A Predictive Theory for Diffusion in Polymer and Protein Solutions

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SCOPE

Recent literature (*1, 5, 11, 19, 26, 27, 30, 32, 44, 46*) has shown that transport of fluids through dilute aqueous polymer solutions is largely affected by the concentration of the polymer in the solution. These investigations suggest that variations in the concentration of any polymeric substance over small concentration ranges might significantly affect the transport of any fluid through the solution. However, the state of the art tends to be more qualitative than quantitative. Although abundant data exist describing diffusion in dilute polymer solutions, this process is not described by any theoretical equation for diffusion in liquid systems. Thus this work is directed toward a better quantitative description of the phenomena.

Such an analysis should include biological polymer solutions, that is, protein solutions, as well as ordinary polymer solutions. Although proteins are macromolecules like polymers, it was believed that their charged nature would alter their physiochemical behavior. However, Booth (*9*), Tanford (*40*), asd Shooter (*38*) have offered evidence that this contention is not valid. Apparently, then, solutions of proteins can be treated similarly to polymer solutions. It also seems plausible that fluid transfer through protein solutions may be affected by the same mechanisms as in polymer solutions, that is, small changes in protein concentrations may produce large changes in transfer rates. Such changes might prove to be of physiological importance.

The major goals of the study were to establish the relative importance of the proteins and polymers on the transfer of fluids through their solutions, and to develop a quantitative predictive theory to describe the transport. The polymer systems employed for the study were the dilute polymeric solution diffusivity data of Li and Gainer (*26*), Osmers (*30*), Weinberg (*44*), and Quinn and Blair (*32*), while the protein systems included the fabricated plasma systems of Connor and Gainer (*12*) and Navari (*28*) and the oxygen-albumin saline data of Goldstick (*19*).

The significant number of investigations of transport in polymer solutions formed a qualitative starting point for the predictive theory. The absolute rate theory developed by Eyring and co-workers (*18, 33*) assumes a cell model for the liquid state, and has been applied successfully by Gainer and Metzner (*17*) to viscous liquids for predicting liquid-liquid diffusion coefficients. In this investigation the Eyring liquid state model has been extended to dilute polymer and protein solutions, and a predictive equation for transport of gases and liquids in these systems has been developed. It is based on solution properties with an emphasis on a priori determinations of the energy of activation for diffusion in the polymer (protein) solutions.

SUMMARY

A theory has been developed for diffusion of fluids in dilute polymer and protein solutions. The development provides some definite conclusions regarding the molecular description of the diffusion process in addition to a method for predicting the diffusivity values. It was found that the ratio of diffusivity in a polymeric or protein solution relative to that in a pure solvent appears to be completely independent of the diffusing solute. This conclusion indicates that the solute diffuses through the solvent, not along the polymer, and is a direct result of the activation energy difference for diffusion being independent of the diffusing species.

The predictive equation, in which the diffusivity ratio is given in terms of solution and polymer properties, appears to predict experimental data for both polymer and protein solutions reasonably well except for very large concentrations in multiple polymer solutions. The only systems in which increasing polymer concentration can result in increasing diffusivities are those with a zero or positive energy of activation difference. No systems reported at this time appear to satisfy this condition.

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An early investigation of transport in polymer solutions was the work of Biancheria and Kegeles (5). This was followed by some experimental studies (*1, 2, 10, 11, 13, 22, 26, 30* to *32, 36, 44, 46*) from which a number of structural models (*11, 13, 26, 27, 30, 42*) were proposed. Most of these are reviewed by Li and Gainer (*26*) and Osmers (*30*), and only the studies directly related to the present work will be discussed.

Li and Gainer (*26*) have proposed the following equation for predicting the diffusion coefficient in polymer solutions:

$$\frac{D_{AS}}{D_{AB}} = \left[\frac{M_B}{M_S}\right]^{1/2}\left[\frac{V_S}{V_B}\right]^{1/3}\left[1 - \frac{\Delta H_M}{\Delta H_{VAP_B}}\right]\left(\frac{K_B}{K_S}\right)\exp\left[\frac{E_{D_{AB}} - E_{D_{AS}}}{RT}\right] \quad (1)$$

They started with a general form of the Eyring equation (*34*) for diffusion of solute *A* through solvent *B* and indicated that since diffusion is a molecular mass transfer process and the system is not under any external force to flow, polymer solutions should approach Newtonian behavior in the diffusing process. Thus the Eyring equation should apply equally well to polymer solutions. In addition, they assume that the polymer and the solvent form a continuum, a solution with properties different from those of the pure solvent.

Applying this equation to systems of four different solutes in seven different polymer solutions at several concentrations of the polymer, they found that it predicted the diffusivities within 15% of the experimental data if the last two terms in the equation were predicted with a viscosity increase function. In addition to predicting correct trends and reasonably accurate values, the equation shows that the diffusivity in the polymer solution relative to that in the pure solvent appears to be independent of the solute.

The difficulties in using this predictive equation are obtaining heat of mixing values and determining the form of the viscosity increase function. Both of these quantities may be difficult to obtain for some systems, especially biological polymer solutions.

The most recent effort in proposing a description of transport in polymer solutions has been made by Osmers (*30*). His approach was to state that the calculation of a transport property is primarily dependent upon the temperature and intermolecular spacing of the system, which are, in turn, related variables. He suggested the effect of a polymer on a solvent can be estimated by considering the change in the solvent intermolecular spacing. The excess volume of mixing of a polymer-solvent system was used to obtain the temperature dependence of the solvent intermolecular spacing.

In order to obtain a predictive equation for a solute diffusion coefficient in a polymer solution, he employed an approach similar to the use of the absolute rate theory by Li and Gainer (*26*) and obtained the expression

$$\frac{D_{AB}^*}{D_{AB}} = \left(\frac{\mu_B}{\mu_B^*}\right)\left(\frac{V_B}{V_B^*}\right)^{1/3}\exp\left[\frac{(E_{\mu B}^* - E_{D_{AB}}^*) - (E_{\mu B} - E_{D_{AB}})}{RT}\right] \quad (2)$$

where those parameters with a superscripted asterisk are to be evaluated at temperature T^*, the temperature of the new intermolecular spacing.

Osmers (*30*) evaluated his approach using data for the diffusion of glycerol and ethanol in aqueous sodium carboxymethyl cellulose (CMC) solutions and of glycerol and allyl alcohol in aqueous AP30 solutions. He concludes that the excess volume of mixing is a good measure of the diffusion of a solute in a polymer solution. However, when one considers the magnitude of the excess volume of mixing of the aqueous CMC and AP30 solutions used in the investigation, one finds that the majority of values are approximately equal to the experimental accuracy of pcynometer method employed to measure them. This is probably the result of the very small values for the excess volume of mixing in these systems. However, small excess volume of mixing values seem to exist for the majority of polymer-solvent systems. This was pointed out by Weinberg (*44*) in his study of cyclohexane diffusing into polystyrene-toluene solutions. Thus it would appear that the prediction of the altered temperature T^* might be better accomplished with an alternate method, since large errors in T^* would cause large errors in the prediction of D_{AB}^*.

No other comprehensive theories appear to have been presented for prediction of mass transfer rates in polymeric systems.

THEORY

The major objective of this investigation was to develop a quantitative predictive theory for transport in all types of polymeric solutions. This would include protein solutions, as well as those consisting of nonbiological polymers. Most previous approaches have used theories of diffusion in ordinary liquids (*17, 24, 33, 45*) as a starting point and extended these to the phenomena of diffusion in polymeric solutions. A number of reviews on diffusion in ordinary liquids are available (*17, 20, 21, 23, 24*) and the reader is referred to these.

Staudinger (*39*) and Kargin et al. (*25*) have shown that polymeric solutions are true solutions and molecular in character. Volkenstein (*42*) discusses a number of similarities between ordinary liquids and polymeric solutions, and Eyring et al. (*15*) show that solutions of most polymeric materials appear to approach Newtonian flow at extremely low rates of shear.

Cussler and Lightfoot (*13*) have used a hydrodynamic model for diffusion in polymeric systems, while Flory (*16*) developed thermodynamic properties of polymer solutions using the lattice model as the starting point. Recent investigations (*11, 26, 27, 30*) have applied Eyring's absolute rate theory to diffusion in polymeric systems and have achieved some qualitative success. In addition, Gainer and Metzner (*17*) have proposed a successful correlation based on work of Eyring and his co-workers for predicting diffusivities in highly viscous mediums. As a result, the quantitative predictive theory of this work has its basis in absolute rate theory.

The Eyring equation for diffusion of a solute into a solution is based on a cell model for the liquid which contains vacancies (*18, 33, 34*). The diffusivity of a solute *A* into a solvent *B* can be expressed as:

$$D_{AB} = \left(\frac{V_B}{N}\right)^{2/3}(\xi_A)^{-1}\left(\frac{k'T}{2\pi m_A}\right)^{1/2}(v_{fAB})^{-1/3}\exp\left(\frac{-E_{D_{AB}}}{RT}\right) \quad (3)$$

ξ has been assumed (*17*) to depend solely on the diffusing of solute *A*. This form of the Eyring equation includes the assumption that the distance between successive

equilibrium positions of the diffusing molecule can be expressed as $(V_B/N)^{1/3}$, and that the rotational and vibrational partition functions of a molecule in the equilibrium state and in the activated state are equal.

Eyring (*18*) suggests that the best way to approximate the free volume of a liquid B (v_{fB}) is to measure the velocity of sound in the liquid (u_B) and use the expression

$$u_B = \left(\frac{V_B}{N}\right)^{1/3} (v_{fB})^{-1/3} \left(\frac{R\,T\,Cp_B}{M_B\,C_{V_B}}\right)^{1/2} \qquad (4)$$

This was derived by making use of the difference in velocity of sound in liquids and gases. Note that $v_{fB} = v_{fAB}$ since diffusion is a process which occurs at infinite dilution of A. Therefore combination of Equations (3) and (4) results in

$$D_{AB} = \left(\frac{V_B}{N}\right)^{1/3} (\xi_A)^{-1} \left(\frac{M_B}{2\pi m_A N}\right)^{1/2} \left(\frac{C_{V_B}}{C_{P_B}}\right)^{1/2} (u_B) \exp\left(\frac{-E_{DAB}}{RT}\right) \qquad (5)$$

A further simplification can be made by recognizing that C_p is approximately equal to C_V for most liquids (*7, 8, 35*) and thus the ratio $(C_V/C_p)^{1/2}$ would be very close to 1 Therefore Equation (5) becomes

$$D_{AB} = \left(\frac{V_B}{N}\right)^{1/3} (\xi_A)^{-1} \left(\frac{M_B}{2\pi m_A N}\right)^{1/2} (u_B) \exp\left(\frac{-E_{DAB}}{RT}\right) \qquad (6)$$

As was previously pointed out, it may be assumed that a polymer solution approaches Newtonian behavior in the diffusion process. As a result, Equation (6) can be applied to diffusion of a solute A in a polymeric solution:

$$D_{AS} = \left(\frac{V_S}{N}\right)^{1/3} (\xi_A)^{-1} \left(\frac{M_S}{2\pi m_A N}\right)^{1/2} (u_S) \exp\left(\frac{-E_{DAS}}{RT}\right) \qquad (7)$$

The diffusivity of a solute A in a solvent B can be compared to the diffusivity of solute A in a polymer solution of solvent B by combining Equations (6) and (7):

$$\frac{D_{AS}}{D_{AB}} = \left(\frac{V_S}{V_B}\right)^{1/3} \left(\frac{M_S}{M_B}\right)^{1/2} \exp\left(\frac{E_{DAB} - E_{DAS}}{RT}\right)\left(\frac{u_S}{u_B}\right) \qquad (8)$$

Measurements of velocity of sound in polymer solutions compared to the same measurement in the pure solvent show that u_S is approximately equal to u_B (*3*). This result further simplifies the ratio of diffusivities expression to

$$\frac{D_{AS}}{D_{AB}} = \left(\frac{V_S}{V_B}\right)^{1/3} \left(\frac{M_S}{M_B}\right)^{1/2} \exp\left(\frac{E_{DAB} - E_{DAS}}{RT}\right) \qquad (9)$$

Therefore the only unknown quantity in Equation (9) needed to predict the diffusivity in a polymer system is E_{DAS}, the diffusion energy of activation for the polymer solution. The molar volumes and molecular weights are easily measured or calculated, and the diffusivity and energy of activation for the solute in the pure solvent are usually known from previous investigations or can be accurately calculated.

In order to obtain an a priori method to predict E_{DAS} or $E_{DAB} - E_{DAS}$, it is necessary to examine the diffusion activation energy in detail. Consider first the diffusion of solute A in a pure solvent. This diffusion process can be viewed as solute A surrounded by a cage of solvent molecules B as shown in Figure 1. As the cage deforms, or as a vacancy is formed, the solute molecule A moves from the cage and into the vacancy. Therefore the energy of activation for diffusion can be expressed in two parts:

$$E_{DAB} = E^H{}_{BB} + E^J{}_{AB} \qquad (10)$$

Using the diffusion cage model as a basis, consider the diffusion of solute A in a polymer solution. This process is viewed as solute A surrounded by a cage of solvent molecules B which are held together by polymer-solvent bonds as well as solvent-solvent bonds as shown in Figure 2. Analogous to the pure solvent case, as the cage deforms or a vacancy is formed, the solute molecule A moves from the cage and into the vacancy. Again, the energy of activation for diffusion can be expressed in two parts, the energy required for cage deformation and the energy required for a solute molecule A to move from the cage:

$$E_{DAS} = E^{H}{}_{(BB+PB)} + E^J{}_{AB} \qquad (11)$$

It is proposed here that the energy required for cage deformation or vacancy formation $E^{H}{}_{(BB+PB)}$ is the energy required to break solvent-polymer bonds as well as solvent-solvent bonds. The energy required for solute molecule A to move from the cage $E^J{}_{AB}$ is assumed to be the same as in the pure solvent case, that is, the solute molecule A must only break solvent bonds and no polymer bonds. This description implies that solute A diffusing in a polymer solution moves through the solvent only and not along the polymer.

Combining Equations (10) and (11), one gets

$$E_{DAB} - E_{DAS} = E^H{}_{BB} - E^{H}{}_{(BB+PB)} \qquad (12)$$

This expression can be used in Equation (9) to obtain

$$\frac{D_{AS}}{D_{AB}} = \left(\frac{V_S}{V_B}\right)^{1/3} \left(\frac{M_S}{M_B}\right)^{1/2} \exp\left(\frac{E^H{}_{BB} - E^{H}{}_{(BB+PB)}}{RT}\right) \qquad (13)$$

It is important to note that this result states that the diffusivity of solute A in a polymer solution relative to that

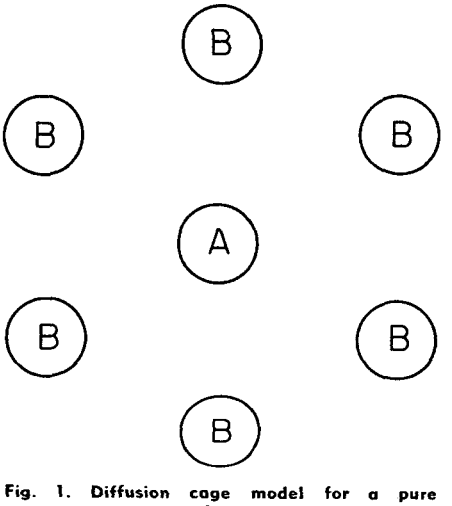

Fig. 1. Diffusion cage model for a pure solvent.

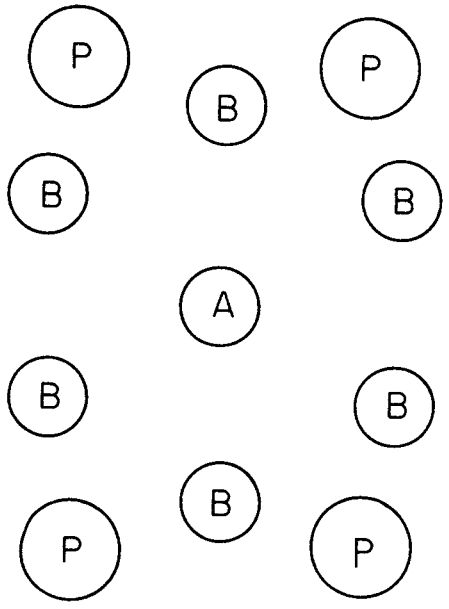

Fig. 2. Diffusion cage model for polymer solutions.

in the pure solvent is independent of the diffusing solute A. In addition, the quantity $\Delta E = E^{H}_{BB} - E^{H}_{(BB+PB)}$ should be very closely related to polymer and solvent physical properties, and it should be possible to predict ΔE from solution properties. ΔE should be a function of the amount of polymer in solution, the type of polymer in solution, and a measure of the strength of the polymer-solvent bonds.

Before Equation (13) can be used to predict diffusivities, the functional form for ΔE must be determined. This was done by calculating values of ΔE from the available literature data on gas and liquid diffusion in polymer and protein solutions and the oxygen and carbon dioxide diffusion values in plasma obtained in this investigation. These calculated values of ΔE were then related to the amount and type of polymer in solution and the strength of the polymer-solvent bonds.

EXPERIMENTAL

Since there appeared to be sufficient data available in the literature to test a predictive equation for diffusion in polymer solutions, the only additional data necessary were those for systems containing biological polymers. In this study diffusivity measurements were made on a solution consisting of all the constituents of human plasma at an average concentration level (*12, 28*).

The gas-liquid diffusivity measurements of oxygen and carbon dioxide in plasma were determined with the steady state diaphragm cell technique developed by Tham, Bhatia, and Gubbins (*41*) and modified by Navari (*28*). The plasma employed was an aqueous solution of all the constituents of normal human plasma. It was prepared by dissolving the various plasma constituents at an average concentration level in completely degassed distilled water at the system temperature. Following dissolution, the solution was buffered to the desired *p*H of 7.41 and maintained at this value throughout all the diffusion measurements.

Density measurements were made on all fabricated plasma solutions in order to determine the magnitude of any change in volume on mixing of the dry protein with fabricated plasma. The measurements show that the change in volume on mixing for each concentration was essentially zero, and the only differences noted were within the experimental accuracy of the pcynometer. These results agree with those of Oncley et al. (29), who also found no volume change on mixing of plasma proteins with an aqueous salt solution. Further details on the experimental procedure can be found elsewhere (*28*).

DISCUSSION OF RESULTS

Diffusing Solute

The predictive equation developed from application of the absolute rate theory, Equation (13), states that the diffusivity of a solute in a polymeric solution relative to that in the pure solvent is independent of the diffusing solute. In order to test this assertion for the fabricated plasmas used in his study, the data obtained were compared with those of Connor and Gainer (*12*) for dextrose-water diffusing into the same fabricated plasma systems. Both sets of data are plotted in Figures 3, 4, and 5 as the ratio of solute diffusivity through the plasma to the solute diffusivity through the solvent water versus the protein concentrations. Figure 3 and 4 show that in the albumin and in the gamma globulin-fabricated plasma systems, the oxygen diffusion coefficient ratios have the same values as the dextrose-water ratios within experimental error. Also, Figure 5 shows relatively good agreement between the carbon dioxide diffusivity ratios and the dextrose-water ratios for the fibrinogen-fabricated plasma system. The lack of agreement at values of fibrinogen concentration above 0.30 g./100 ml. may be due to experimental error (*p*H changes) and to the difficulty encountered in dissolving fibrinogen at higher concentrations. The fact that there is good agreement among the diffusivity ratios for different diffusing solutes supports the assertion that the diffusivity ratio is independent of the diffusing species.

In order to investigate this assertion for nonbiological polymer solutions, the data of Osmers (*30*) for ethanol and glycerol diffusing into aqueous carboxymethyl cellu-

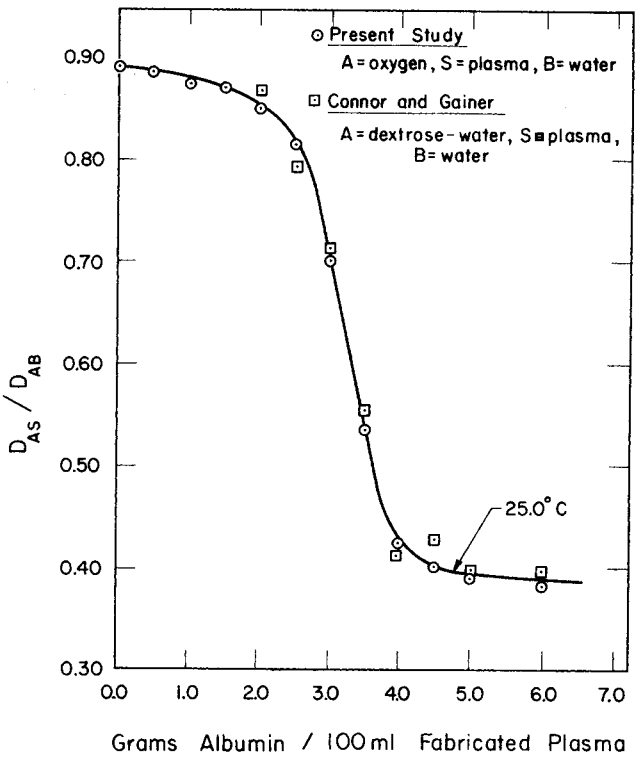

Fig. 3. Variation of ratios of diffusivity in plasma with albumin concentration.

lose (CMC) solutions and Quinn and Blair (*32*) for carbon dioxide diffusing into the same CMC solutions were compared. Figure 6 shows that the ratio of the solute diffusivity through the aqueous-CMC solution to the solute diffusivity through the solvent water is independent of the nature of the diffusing solute. These results and those of Figures 3 to 5 confirm one of the major assumptions of Equation (13), and suggest that it may be possible to predict the diffusivity ratio from solution properties only.

Activation Energy Difference

In order to obtain an a priori method to predict $\Delta E = E^H_{BB} - E^H_{(BB+PB)}$, values were calculated from diffusivity data using Equation (13). This was done for the oxygen and carbon dioxide diffusion data in the fabricated plasma solutions, for the oxygen-albumin saline diffusivity data of Goldstick (*19*), and for the dilute polymeric solution diffusivity data of Li and Gainer (*26*), Osmers (*30*), Weinberg (*44*), and Quinn and Blair (*32*). These polymeric systems were chosen because diffusivity values were reported for a number of concentrations.

The result for all the systems employed was that the logarithm of the activation energy difference (ΔE) varied linearly with the reciprocal of the polymer or protein weight fraction (c). When we express this mathematically, the activation energy difference is

$$\Delta E = \Delta E_M \exp(-k/c) \qquad (14)$$

where ΔE_M and $(-k)$ are the intercept and slope respectively of a $\ln(\Delta E)$ versus $(1/c)$ plot. Note that as c approaches zero, ΔE approaches zero, that is, $E^H_{BB} = E^H_{(BB+PB)}$, the expected result for no polymer in the solution.

There are a number of important aspects of Equation (14). Figure 7 is a plot of the equation for the various systems used by Li and Gainer (*26*) and Weinberg (*44*). Note that the intercept is the same for each particular polymer in solution, regardless of the diffusing species or the solvent. This is equivalent to stating that ΔE_M is a function of the polymer in the solution only and not of the solvent. It follows that since the slopes of the plots are significantly different, the slope is a function of the solvent or of the polymer-solvent interactions.

The fact that Equation (14) was applicable to the data of Goldstick (*19*) illustrated that the dilute protein solution of albumin in saline could be treated in the same way as dilute polymer solutions; the logarithm of ΔE is a linear function of the reciprocal weight fraction.

It was also found that the fabricated plasma systems of this investigation could be described by Equation (14). Small deviations occurred at high concentrations of protein in the albumin and gamma globulin systems, and this may be due to the fact that the fabricated plasma is actually a solution of many proteins, rather than only a single macromolecule in solution as in the other systems employed in the analysis. At the higher albumin and gamma globulin concentrations, the protein-protein interactions appear to become important, resulting in deviations from a linear relationship between $\ln(\Delta E)$ and reciprocal protein concentration. It is interesting to note, however, that the lower concentrations of the albumin-plasma system give an intercept value of $\Delta E_M = 3{,}600$ cal./mole, the same value of the intercept in the albumin-saline solution. This again indicates ΔE_M to be solely a function of the polymer or protein in solution.

The albumin and gamma globulin-fabricated plasma systems show ΔE to be a stronger function of temperature at higher concentrations of the respective proteins than at low concentrations. This may mean that temperature

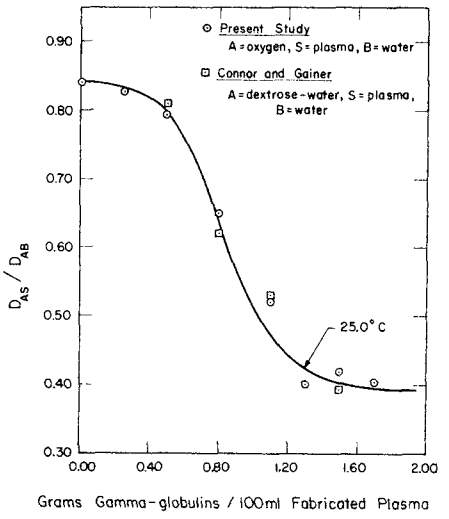

Fig. 4. Variation of ratios of diffusivity in plasma with gamma globulin concentration.

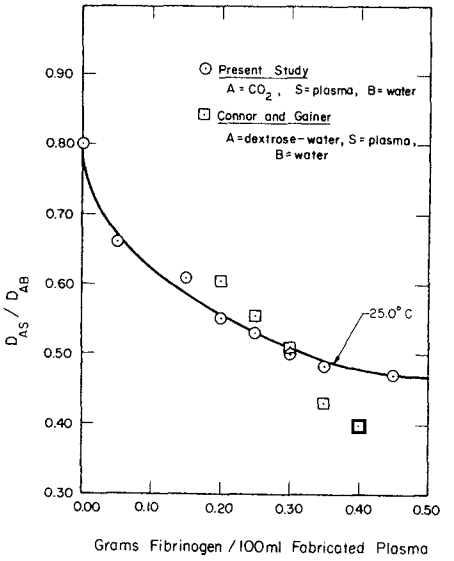

Fig. 5. Variation of ratios of diffusivity in plasma with fibrinogen concentration.

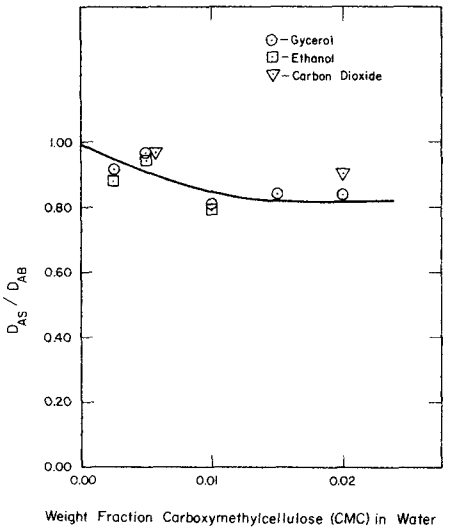

Fig. 6. Variation of ratios of diffusivity in aqueous CMC solutions with CMC concentration at 25°C

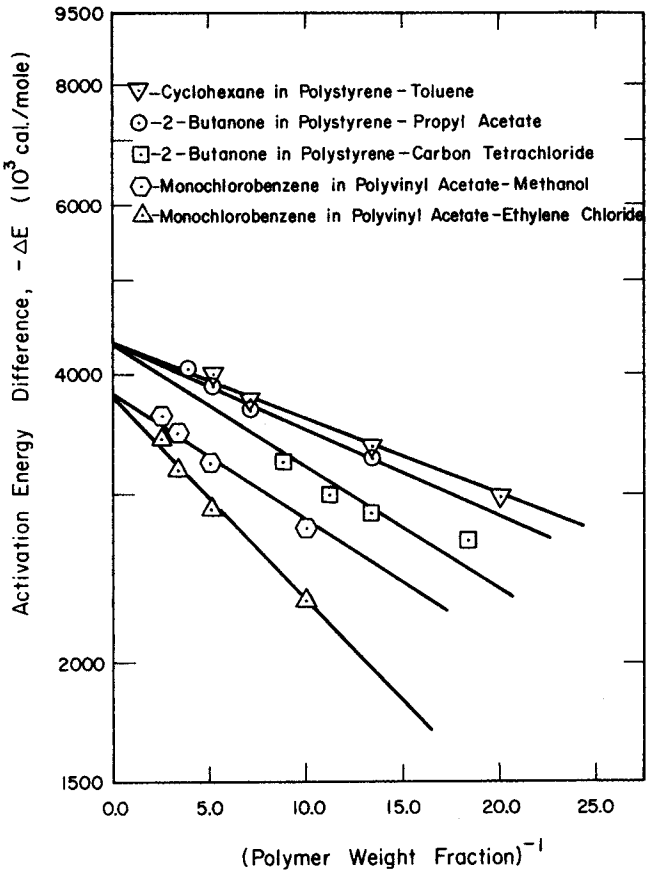

Fig. 7. Variation of activation energy difference in polymer solutions with polymer concentrations at 25°C.

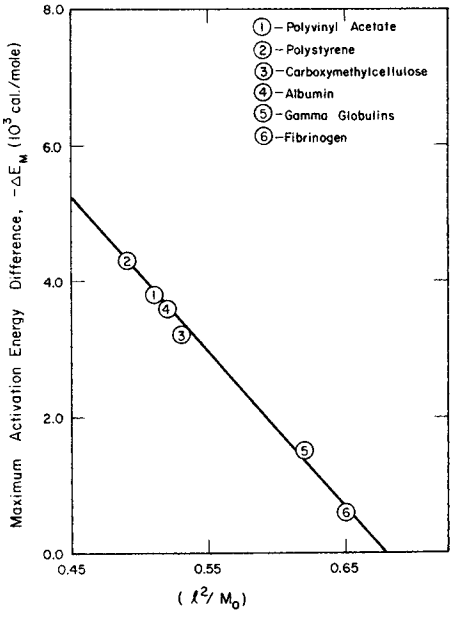

Fig. 8. Variation of maximum activation energy difference with (l^2/M_0).

has a much larger effect on protein-protein interactions than protein-solvent interactions.

In order to have an a priori method of predicting ΔE, it is necessary to have values for ΔE_M and k for any system. The analysis of the various systems indicated that ΔE_M is a function of the polymer only, while k is a measure of the polymer-solvent interactions. Thus it seems plausible that ΔE_M might be related to a polymer property, and that k could be related to a solution property.

For a polymer in a solution, the root-mean-square end to end distance between the ends of a polymer chain usually consists of two factors, one containing terms depending only on the nature of the polymer, such as bond length, the bond angle, and/or the degree of restriction of rotation; the other independent of the nature of the polymer, depending only on chain length (*6, 16, 40*). This can be expressed mathematically as

$$\overline{r^2} = (l^2)\ (x) \qquad (15)$$

Rewriting Equation (15) with x in terms of molecular weights, one obtains

$$(l^2/M_0) = (\overline{r^2}/M_p) \qquad (16)$$

It thus appears that ΔE_M could be related directly to l, l^2, or (l^2/M_0), which are all functions characteristic of the polymer only. Figure 8 shows a plot of (l^2/M_0) versus values of ΔE_M for both the polymer solutions and the protein solutions. If l or M_0 cannot be determined experi-

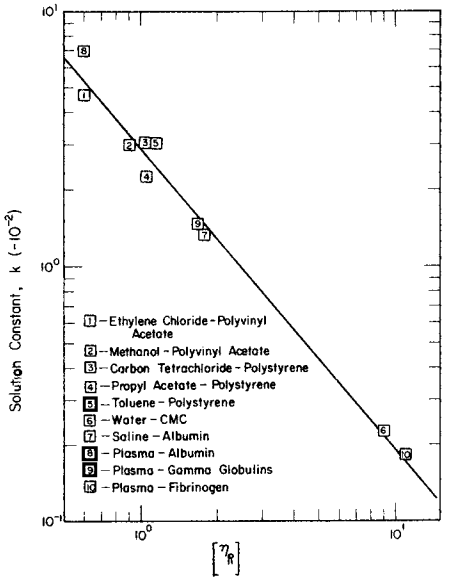

Fig. 9. Variation of k with η_R.

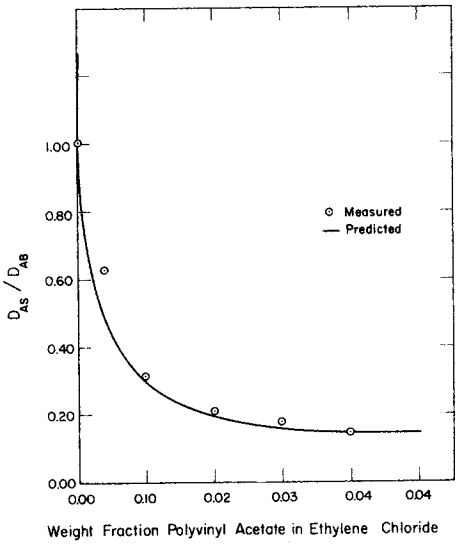

Fig. 10. Diffusivity of monochlorobenzene in polyvinyl acetate-ethylene chloride solutions at 24 ± 1°C.

mentally, (l^2/M_0) can be estimated from intrinsic viscosity measurements (40). The plot demonstrates that there is a good correlation between ΔE_M and (l^2/M_0) of the following form:

$$\Delta E_M = C_1 (l^2/M_0) + C_2 \qquad (17)$$

This correlation gives a way to predict ΔE_M for both the proteins and the polymers.

As a result of the apparent success in predicting ΔE_M, it appears that the final step in obtaining an a priori method to predict ΔE is predicting the values of the solution constant k. As previously noted, k should be a direct measure of the solvent-polymer (protein) interactions. There are a number of physical properties of a polymer solution which could be used to correlate k, but a viscosity function should give a more direct measure of the polymer-solvent interactions. As a result, k was correlated with a solution viscosity function of the form

$$\eta_R = \left(2\eta/\eta_0 c - 1/\eta_0 \frac{d\eta}{dc}\right) \text{ for large } c$$

It is noteworthy that for large values of η/η_0, η_R will approximate the intrinsic viscosity. Figure 9 shows values of k plotted against corresponding values of η_R for the polymer and protein systems. The plot can be represented by the equation

$$\ln(k) = C_3 \ln(\eta_R) + C_4 \qquad (18)$$

Predictive Equation

Since values of ΔE_M and k can be obtained from Equations (17) and (18) respectively, Equation (14) can be used to find values of the activation energy difference for polymer solutions. These values can then be employed with Equation (13) to predict the ratio of diffusivity of a solute in a dilute polymer solution relative to that in the pure solvent. Figures 10 to 20 compare the experimental data with the predicted values of Equation (13). The comparison shows good agreement between the predicted and experimental values, except at high concentrations of albumin and gamma globulin in the fabricated plasma where the deviations tend to be larger than those over the entire range. As discussed previously, this is probably due to increasing interactions among the proteins in the multiprotein fabricated plasma.

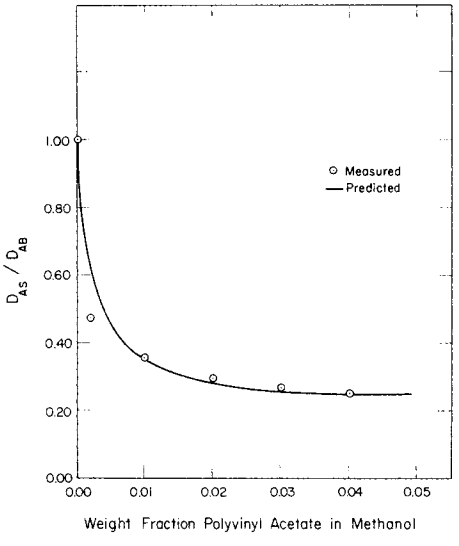

Fig. 11. Diffusivity of monochlorobenzene in polyvinyl acetate-methanol solutions at 24 ± 1°C.

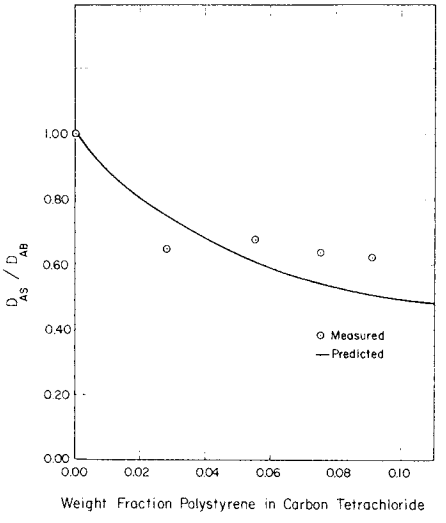

Fig. 12. Diffusivity of 2-butanone in polystyrene-carbon tetrachloride solutions at 24 ± 1°C.

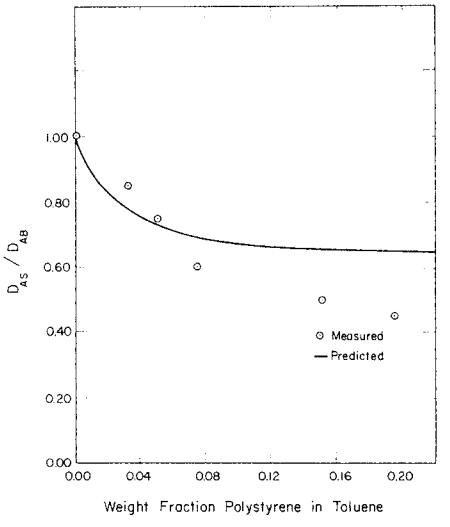

Fig. 13. Diffusivity of cyclohexane in polystyrene-toluene solutions at 25°C.

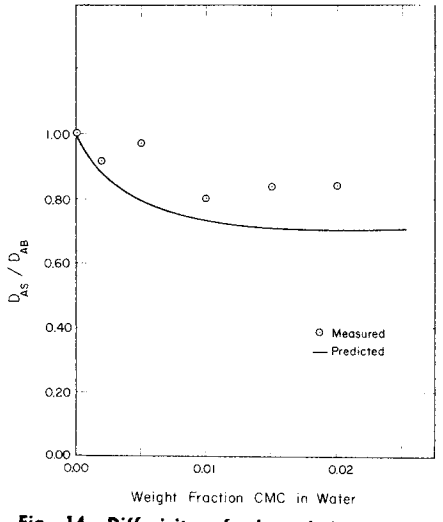

Fig. 14. Diffusivity of glycerol in aqueous carboxymethylcellulose solutions at 24 ± 1°C.

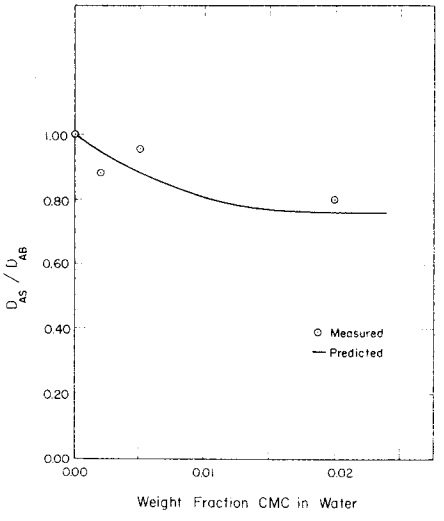

Fig. 15. Diffusivity of ethanol in aqueous carboxymethylcellulose solutions at 25.0°C.

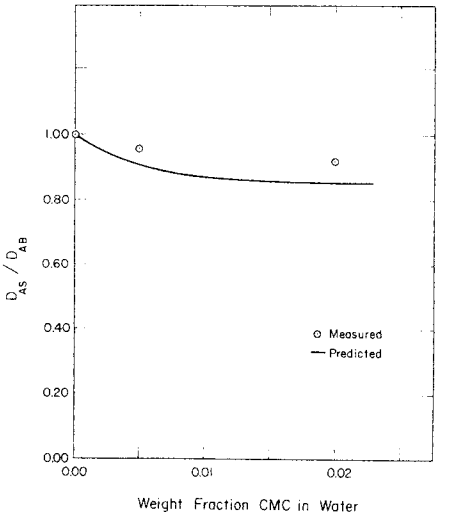

Fig. 16. Diffusivity of carbon dioxide in aqueous carboxymethylcellulose solutions at 25.0°C.

Diffusivity Maxima

Most data reported to date have shown decreases in gas or liquid diffusivity with increased polymer concentration. However, a few investigators have reported increased diffusivities with increased polymer concentration. Astarita (*1*) and Zandi and Turner (*46*) have found increased gas diffusivities with increases in the concentration of polymers carboxymethyl cellulose (CMC), carboxypolymethylene, and ET597 in aqueous solutions. Li and Gainer (*26*) reported that unpublished data of Astarita, Osmers, and Metzner showed increased liquid diffusivities with increased CMC concentration. However, Osmers (*30*) has since shown that by applying a necessary correction developed by Duda and Vrentas (*14*) to these microinterferometric data, the liquid diffusivities actually decreased with increased CMC concentration. Osmers (*30*) has also reported that he was unsuccessful in duplicating the data of the one system in which Li and Gainer (*26*) found an increase in diffusivity with increased polymer concentration, indicating that this increase may have been due primarily to experimental errors. Thus the only unexplained maxima are those of Astarita (*1*) and Zandi and Turner (*46*).

Due to the existence of these reported maxima, Equation (13) was investigated for possible maxima or minima. It was found that in order to have the diffusivity increase with increasing polymer concentration, the value of the activation energy difference must be non-negative. This condition did not hold for any of the polymers in this investigation, nor does it appear to exist for any of the systems reported in the literature, including those of Astarita (*1*) and Zandi and Turner (*46*).

It is interesting to note that these two investigations employed the laminar liquid jet technique developed by Scriven and Pigford (*37*) for Newtonian liquids. When a solution of polymer material is used in the jet, a number of second-order effects, such as nozzle outlet, jet shrinkage, and jet expansion, due to the relaxation of elastic stresses exist and must be considered (*1, 4*) in analysis. As the polymer concentration is increased, these effects may become increasingly important, requiring a detailed knowledge of the fluid mechanical behavior of the jet and rendering the results questionable. Both Astarita (*1*) and Zandi and Turner (*46*) obtained the largest maxima at the highest polymer concentration employed.

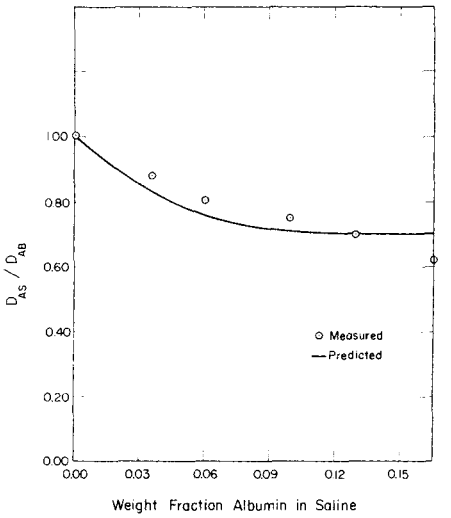

Fig. 17. Diffusivity of oxygen in albumin-saline solutions at 25.0°C.

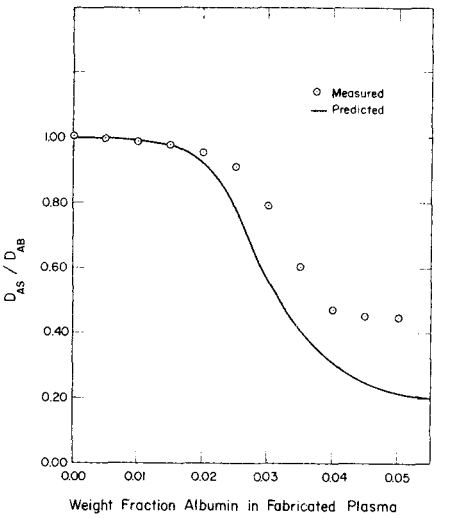

Fig. 18. Diffusivity of oxygen in albumin-fabricated plasma solutions at 25.0°C.

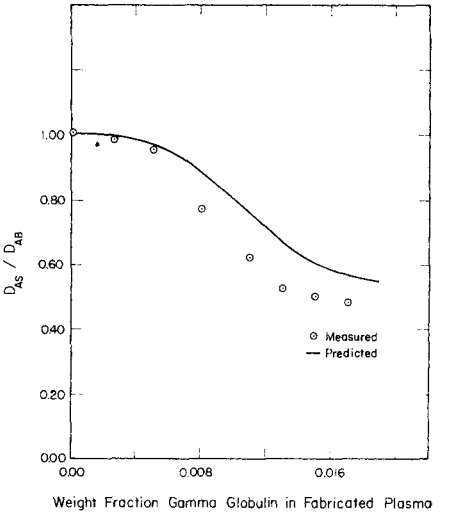

Fig. 19. Diffusivity of oxygen in gamma globulins-fabricated plasma solutions at 25.0°C.

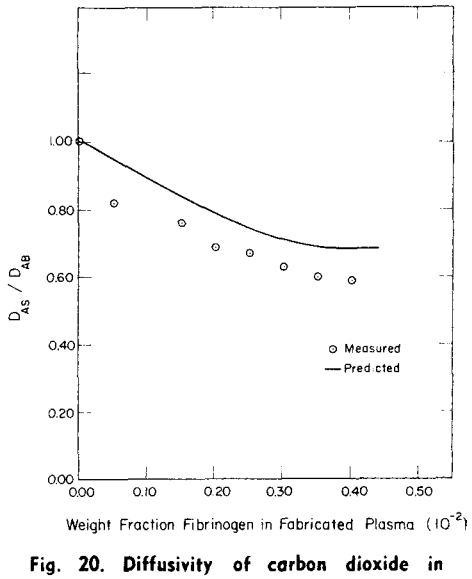

Fig. 20. Diffusivity of carbon dioxide in fibrinogen-fabricated plasma solutions at 25.0°C.

NOTATION

c = polymer or protein weight fraction
C_p, C_v = heat capacities
D = diffusion coefficient
E_D = energy of activation for diffusion
E_μ = energy of activation for viscosity
$E^H{}_{BB}$ = energy required for cage deformation or vacancy formation caused by breaking solvent-solvent bonds
$E^J{}_{AB}$ = energy required for solute molecule A to move from the solvent B cage caused by breaking solute-solvent bonds
$E^H{}_{(BB+PB)}$ = energy required for cage deformation or vacancy formation caused by breaking solvent-solvent bonds and solvent-polymer bonds
ΔE = activation energy difference, $E^H{}_{BB} - E^H{}_{(BB+PB)}$
ΔE_M = maximum activation energy difference
ΔH_M = molar heat of mixing of the polymer solution
ΔH_{VAP_B} = molar heat of vaporization of the pure solvent B
K = constant which depends on the molecular packing of the liquid
k' = Boltzman's constant
k = solution constant
l = effective bond length of the repeating units of the polymer
M = molecular weight
M_p = polymer molecular weight
M_0 = molecular weight of the repeating unit of the polymer
m = mass of the diffusing molecule
N = Avogadro's constant
R = gas constant
$(\bar{r^2})^{1/2}$ = root-mean-square end to end distance between the ends of the polymer
T = absolute temperature
u = velocity of sound in a liquid
V = molar volume
v_{fAB} = free volume of molecule A surrounded by neighbor molecules B
x = number of repeating units of a polymer

Greek Letters

ξ = parameter which describes the geometrical configuration of the diffusing molecules and its nearest neighbors
μ = fluid viscosity
η = polymer or protein solution viscosity
η_0 = solvent viscosity

Subscripts

A = diffusing solute
B = liquid solvent
S = solution (polymer or protein plus solvent)

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