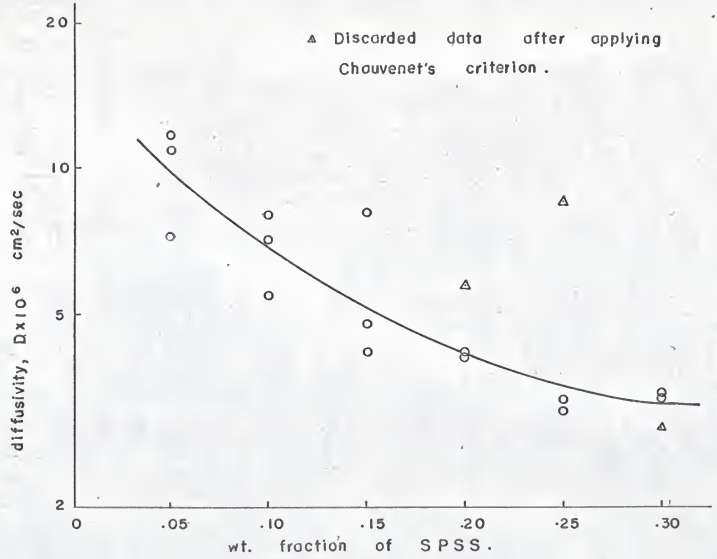


Fig. 21. Diffusivity vs. concentration for SPSS system at 25° C.

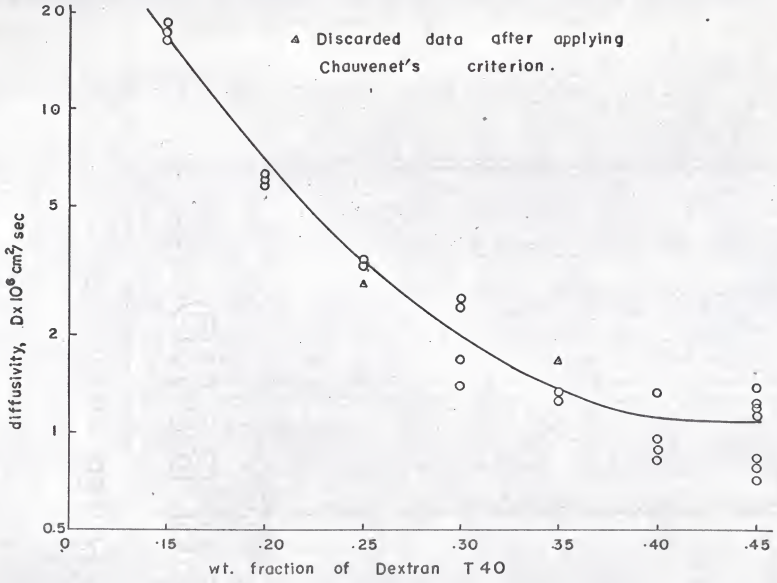


Fig. 22. Diffusivity vs. concentration for Dextran T40 system at 25°C.

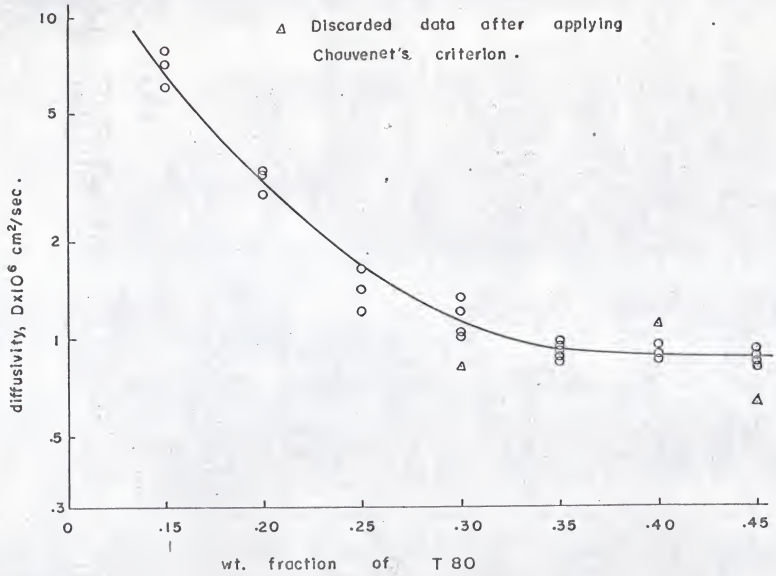


Fig. 23. Diffusivity vs. concentration for Dextran T80 system at 25° C.

CHAPTER VI

ANALYSIS OF DIFFUSIVITY DATA AND CONCLUSION

When the value of a quantity is to be determined, habitually a series of identical experiments is carried out independently, and the arithmetic mean of the measurements is taken as the value of that quantity. Occasionally, some of the measurements will deviate considerably from the mean. If a large number of measurements are made, a single incorrect result will introduce only a small error in the mean. But when the total number of measurements is small, the error introduced by an incorrect result will lead to an erroneous mean. Obviously some criterion must be used in deciding whether a result of measurement should be included or discarded. The method known as Chauvenet's criterion (17) is often employed for this purpose. The statistical basis of this criterion is presented in the first section of this chapter. Chauvenet's criterion is still not satisfactory for a case in which only 3 or fewer measurements are carried out. Some amendments were made to this criterion for the case in which the quantity to be determined depended on some variables like time, concentration, coordinates and so on. The revised criterion was employed in this study for analyzing the measured diffusivity data. The revised findings are presented in Section 2. The diffusivity data, after all the invalid measurements were discarded are discussed for their significance in Section 3. In the last section, the conclusion reached in this study and the recommendation for future work are presented.

(1) Chauvenet's criterion for discarding invalid measurements

If a series of identical experiments is carried out independently on a

quantity, the results of measurement, known as random sample of size N, are taken to be normally distributed (17). The random sample is denoted by X_i, $i = 1, 2, \cdots, N$, where N is the number of measurements, and the mean and the variance of the normal distribution by α and σ^2 respectively as shown in Figure 24 (a). The mean and the variance of the random sample are defined as follows:

$$\bar{X} = \frac{1}{N} \sum_{1}^{N} X_i$$

$$S^2 = \frac{1}{N} \sum_{1}^{N} (\bar{X} - X_i)^2$$

Based on the theory of statistics it is known that (18) the distribution of $\bar{X}$ is $n(\alpha , \sigma^2/N)$ and the distribution of NS^2/σ^2 is $\chi^2(N-1)$. Therefore the mean of $\bar{X}$ is α. So α, the value of the quantity to be determined, can be approximately estimated by $\bar{X}$, i.e.

$$\alpha \doteq \bar{X}$$

$$\doteq \frac{1}{N} \sum_{1}^{N} X_i \qquad (24)$$

The mean of NS^2/σ^2 is N-1. Thus, σ^2 is approximated to be

$$\sigma^2 \doteq \frac{NS^2}{N-1}$$

$$\doteq \frac{1}{N-1} \sum_{1}^{N} (\bar{X} - X_i)^2$$

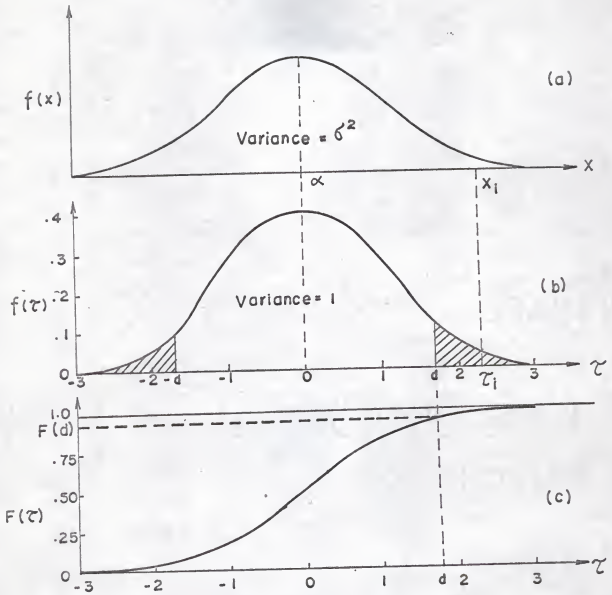


Fig. 24. Distribution of random sample.

(a) Probability density function of original random sample $n(\alpha, \sigma^2)$.

(b) Probability density function of random sample after being converted to $n(0,1)$.

(c) Distribution function of $n(0,1)$.

Therefore the standard deviation of the normal distribution is

$$\sigma = \left[\frac{1}{N-1} \sum_{1}^{N} (\bar{X}-X_i)^2 \right]^{\frac{1}{2}} \qquad (25)$$

According to the central limit theory, once the α and σ are determined, the distribution of X_i can be converted to the standard form of normal distribution by substracting α from X_i and dividing the result by σ , i.e. the distribution of $(X_i-\alpha)/\sigma$ is n(0,1) as shown in Figure 24 (b).

The problem of discarding invalid measurements will now be discussed. Concerning equation (24) it is evident that an incorrect X_i in the random sample will lead to an erroneous mean if the number of measurements, N, is small. Such an incorrect measurement must obviously be excluded in calculating the mean according to equation (24). Of the several criteria developed for rejecting such an invalid measurement, that one formulated by Chauvenet seems to be most generally accepted. This criterion states (17) that a measurement should be discarded if the probability of its occurence is equal to or less than 1/2N. Expressed partly in equation form, it states that if the "deviation from the mean of a certain measurement", τ_i, which is defined as $\frac{|X_i-\alpha|}{\sigma}$, is greater than the normal deviation, d, where d is defined according to the following equations

$$2\left(1 - F(d)\right) = \frac{1}{2N}$$

F(d) = The distribution function of standard normal distribution

$$= \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{d} e^{-\frac{x^2}{2}} dx$$

then X_i should be rejected as shown in Figure 24 (c). The normal deviation

can be calculated from the normal distribution table. Some values with corresponding numbers of measurement are shown in Table 12.

A summary of the procedures for employing Chauvenet's criterion follows:

(i) Compute the mean

$$\alpha = \overline{X}$$

$$= \frac{1}{N} \sum_{1}^{N} X_i$$

(ii) Compute the standard deviation

$$\sigma = \left(\frac{1}{N-1} \sum_{1}^{N} (\alpha - X_i)^2 \right)^{\frac{1}{2}}$$

(iii) Compute the deviation from the mean for each X_i

$$\gamma_i = \frac{|X_i - \alpha|}{\sigma}$$

(iv) Find the normal deviation, d, corresponding to the number of measurement, N, from Table 12.

(v) Test γ_i against d and discard any measurement for which γ_i is greater than d.

(vi) Repeat testing all the remaining data with a new N which is equal to the original N less the number of X_i discarded.

(2) Application of Chauvenet's criterion to the analysis of diffusivity data

The validity of Chauvenet's criterion lies in the estimation of the actual value of the quantity to be determined by the arithmetic mean of the measurements as shown in equation (24). If the total number of measurements is small, such as 3 or fewer, the confidence of estimation in taking $\overline{X}$ to be

Table 12. Chauvenet's criterion for rejection of invalid data.

Number of measurements, N	Normal deviation, d
2	1.15
3	1.38
4	1.54
5	1.65
6	1.73
7	1.80
8	1.86
9	1.91
10	1.96
15	2.13
20	2.24
25	2.33
30	2.40
40	2.50
50	2.58
60	2.63
70	2.69
80	2.73
90	2.77
100	2.80

α is not high. That is, in such a case α may not be satisfactorily represented by $\bar{X}$. Refinement can be made only by increasing the total number of measurements. But if the quantity to be determined depends on some variables like time, coordinates, concentration and so on, the confidence of estimation can be improved even in the case of a small number of measurements if the correlation between the quantity and the variable on which it depends is known or can be determined. For this purpose the least-square method (19) is usually employed. Denote the quantity to be determined by X and the variable on which it depends by Y. For the determination of the values of X which depend on Y, measurements are made at various values of Y. The results of the measurements of X are plotted against those of Y to determine the correlation between them, if the correlation is not well known. An empirical equation is then used to fit these data. The values of X at various values of Y can then be determined from the empirical equation. When these values of X are used as the mean in Procedure (i) of the previous section, they yield better estimations of the values of the quantity to be determined even if the number of measurements at a certain Y is small. With this revised method of determining the mean the same procedures for the rest of Chauvenet's criterion can then be followed to achieve better satisfaction.

Some of the empirical equations usually employed are the following:

$$X = a + bY \qquad (26)$$

$$X = a + bY + cY^2 \qquad (27)$$

$$X = a + bY + cY^2 + dY^3 \qquad (28)$$

$$X = a \ \mathrm{Exp}\ (bY) \qquad (29)$$

$$X = a \ \mathrm{Exp}\ (bY + cY^2) \qquad (30)$$

and so on depending on a well known relationship between X and Y or the pat-

tern of the data when X is plotted versus Y. The designations a, b, c and d in the above equations are parameters to be chosen so as to minimize the sum of the squares of the deviations of the measurements from the values calculated from the empirical equation.

As far as this study is concerned the quantity to be determined is diffusivity, D. Usually diffusivity depends on the concentration of the solution, C, under constant temperature. To determine the diffusivities, measurements were made at various values of C. The results are plotted in Figures 21, 22 and 23. Equations (29) and (30) were used to fit these data as discussed in the ensuing section. The value calculated from the empirical equation was taken as the average value of diffusivity at a certain concentration. The revised Chauvenet's criterion was then employed to discard all the invalid measurements. A computer program for this purpose and its flow diagram are presented in the Appendix. The final results are shown in Tables 9, 10 and 11.

(3) Discussion of diffusivity data

The experimental diffusivity measurements are catalogued in the previous sections. In this section an analysis of the data after invalid measurements were discarded and the discussion of the significance of the data are presented.

The first and foremost result is the significant concentration dependence of diffusivity which was observed in each of the three systems as shown in Figures 21, 22 and 23. Representing the diffusivity data as a function of concentration by an empirical equation was attempted. Equations (26) through (28) were first tried. The linear, quadratic or cubic regression of the data resulted in a high correlation coefficient. These equations also predicted negative values of diffusivity at some concentrations or showed an increase of

diffusivity at both ends of the concentration range. These are not physically meaningful. Therefore, equations (29) and (30) are used to represent the diffusivity-concentration relationship and are listed in Tables 9 through 11. This approach is justified by the present absence of theoretical equations which can describe the variation of the diffusivity over the concentration range in the three systems studied.

Secondly a discussion of diffusivities of the three systems through the application of an available theory of diffusion for liquids is presented. From hydrodynamic theory an equation relating the physical properties of a large spherical molecule diffusing through a solvent has been developed as indicated in the following equation (20, 21)

$$\frac{D\mu_1}{kT} = \frac{1}{6\pi R_A} \tag{31}$$

in which μ_1 is the viscosity of the pure solvent, T is the absolute temperature, k is Boltzmann's constant and R_A is the radius of the diffusion molecule. This equation is called the Stokes-Einstein equation. The viscosity in the Stokes-Einstein equation is often replaced by the viscosity of the solution μ. Equation (31) can then be written as

$$D\mu = \frac{kT}{6\pi R_A} \tag{32}$$

Under the condition of constant temperature, it is seen that the product of the diffusivity and the solution viscosity is a constant.

Equation (32) was tested with the diffusivity and viscosity data for each of the three systems. The results are listed in Tables 13 and 14 and are plotted versus concentration in Figures 25 and 26. These figures reveal that in

Table 13. The product of diffusivity and viscosity for SPSS system at 25°C.

Concentration, Wt. fraction of SPSS	Viscosity, μ poises	Diffusivity, $Dx10^6$ $cm^2/sec.$	$D\mu x10^5$ dyne
0.050	1.87	9.868	1.845
0.100	8.50	6.938	5.897
0.150	22.6	5.214	11.78
0.200	50.5	4.187	21.14
0.250	128.	3.594	46.03
0.300	254.	3.297	83.74

Table 14. The product of diffusivity and viscosity for dextran systems at 25°C.

	Concentration, Wt. fraction of dextran	Viscosity, μ Centipoises	Diffusivity, $Dx10^6$ $cm^2/sec.$	$D\mu x10^6$ Dyne
	0.150	9.713	16.83	1.635
	0.200	19.30	6.961	1.343
	0.250	36.22	3.407	1.234
T40	0.300	71.28	1.990	1.418
	0.350	138.3	1.372	1.897
	0.400	286.0	1.128	3.226
	0.450	592.0	1.099	6.506
	0.150	17.22	6.683	1.151
	0.200	37.36	3.084	1.152
	0.250	76.54	1.700	1.301
T80	0.300	157.8	1.120	1.767
	0.350	335.5	0.9185	3.082
	0.400	681.0	0.8949	6.094
	0.450	1702.	0.8719	14.84

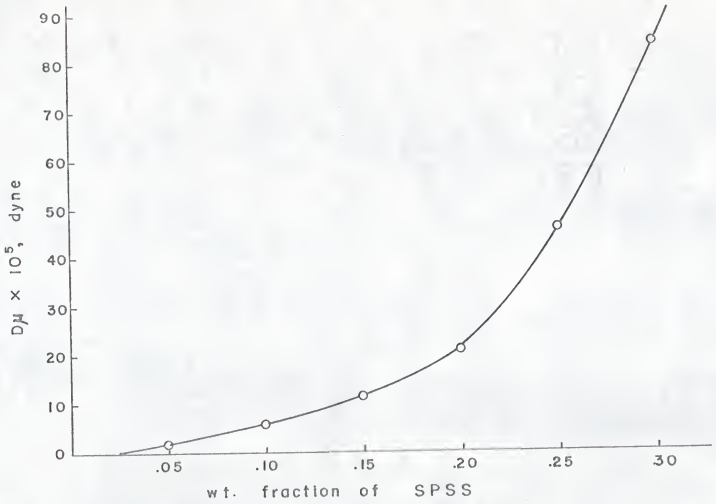


Fig.25. The product of diffusivity & viscosity vs. concentration for SPSS system at 25° C.

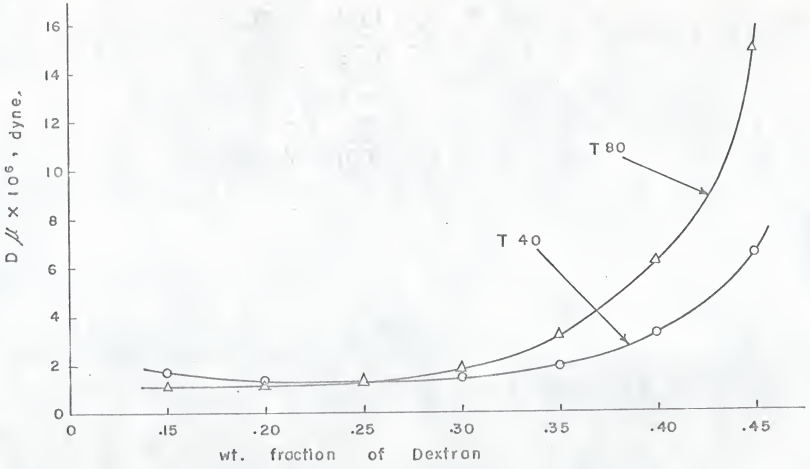


Fig. 26. The product of diffusivity & visicosity vs. concentration for Dextran systems at 25° C.

none of the three systems is the diffusivity-viscosity product constant over the whole range of concentration. An increase of the diffusivity-viscosity product with an increase of concentration was observed for all three systems.

Finally the effect of molecular weight on diffusivity is discussed. The two dextran systems were so selected that the T80 polymer has an average molecular weight about twice that of the T40 polymer. Comparison of the diffusivity data of these two systems revealed that half (1/2.17, to be exact) the average molecular weight gives the T40 polymer a diffusivity 2.52 times higher than that of the T80 polymer at the lower end of the concentration range to 1.26 times at the higher end of the concentration range as shown in Figure 27. This confirms the fact that smaller molecules diffuse faster if all other conditions are the same.

(4) Conclusion and recommendation

Because of the lack of experimental data in the literature, no reported diffusivities for these three systems are available for comparison. But a comparison with other branched dextrans (22) and other polymer solutions (23, 24) shows that the order of magnitude of these measured diffusivities lies within a reasonable range. The reliability of measured diffusivities is higher at the higher concentration range because the relationship between the position of intersection, x, and the dimensionless refractive index, $\bar{n}$, is observed to be strictly linear. The reliability at the lower concentration range is poorer because of the low viscosity at this end. The standard deviations of the diffusivity data range from 2.5×10^{-6} and 10^{-6} $cm^2/sec.$ at the lower concentration range for the SPSS and dextran systems respectively (where the diffusivities are of the order of 10^{-5} $cm^2/sec.$), to 2.7×10^{-7} and 0.5×10^{-7} $cm^2/sec.$ at the higher concentration range (where the diffusivities are of the order of 3×10^{-6} and 10^{-6} $cm^2/sec.$ for the SPSS and dextran systems respec-

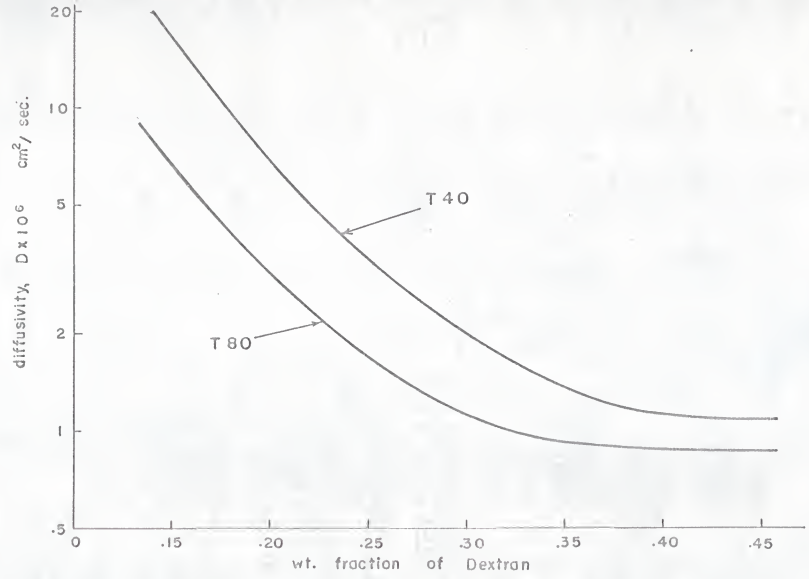


Fig. 27. Comparison of diffusivities for the two Dextran systems at 25° C.

tively). Those are within the estimated accuracy of the equipment (25 % maximum error at the lower concentration range to 10 % maximum error at the higher concentration range). These measured data also indicate that the diffusivities of the three systems studied are highly concentration dependent. It is thus incorrect to take them to be constant for a wide concentration range.

The range of applicability of the microinterferometric method will now be discussed. Before experiments with these three systems were performed, diffusivity measurements of several other systems had been made with little success. Among them were the di-sodium salt of fluorescein-water, polypropylene glycol-dimethyl sulfoxide (DMSO), polypropylene glycol-paraxylene, ribonucleic acid (RNA)-1 % NaCl aqueous solution, deoxyribonucleic acid (DNA)-1 % NaCl aqueous solution systems and others. The difficulties encountered in these systems together with those in the SPSS and the two dextran systems revealed some of the restrictions of the microinterferometric method to be as follows:

(i) The successful employment of the microinterferometric method requires that the refractive index difference between the two diffusing liquids placed in the optical wedge diffusion cell should be high enough to yield a reasonable interference fringe pattern. If the refractive indices of the two liquids are only slightly concentration dependent, this method is not recommended for measuring their diffusivity. In addition, constant diffusivity is assumed in evaluating the diffusion pictures. Therefore, the concentration gradient of the two liquids should be kept as low as possible if the diffusivity is highly concentration dependent. This requirement should be met unless some other method for evaluating the diffusivity is developed.

(ii) If a solid solute is used, as in the three systems studied, its solubility in the solvent should be high enough to give both a reasonable refractive index difference and diffusivity data in a wide concentration range.

(iii) The viscosity of the solution should be neither too low nor too high. The mixing disturbence of forced diffusion caused by low viscosities usually yields a tremendously high diffusivity which is apparently erroneous. A high viscosity makes the operation of the experiment hard to handle. The optimal range of viscosity was estimated to be from 10 cp. to 25,000 cp..

(iv) The solution should be clear and colorless to make possible the evaluation of diffusion pictures taken in diffusivity measurement runs.

(v) As the sides of the diffusion cell are partially open, the solvent used should not be a highly volatile chemical in order to prevent a concentration change during the experimental runs.

(vi) The solutions should form spheroidal drops on the surface of a diffusion slide before the two liquids contact physically. Systems with a solvent which has a low surface tension are not suitable for use with this method (para-xylene has a surface tension of 28.37 dyne/cm at 20°C, compared with that of 73 dyne/cm for water at the same temperature).

Despite numerous limitations and its narrow spectrum of applicability, the microinterferometric method provides a rapid way for determining the diffusivity of viscous materials. It is believed that this method may help to remedy the current lack of diffusivity data of high molecular weight polymer solutions in the literature.

The restrictions (i) through (iv) listed above indicate inherent limitations in this method. No improvements seem to be possible at present. But the restrictions (v) and (vi) can be avoided if the diffusion takes place in a closed cell. Further study in this field should therefore be directed towards using a closed diffusion cell such as has been developed by E. Travnicek (25).

NOMENCLATURE

Symbols

C	Concentration
C_o', C_o''	Initial concentration
$\overline{C}$	Dimensionless concentration, $(C-C_o'')/(C_o'-C_o'')$
D	Diffusivity
d	Normal deviation
J	Flux of mass transfer through a unit area
k	Boltzmann's constant
$\overline{M}_n$	Number average of molecular weight
$\overline{M}_w$	Weight average of molecular weight
N	Number of measurements
n	Refractive index
n_o', n_o''	Initial refractive index
$\overline{n}$	Dimensionless refractive index, $(n-n_o'')/(n_o'-n_o'')$
R_A	Radius of a spherical molecule
S^2	Variance of random sample
T	Absolute temperature
t_o	Time difference between t' and t
t'	Observed time
t	Apparent time
X	Value of random sample
$\overline{X}$	Mean of random sample
x	Coordinate

NOMENCLATURE -- Continued

α Mean of a normal distribution

λ Wavelength of incident light

η Dimensionless parameter, $x/\sqrt{4Dt}$

θ Wedge angle

μ Viscosity

σ^2 Variance of a normal distribution

σ Standard deviation of a normal distribution

τ Deviation from the mean

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APPENDIX

COMPUTER PROGRAM FOR THE ANALYSIS OF MEASURED DIFFUSIVITY DATA

The discarding of invalid measurements of diffusivity data together with the least-square fitting of the empirical equations were accomplished through the use of the IBM 360/50 computer at the Kansas State University Computing Center. The computer program for these purposes consisted mainly of two parts. The first part is the least-square fitting of these diffusivity data using a quadratic logarithmic equation. The diffusivity at a certain concentration is then computed using the empirical equation and the finding is taken as the mean value of diffusivity at that concentration as dissussed in Section VI-2. In the second part the computed diffusivities were used with Chauvenet's criterion presented in Section VI-1 in order to discard all the invalid measurements. Figure A-1 shows the flow diagram of the computer program which is presented in Table A-1. For illustration, the data deck of the dextran T40 system is included at the end of the source deck of the computer program. The nomenclature for this computer program is listed in Table A-2.

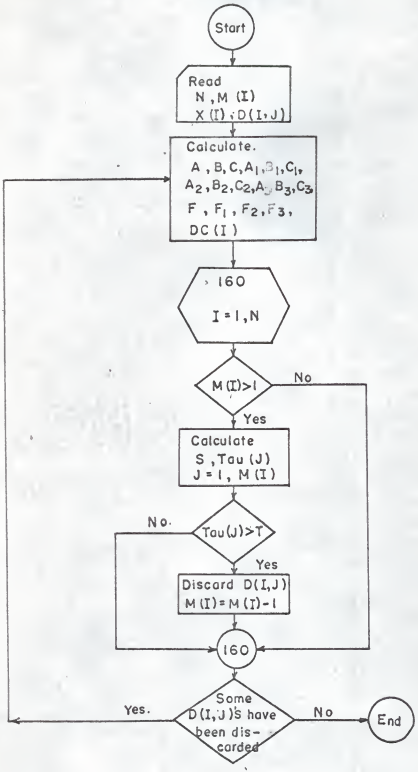

Fig. A-1. Flow diagram for the data analysis computer program.

Table A-1. Computer program for data analysis.

```
      DIMENSION D(100,100),DC(100),M(100),X(100),GM(100),T(100),TAU(100)
   11 FORMAT (I2)
   12 FORMAT (10(I2,1X))
   15 FORMAT (/,/,/,7X,70HTHE FOLLOWING IS THE LEAST SQUARE FITTING USIN
     1G A LOGARITHMIC EQUATION,/,/,/)
   20 FORMAT (1H1,/,/,/,10X,20HLEAST SQUARE FITTING,/,/,/)
   21 FORMAT (6E12.5)
   22 FORMAT (/,5X,17HAT CONCENTRATION=,F6.3,2H %,/,/)
   23 FORMAT (10X,12HDIFFUSIVITY=,E12.5,12H CM SQ./SEC.)
   24 FORMAT (/,/,7X,3HD=(,E10.3,7H)*EXP((,E10.3,6H)*C +(,E10.3,7H)*C**2
     1),/,/,/)
   25 FORMAT (5X,17HDIFFUSIVITY AT C=,F6.3,1X,5H% IS ,E12.5,12H CM SQ./S
     1EC.)
   30 FORMAT (/,/,/,/,20X,18HEND OF THIS SYSTEM)
  100 FORMAT (/,/,10X,57HCHAUVENET'S CRITERION FOR DISCARDING INVALID ME
     1ASUREMENTS,/,/,/)
  101 FORMAT (/,/,7X,26HTHE MEAN DIFFUSIVITY AT C=,F6.3,6H % IS ,E12.5,1
     12H CM SQ./SEC.,/)
  102 FORMAT (7X,25HTHE STANDARD DEVIATION IS,E10.3,/)
  103 FORMAT (5X,17HTHE DEVIATION OF ,E12.5,12H CM SQ./SEC.,1X,16HFROM T
     1HE MEAN IS,1X,F8.3)
  104 FORMAT (/,/,5X,16HTHE DEVIATION OF,E12.5,12H CM SQ./SEC.,1X,36HIS
     1GRFATER THAN THE NOAMAL DEVIATION,/)
    1 READ (1,11) N
      READ (1,12) (M(I),I=1,N)
      READ (1,21) (X(I),I=1,N)
      DO 2 I=1,N
      L=M(I)
    2 READ (1,21) (D(I,J),J=1,L)
    3 WRITE (3,20)
      DO 32 I=1,N
      WRITE (3,22) X(I)
      L=M(I)
      DO 31 J=1,L
   31 WRITE (3,23) D(I,J)
```

Table A-1. Computer program for data analysis.

(Continuation number 1)

```
   32 CONTINUE
      DO 40 I=1,N
   40 GM(I)=M(I)
      WRITE (3,15)
C     THE FOLLOWING IS THE LEAST SQUARE FITTING
C     USING A LOGARITHMIC EQUATION
C        DC(I)=F*EXP(F2*X(I)+F3*X(I)**2)
C        THAT IS
C        LOG(DC(I))=LOG(F)+F2*X(I)+F3*X(I)**2
C                  =F1+F2*X(I)+F3*X(I)**2
C     THE NORMAL EQUATIONS ARE
C        A=A1F1+A2F2+A3F3
C        B=B1F1+B2F2+B3F3
C        C=C1F1+C2F2+C3F3
      A=0
      DO 61 I=1,N
      L=M(I)
      DO 60 J=1,L
   60 A=A+ALOG(D(I,J))
   61 CONTINUE
      B=0
      DO 63 I=1,N
      L=M(I)
      DO 62 J=1,L
   62 B=B+ALOG(D(I,J))*X(I)
   63 CONTINUE
      C=0
      DO 65 I=1,N
      L=M(I)
      DO 64 J=1,L
   64 C=C+ALOG(D(I,J))*X(I)**2
```

Table A-1. Computer program for data analysis.

(Continuation number 2)

```
65 CONTINUE
   A1=0
   DO 70 I=1,N
70 A1=A1+GM(I)
   A2=0
   DO 71 I=1,N
71 A2=A2+X(I)*GM(I)
   B1=A2
   A3=0
   DO 72 I=1,N
72 A3=A3+GM(I)*X(I)**2
   B2=A3
   C1=A3
   B3=0
   DO 73 I=1,N
73 B3=B3+GM(I)*X(I)**3
   C2=B3
   C3=0
   DO 74 I=1,N
74 C3=C3+GM(I)*X(I)**4
   FD=A1*B2*C3+A2*B3*C1+A3*B1*C2-A1*B3*C2-A2*B1*C3-A3*B2*C1
   FN1=A*B2*C3+A2*B3*C+A3*B*C2-A*B3*C2-A2*B*C3-A3*B2*C
   FN2=A1*B*C3+A*B3*C1+A3*B1*C-A1*B3*C-A*B1*C3-A3*B*C1
   FN3=A1*B2*C+A2*B*C1+A*B1*C2-A1*B*C2-A2*B1*C-A*B2*C1
   F1=FN1/FD
   F=EXP(F1)
   F2=FN2/FD
   F3=FN3/FD
   WRITE (3,24) F,F2,F3
   DO 80 I=1,N
   DC(I)=F1+F2*X(I)+F3*X(I)**2
   DC(I)=EXP(DC(I))
80 WRITE (3,25) X(I),DC(I)
```

Table A-1. Computer program for data analysis.

(Continuation number 3)

```
C         THE FOLLOWING IS CHAUVENET'S CRITERION
C         FOR DISCARDING INVALID MEASUREMENTS
  131 WRITE (3,100)
      DO 160 I=1,N
      L=M(I)
      WRITE (3,101) X(I),DC(I)
      IF (L-1) 160,160,132
  132 DD=0
      DO 133 J=1,L
  133 DD=DD+(D(I,J)-DC(I))**2
      S=SQRT(DD/(GM(I)-1.))
      WRITE (3,102) S
      T(2)=1.15
      T(3)=1.38
      T(4)=1.54
      T(5)=1.65
      T(6)=1.73
      T(7)=1.80
      T(8)=1.86
      T(9)=1.91
      T(10)=1.96
      MA=L
      DO 134 J=1,L
      TAU(J)=ABS(D(I,J)-DC(I))/S
  134 WRITE (3,103) D(I,J),TAU(J)
      DO 140 J=1,L
      IF (T(L)-TAU(J)) 135,135,140
  135 WRITE (3,104) D(I,J)
      DO 139 K=1,L
      IF (K-J) 136,137,138
  136 D(I,K)=D(I,K)
      GO TO 139
```

Table A-1. Computer program for data analysis.

(Continuation number 4)

```
137 DD=D(I,K)
    GO TO 139
138 D(I,K-1)=D(I,K)
139 CONTINUE
    D(I,L)=DD
    MA=MA-1
140 CONTINUE
    M(I)=MA
160 CONTINUE
    DO 170 I=1,N
170 GM(I)=M(I)
    AM=0
    DO 175 I=1,N
175 AM=AM+GM(I)
    IF (AM-A1) 3,180,180
180 WRITE (3,30)
    GO TO 1
    END
7
3  3  3  4  3  6  7
0.15000E 02 0.19990E 02 0.25000E 02 0.29970E 02 0.35010E 02 0.39980E 02
0.45000E 02
0.17326E-04 0.16604E-04 0.16711E-04
0.50790E-05 0.68220E-05 0.52990E-05
0.34100E-05 0.33030E-05 0.28820E-05
0.24600E-05 0.14040E-05 0.26100E-05 0.16880E-05
0.12720E-05 0.16730E-05 0.13400E-05
0.11310E-05 0.90220E-06 0.82430E-06 0.13350E-05 0.89400E-06 0.95880E-06
0.71950E-06 0.12750E-05 0.13860E-05 0.11320E-05 0.84150E-06 0.68030E-06
0.12170E-05
```

Table A-2. Nomenclature for the data analysis computer program.

The empirical logarithmic equation is

$$DC(I) = F \, Exp \left[F_2 \, X(I) + F_3 \, X(I)^2 \right]$$

i.e.

$$\ln \left[DC(I) \right] = \ln (F) + F_2 \, X(I) + F_3 \, X(I)^2$$
$$= F_1 + F_2 \, X(I) + F_3 \, X(I)^2$$

where $F_1 = \ln (F)$.

The normal equations for least-square fitting are

$$A = A_1 \, F_1 + A_2 \, F_2 + A_3 \, F_3$$
$$B = B_1 \, F_1 + B_2 \, F_2 + B_3 \, F_3$$
$$C = C_1 \, F_1 + C_2 \, F_2 + C_3 \, F_3$$

Program symbol	Designation
N	Number of concentrations in one system
M(I)	Number of measurements at concentration X(I)
X(I)	Concentration
D(I,J)	Diffusivity of J^{th} measurement at concentration X(I)
DC(I)	Diffusivity at concentration X(I) calculated by use of the empirical equation
S	Standard deviation
T	Normal deviation from the mean
TAU(J)	Deviation of the J^{th} measurement from the mean

MEASUREMENT OF LIQUID PHASE DIFFUSIVITIES OF SODIUM POLYSTYRENE SULFONATE, DEXTRAN T40 AND DEXTRAN T80 AT 25°C

by

HSIN-I HUANG

B.S., National Taiwan University, 1965

Taipei, Taiwan

AN ABSTRACT OF A MASTER'S THESIS

submitted in partial fulfillment of the

requirements for the degree

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KANSAS STATE UNIVERSITY
Manhattan, Kansas

1969

ABSTRACT

Accurate diffusivities are needed for chemical equipment designs involving diffusion processes. Experimental data of diffusivities of high molecular weight chemicals are seldom available in the literature because of the excessive time and difficulties involved in diffusivity measurement. The microinterferometric method developed by Nishijima and Oster serves to provide a fast way for determining diffusivities.

The purposes of this study were to find the range of applicability of the microinterferometric method and its application in determining the diffusivities of sodium polystyrene sulfonate (SPSS), dextran T40 and dextran T80 in aqueous systems.

The SPSS system was measured with an average concentration of 5 % to 30 % SPSS by weight and the two dextran systems were from 15 % to 45 % dextran by weight. All were at ambient pressure and at a temperature of 25°C.

The microinterferometric method was found to be suitable for measuring the diffusivity of highly viscous materials. If the viscosity of the solution is low, it is suggested that other devices be used. The experimental data indicates that the diffusivities of these three systems are highly concentration dependent.

It is recommended that a closed diffusion cell be employed to replace the partially open cell currently used.