Diffusion in Glycerol-Water Mixture

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When the diffusion coefficient is concentration dependent, the diffusion curve, in which the concentration gradient is plotted against distance, will no longer be symmetric with respect to the position of the original boundary. In such a skewed curve, the maximum position of the concentration gradient is displaced to the solvent side or to the solution side depending on whether the concentration dependence is positive or negative, respectively. The degree of skewness of the curve is a measure of the extent of the concentration dependence of the diffusion coefficient.

The concentration dependence of diffusion coefficient, especially in the case of polymer solutions, has been studied[1-4].

This dependence is attributed to a thermodynamic factor and to a hydrodynamic factor. In most cases, these factors act in opposite directions and partly counterbalance the resultant concentration dependence of the diffusion coefficient. The thermodynamic factor is due to the non-ideality of the solution and usually contributes to the positive dependence, that is, to increase the rate of diffusion with increasing concentration. On the other hand, the hydrodynamic factor tends to slow down the diffusion rate with increasing concentration. This factor is attributed to the concentration dependence of the frictional coefficient of the diffusing particles. When the size and shape of the diffusing particles are independent of the concentration, the hydrodynamic factor can be estimated from the local viscosity of the medium in which the particles are diffusing[5]. It has not been entirely clear, however, how one can determine the local viscosity of the medium. In the case of very dilute solutions, the local viscosity is approximated by the solvent viscosity, whereas, at higher solute concentrations, the local viscosity is apparently somewhere between the solvent viscosity and the solution, or macroscopic, viscosity. In the case of solutions of small molecules such as glycerol-water mixtures, we have found that the local viscosity, obtained from fluorescence measurements of Auramine O, equals the macroscopic viscosity of solution[6].

It is the purpose of the present paper to investigate the concepts mentioned above using the glycerol-water system as an example, and

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covering a wide range of concentrations. The diffusion measurements were carried out in an interferometric micro-diffusion apparatus[5].

Experimental

Apparatus.—We have developed a simple interferometric microdiffusion method which employs an ordinary light microscope. The diffusion cell is an optical wedge consisting of two partially-reflecting microscope slides and placed on the microscope stage. Small drops of the liquids are introduced into the cell to form a sharp boundary readily. Since the cell is very thin, convection currents are eliminated and hence rigid temperature control is unnecessary and the temperature was maintained in the vicinity of 25°C. The time required for diffusion measurements in the micro method is reduced by several thousand-fold that required in a conventional diffusion apparatus. The interference fringes produced in the cell are photographed every minute. Since each fringe represents a contour line of constant optical path in the wedge, the refractive index gradient is easily determined. The details of this method have been treated elsewhere[5].

Results

To insure high accuracy, the diffusion measurements were carried out between several pairs of glycerol-water mixtures varying in concentrations ranging from pure water to 93% glycerol by weight. An example of a normalized diffusion curve obtained by our method is given in Fig. 1. For higher glycerol concentrations the curve is even more skewed in the direction of the higher concentration side.

The diffusion coefficient $D(c)$ as a function of concentration may be calculated from Boltzmann's equation[7]

$$D(c)=-\frac{1}{2t}\cdot\frac{\mathrm{d}x}{\mathrm{d}c}\int_0^c x\mathrm{d}c \qquad (1)$$

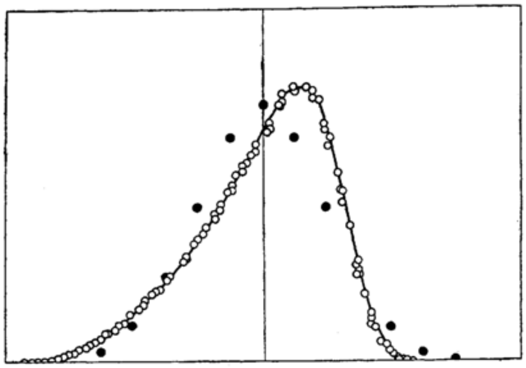

Fig. 1. Normalized diffusion curve: 62% glycerol against pure water (water on left); Open circles: experimental points. Black dots: Gaussian curve.

where c is the concentration, x is the distance along the direction of diffusion, and t is the time. In the present study, the diffusion coefficients were calculated from Boltzmann's equation utilizing normalized coordinates. The diffusion coefficient as a function of glycerol concentration is given in Fig. 2. The fact that the slope is negative, shows that the hydrodynamic factor is predominant. Since this curve is not linear, simple graphical methods for evaluating the concentration dependence[3,8] are not valid because such methods assume linearity. A general statistical method for analyzing slightly skewed curves has been developed[9], but is not valid for high glycerol concentration since the diffusion curves are highly skewed (see, for example, Fig. 1).

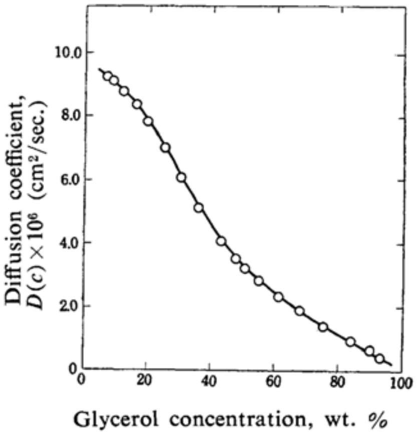

Fig. 2. Diffusion coefficient of glycerol as a function of concentration.

Discussion

The diffusion coefficient in non-ideal solution is given by the equation[10]

$$D(c)=\frac{\boldsymbol{RT}}{f}\cdot\frac{\mathrm{d}\ln a_2}{\mathrm{d}\ln c} \qquad (2)$$

where f is the frictional coefficient of the diffusing particles, a_2 is the activity of the solute at concentration c, $\boldsymbol{R}$ is the gas constant, and T is the absolute temperature. We have calculated the thermodynamic factor, $\mathrm{d}\ln a_2/\mathrm{d}\ln c$, in Eq. 2 from literature values of the vapor pressures of glycerol-water mixtures[11]. The frictional coefficient f is proportional to the local viscosity of the medium. Hence, if the local viscosity is identical with the macroscopic, or solution, viscosity this hydrodynamic

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TABLE I. CORRECTION FACTORS FOR THE DIFFUSION COEFFICIENT

Glycerol conc. (wt. %)	10	20	30	40	50	60	70	80	90
$(d \ln a_2/d \ln c)$	1.0	1.2	1.4	1.7	2.0	2.3	2.8	3.2	3.5
Viscosity	1.15	1.54	2.16	3.18	5.04	8.82	17.96	45.86	163.6

factor should be proportional to observed viscosities of the glycerol-water mixtures. These correction factors are given in Table I. Applying these correction factors to the data of Fig. 2, we obtain the curve shown in Fig. 3.

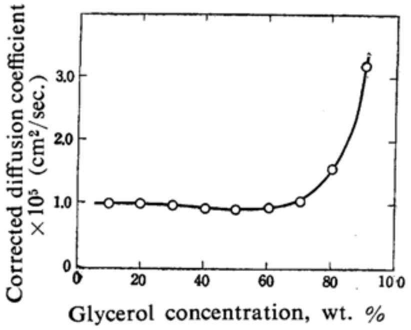

Fig. 3. Corrected diffusion coefficient of glycerol.

The corrected diffusion coefficient illustrated in Fig. 3 is sensibly independent of concentration up to 70% glycerol above which it rises rapidly. The increased mobility at very high glycerol concentrations could be due to a decreased hydration of the glycerol molecules. Vapor pressure measurements of glycerol-water mixtures have been interpreted in terms of a decrease of hydration with increasing concentration of glycerol[12]. More direct measurements, however, such as obtained from nuclear magnetic resonance, could better indicate changes in hydration.

Summary

Diffusion studies of glycerol in glycerol-water mixtures ranging from zero to 93% glycerol were carried out using the micro-interferometric method. For higher concentration of glycerol the diffusion coefficient decreases strongly with increasing concentration and the diffusion curves are highly skewed. Applying thermodynamic and hydrodynamic correction obtained from vapor pressure measurements and solution viscosities, respectively, the diffusion coefficient was found to be sensibly independent of glycerol concentration up to about 70% after which it rises. The increased mobility at very high glycerol concentrations is attributed to a decreased hydration of the glycerol molecules under these conditions.

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