V	molar volume, cm^3 mol^{-1}
V^E	molar excess volume, cm^3 mol^{-1}
x_i	mole fraction of component i
Z^E	excess value of quantity Z

Greek Letters

δ_{max}	maximum deviation in units of fitted data
ρ	density, g cm^{-3}
σ	standard deviation in units of fitted data

Subscripts

m,f	measured or fitted values

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Received for review October 31, 1990. Accepted February 25, 1991. Partial financial support by the Ministry of Science and Research of Nordrhein-Westfalen is gratefully acknowledged.

Infinite Dilution Diffusion Coefficients of Poly(ethylene glycol) and Poly(propylene glycol) in Water in the Temperature Range 303–318 K

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In this paper, the infinite dilution diffusion coefficients of poly(ethylene glycol) and poly(propylene glycol) in water were measured by using the Taylor dispersion technique. For poly(ethylene glycol), the measurements were performed in the temperature range of 303–318 K at four different polymer molecular weights. The diffusion coefficient was found to increase linearly with temperature but decrease exponentially with molecular weight. In addition, the diffusion coefficient of poly(propylene glycol) (*M* = 400) was found to be lower than that of poly(ethylene glycol) at the same molecular weight but has the same temperature dependence.

1. Introduction

Diffusion coefficient measurements provide fundamental information needed in various engineering and industrial operations. For example, diffusion is important in the design of chemical reactors, liquid–liquid extractors, and absorbers, as well as distillation columns. In addition, the study of fluid-state theory, mass-transfer phenomena, and molecular interactions can be further aided by accurate determinations of diffusion coefficients.

There are many well-established methods for the determination of diffusion coefficients in liquids (*1*). The most accurate measurements of the mutual diffusion coefficients of binary liquid mixtures are performed by the interferometric method (*1*). However, this technique has been proven to be tedious and difficult to be applied to conditions far from ambient (*1,2*). Instead, the Taylor dispersion technique based on chromatographic peak broadening is used in the present work for the determination of the diffusion coefficient. This technique is direct and offers the advantage of speed and simplicity. In fact, it has been established as an absolute method for liquid diffusivity measurements (*3–5*).

Earlier studies on the poly(ethylene glycol)/water system show that, at low concentration, the diffusion coefficient depends on the polymer molecular weight and not on the concentration (*6*). However, no experimental data for diffusion coefficient as a function of temperature is available for this system. In the present paper, the infinite dilution diffusion coefficients of poly(ethylene glycol) in water at different molecular weights and at different temperatures are investigated. In addition, the infinite dilution diffusion coefficients of poly(propylene glycol) at four different temperatures are measured to study the effect of branching on diffusion.

2. Experimental Section

The ideal model of the instrument for the measurement of the diffusion coefficient by the Taylor dispersion technique consists of an infinitely long straight tube of uniform circular cross section, radius a_0, through which a fluid mixture passes in laminar flow with mean velocity, $\bar{u}_0$. A δ-function pulse of a liquid mixture is injected at a distance L from the detection point. The mutual diffusion coefficient of the liquid mixtures, D_{12}, is given by

$$D_{12} = \frac{A}{24\pi t_{id}}\left[\frac{[1 + 4\sigma_{id}^2/t_{id}^2]^{1/2} + 3}{[1 + 4\sigma_{id}^2/t_{id}^2]^{1/2} + 2\sigma_{id}^2/t_{id}^2 - 1}\right] \times [1/2 + 1/2(1 - \delta_a)^{1/2}] \quad (1)$$

where A = cross section area of the tube; t_{id} = first raw

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0021-9568/91/1736-0329$02.50/0

Table I. Characteristics of the Instrument

item	symbol	dimension
diffusion tube length	L/m	12.265
diffusion tube internal radius	a_0/mm	0.5527
coil radius	R_c/m	0.305
volume of injected sample	V_i/μL	20
volume of detector cell	V_c/μL	10
length of connecting tube	l/m	0.35
radius of the connecting tubing	r/mm	0.1143

moment of the distribution; σ_{id}^2 = second central moment of the distribution; $\delta_a = 12.7997\bar{u}_0 a_0{}^2/48LD_{12}$; L = length of the tube; and $\bar{u}_0$ = mean velocity.

The characteristics of the instrument are listed in Table I. The diffusion tube, made from approximately 12 m of stainless steel tubing that has a nominal internal diameter of about 0.55 mm, was wound in a smooth helical coil on a metal mould. The metal mould was then filled with molten solder to ensure good thermal contact after which it was placed in a water bath. Its temperature was maintained by a thermostat (Thermomix U, Bruan, West Germany) to ±0.1 °C. At its upstream end, the diffusion tube was directly connected to an injection valve (Rheodyne Model 7010) that was fitted with a sample loop of nominal volume of 20 μL. At its downstream end, the diffusion tube was coupled to one side of a differential refractometer (Model R401, Waters Associate) by means of a short length of insulated connecting tubing. This carrier fluid flow was maintained by the hydrostatic pressure provided by the reservoir of fluid, whose level was adjusted to give the desired flow rate.

The data recorded during a single measurement represents the distribution of the perturbation of the concentration of the flowing stream at the end of the diffusion tube as a function of time. For application of the Taylor dispersion equation in determining the corresponding diffusion coefficient, D_{12}, the moments of the distribution may in principle be determined by direct integration of the concentration profile $C(t_i)$ recorded at discrete times t_i. However, this procedure has not proved to be as precise as another method where the eluted concentration distribution departs negligibly from a Gaussian distribution under the conditions employed in the measurements:

$$C(t) = A\exp(-(t-\bar{t})/2\sigma^2) \qquad (2)$$

Consequently, the moments $\bar{t}$ and σ^2 may be determined by considering them as parameters of the diffusion time and the ratio of peak area to peak height, respectively.

Poly(ethylene glycol) of molecular weights of 200 ± 10, 300 ± 15, 400 ± 20, and 600 ± 30 (Fluka Chemika, Switzerland) were employed in the present study. Each sample was dissolved in water to give a mole fraction of 0.0125. The mole fraction was kept low to ensure that the value of the diffusion coefficient would be independent of concentration and to give a sample peak of reasonable size.

The samples prepared were first filtered through a membrane of pore size 0.45 μm to exclude impurities before each of them was injected into the sample loop. Distilled water was filtered before being poured into the reservoir to eliminate impurities that might clog up the diffusion coil. Degassing of solvent by helium was also performed to prevent formation of bubbles in the system.

As a laminar stream of water was flowing through the system, a sample was injected. Measurements were carried out at temperatures 303, 308, 313, and 318 K for each molecular weight. In addition, the measurement was repeated with poly(propylene glycol) of molecular weight 400 at four temperatures. The experimental working range for the instrument had been tested, and it was found that diffusion coefficients obtained from measurements carried out with diffusion times of between 100 and 150 min departed from a constant value by no more than ±0.7% (*7*). Hence, the measurements were conducted within this range. The first moment and the variance are reproducible to within ±0.2 and ±0.5%, respectively. With small corrections (*2*) due to nonzero volumes of the detector and injection sample being taken into account and from the small length of connecting tubing between the diffusion tube and the detector, the accuracy of the experimental data is estimated to be better than ±1.5%.

Table II. D_{12} Values for Different Molecular Weights of Poly(ethylene glycol) and for Poly(propylene glycol) of Molecular Weight 400 at Different Temperatures

molecular weight	$D_{12}/(10^{-10}\ \mathrm{m^2\ s^{-1}})$			
	303 K	308 K	313 K	318 K
PE 200	6.53 ± 0.08	7.34 ± 0.09	8.03 ± 0.10	9.15 ± 0.08
PE 300	5.44 ± 0.07	6.15 ± 0.07	6.89 ± 0.09	7.40 ± 0.08
PE 400	5.13 ± 0.08	5.63 ± 0.08	6.21 ± 0.09	7.00 ± 0.09
PP 400	4.40 ± 0.07	4.87 ± 0.07	5.56 ± 0.07	6.20 ± 0.08
PE 600	4.75 ± 0.07	5.11 ± 0.07	5.68 ± 0.06	6.01 ± 0.07

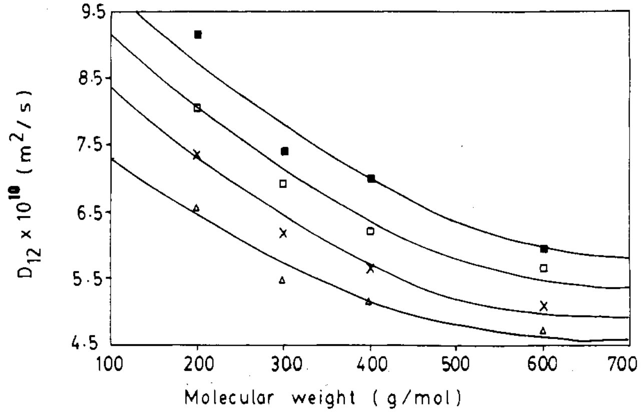

Figure 1. Molecular weight dependence of the infinite dilution diffusion coefficient of poly(ethylene glycol): (Δ) 303 K; (×) 303 K; (□) 313 K; (■) 318 K.

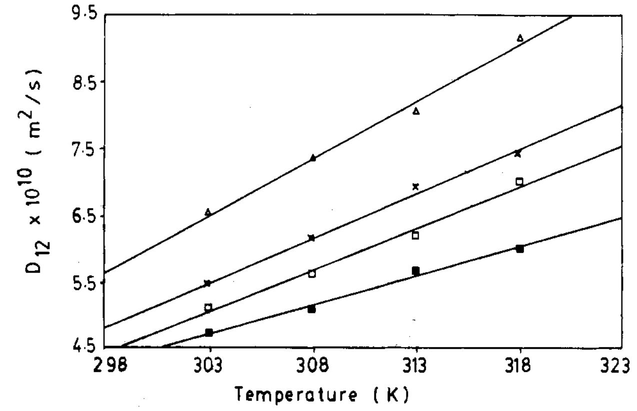

Figure 2. Temperature dependence of the infinite dilution diffusion coefficient of poly(ethylene glycol): (Δ) PE 200; (×) PE 300; (□) PE 400; (■) PE 600.

3. Results and Discussion

The experimental results are summarized in Table II. A plot of diffusion coefficient, D_{12}, vs molecular weight, M, at different temperatures is shown in Figure 1. The results showed that D_{12} varies nonlinearly with molecular weight at infinite dilution. A plot of D_{12} vs temperature, at different molecular weights, is shown in Figure 2. A nonlinear relationship was observed.

(***a***) ***Molecular Weight Dependence of Diffusion Coefficient.*** From both Figures 1 and 2, it can be seen that as molecular weight increases, the diffusion coefficient decreases. This can be simply explained by the fact that generally as M increases, size also increases and the mobility decreases, leading to a

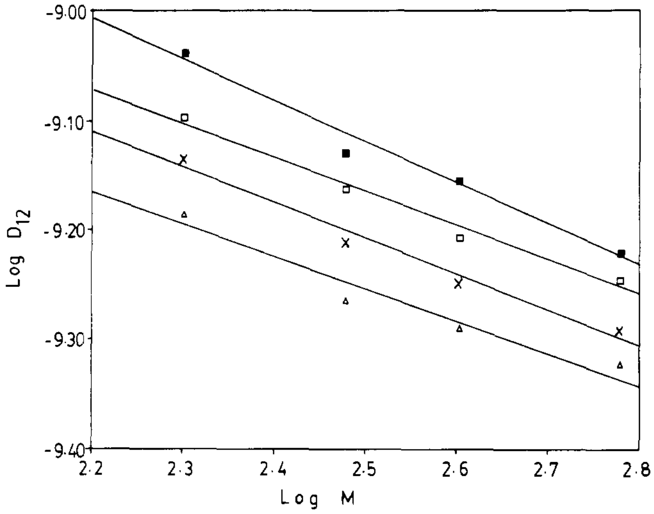

Figure 3. log D_{12} vs log M for poly(ethylene glycol): (△) 303 K; (×) 303 K; (□) 313 K; (■) 318 K.

decrease in D_{12}. Attempts were made to search the literature for previous work done on the diffusion coefficient of poly(ethylene glycol) in water but without success. However, from light-scattering experiments, Yuko and Chikako (*6*) found that, at low concentrations, the molecular weight dependence of the diffusion coefficient of poly(ethylene oxide) can be expressed as $D_{12} \propto M^{-0.39}$. In our experiments, the minute amount of sample injected into the flowing stream of water may be regarded as the condition of infinite dilution. Under such conditions, the diffusion coefficient would be expected to depend on molecular weight. The plot of log D_{12} vs log M in Figure 3 shows that the infinite dilution diffusion coefficient of poly(ethylene glycol) is proportional to $M^{-0.32}$, which is in good agreement with the earlier findings from light-scattering experiments (*6*).

(*b*) *Temperature Dependence of Diffusion Coefficient*. Figure 2 also shows that, at any molecular weight, D_{12} increases with temperature. This is a phenomenon expected and can be attributed to the kinetic considerations. As temperature increases, thermal motion also increases which could in turn cause an increase in diffusion coefficient with increasing temperature.

(*c*) *Effect of Branching on Diffusion Coefficient*. Recent studies on the influence of molecular structure on diffusion revealed that diffusion coefficients of alkane isomers decrease significantly with increasing branching (*7*,*8*). Figure 4 shows that, at the same average molecular weight of 400, the values of D_{12} for poly(ethylene glycol) are higher than that of poly(propylene glycol) for all temperatures. This is consistent with the observation that D_{12} decreases with branching. In addition, the temperature dependence of D_{12} of poly(ethylene glycol) and poly(propylene glycol), as indicated by the gradient of the graph, are also found to be the same.

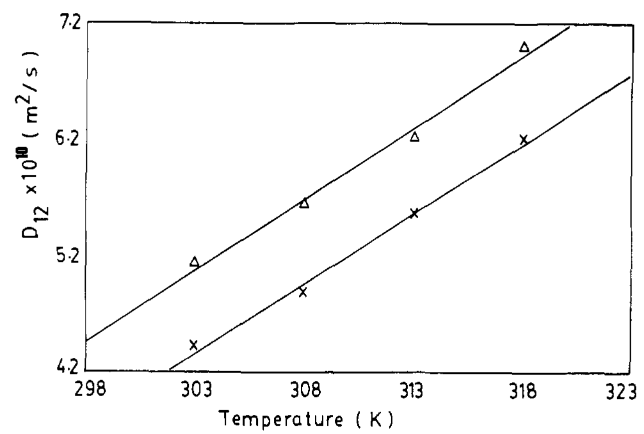

Figure 4. Effect of branching on D_{12}: (△) PE 400; (×) PP 400.

In summary, the infinite dilution diffusion coefficients of poly(ethylene glycol) in water as a function of temperature and polymer molecular weight were measured by using an instrument based on the Taylor dispersion technique. This technique is simpler and faster than many other method. The results obtained indicated that the infinite dilution coefficient of poly(ethylene glycol) decreases exponentially with increasing molecular weight in the range of 200–600 and varies linearly with increasing temperature in the range of 303–318 K.

Glossary

D_{12}	infinite dilution diffusion coefficient of solute 1 in solvent 2
M	molecular weight
PE X	poly(ethylene glycol) of molecular weight X
PP X	poly(propylene glycol) of molecular weight X

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Received for review January 7, 1991. Accepted April 8, 1991.