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Self-Diffusion of Oligo- and Poly(ethylene glycol)s in Poly(vinyl alcohol) Aqueous Solutions As Studied by Pulsed-Gradient NMR Spectroscopy

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ABSTRACT: We have measured the self-diffusion coefficients of a series of solute probes, including ethylene glycol and its oligomers and polymers in aqueous solutions and gels of poly(vinyl alcohol) (PVA) using the pulsed-gradient spin−echo NMR techniques. In an effort to link the diffusion properties of small and large molecules in polymer systems, we have selected this group of diffusant probes with various molecular weights, ranging from 62 to 4000. The self-diffusion coefficients of the solute probes decrease with increasing PVA concentrations (from 0 to 0.38 g/mL) and with increasing molecular size of the probes. The temperature dependence of the self-diffusion coefficients has also been studied for ethylene glycol and poly(ethylene glycol)s of molecular weights 600 and 2000. Energy barriers of 30.0, 36.5, and 39.0 kJ/mol have been calculated respectively for the probes, in the temperature range 23−53 °C. The experimental data are used to fit a new physical model of diffusion (Petit *et al. Macromolecules*, **1996**, *29*, 6031), which is shown to be successful in describing the effects of polymer concentration, temperature, and molecular size of the diffusants on the self-diffusion coefficients of small and large molecular probes in the polymer system.

Introduction

The study of diffusion of solute molecules in polymers is important to the application of the materials. The addition of plasticizers in polymers, the permeability through polymer membranes, the miscibility of polymers, and the release of drugs and other molecules from polymers are all related to the diffusion in polymer matrixes.[1−3] With the development of pulsed field-gradient NMR spectroscopic methods,[4,5] self-diffusion of various diffusants in polymer systems can be much more easily determined. The diffusion of solute molecules in polymer gels is influenced by many factors: polymer concentration, size and shape of the diffusant, temperature, and any specific interactions in the polymer networks. Physical models describing the self-diffusion of a solute in polymer systems are needed to understand the diffusion phenomena in polymers and to describe and estimate the mobility and diffusion rates of a component in a given polymer mixture. A number of physical models of diffusion for polymer systems have already been proposed, including those based on the concepts of free-volume theory,[6−9] obstruction effects,[10,11] and hydrodynamic interactions.[12−14] The free-volume model introduced by Fujita[6] and its modified version for aqueous systems by Yasuda *et al.*[7] showed significant deviation when used to describe diffusion of large probes, such as poly(ethylene glycol)s.[15] The model of Vrentas and Duda[8,9] seems more adequate to describe the diffusion of solvents or polymers in polymer systems.[16,17] The use of this model, however, requires the knowledge of many free-volume parameters.[17,18] Some of these parameters have been reported in the literature for some solvents as well as polymers such as polystyrene[17] and poly(methyl methacrylate),[19] but these parameters are not readily available for many other polymers, solvents, and solutes and would need to be determined by various physicochemical experiments. The application of the models based on obstruction effect by Mackie and Meares[10] and Ogston *et al.*[11] is limited to very small diffusants or dilute systems.[15,16] Won and Lodge[20] reported similar problems with the models of Cukier[12] and of Altenberger and Tirrell[13] based on hydrodynamic interactions. The “universal equation” proposed by Phillies intends to describe the diffusion of macromolecular probes over a wide range of polymer concentrations and demonstrated good agreement between the experimental data and the model.[14] We have used this model to fit the self-diffusion data of selected solute probes in poly(vinyl alcohol) (PVA) aqueous systems,[15] but questions were raised as to the applicability of the model for small diffusants and the interpretation of the fitting parameters. We have shown previously the limitations encountered in the application of selected models in the treatment of the diffusion data obtained in aqueous solutions of PVA.[15,21] It seems fair to say that the physical models of diffusion are useful in many circumstances but are limited in others. It was our wish to find a physical model that can be used to describe the self-diffusion data of both small or large diffusants, including small molecules and polymers, in dilute and concentrated polymer systems.

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We have proposed a new physical model for the interpretation of the diffusion of some solvent and solute molecules in selected polymer solutions and gels.[21] In this model, the polymer matrix is represented by a transient statistical network with a certain mesh size. The diffusing molecule is considered as a particle residing temporarily in a cavity and the diffusion occurs when the particle has enough energy to overcome a certain potential barrier. The self-diffusion coefficient, D, is related to the concentration of the polymer, c, and temperature, T, by the following equation:

$$\frac{D}{D_0} = \frac{1}{1 + ac^{2\nu}} \tag{1}$$

Here D_0 is the self-diffusion coefficient of the solute probe in the absence of the polymer matrix, $a = D_0/k\beta^2$, β and ν can be regarded as constants which are characteristic of the system, and k represents the jump frequency over the energy barriers and is given by

$$k = F_p \exp\left(-\frac{\Delta E}{k_B T}\right) \tag{2}$$

where F_p can be considered as a constant, ΔE is the energy barrier of diffusion, and k_B is the Boltzmann constant.

This model has been used successfully[21] to reproduce the polymer concentration dependence of the self-diffusion of various solvents and solute molecules in binary and ternary polymer solutions.[15,21−23] The diffusant probes used previously were generally small molecules. To make a link between the diffusion of small molecules and that of larger diffusants such as oligomers and polymers, we selected a series of solute probes including ethylene glycol and its oligomers and polymers and measured their self-diffusion coefficients in aqueous solutions and gels of poly(vinyl alcohol) using the pulsed-gradient spin−echo (PGSE) NMR techniques. Poly(ethylene glycol)s were selected since (1) they are soluble in water and miscible with aqueous PVA gels, (2) they have distinct NMR signals which do not overlap with the PVA and water signals and their NMR relaxation times (mainly T_2) are long enough so that their diffusion is easily studied by the PGSE NMR method, and (3) PEG samples are readily available with a variety of molecular weights and with narrow molecular weight distributions (nearly monodisperse). By examining the effects of polymer concentration, probe size, and temperature on the self-diffusion of these probe molecules, we can test the validity of the new model of diffusion for the case of larger diffusant molecules such as oligomers and polymers.

Experimental Section

Ethylene glycol (EG) and its oligomers (OEG) and polymers (PEG) as well as the poly(vinyl alcohol) (PVA) sample used (M = 50 000, 99% hydrolyzed) were all purchased from Aldrich (Milwaukee, WI) and used as received. Size exclusion chromatography (SEC) of the oligo- and poly(ethylene glycol)s were carried out to determine their molecular weights (M) on a Waters SEC system, equipped with three Ultrastyragel columns of nominal porosities of 1000, 500, and 100 Å, respectively. The molecular weights (M_n and M_w) of each of the OEG and PEG samples are quite narrowly distributed, as shown in Table 1 (M_w/M_n < 1.1). The OEG and PEG samples include tri-, tetra-, penta-, and hexa(ethylene glycol)s as well as PEG-200, PEG-400, PEG-600, PEG-1000, PEG-2000, and PEG-4000. The molecular weight of PEG is represented by the number following PEG.

Table 1. Number- and Weight-Average Molecular Weights (M_n and M_w) of OEG and PEG Samples Used in the Diffusion Studies as Determined by SEC

sample	theoretical MW	average MW M_n	average MW M_w	M_w/M_n
EG	62			
$(EG)_3$	150	182	182	1.00
$(EG)_4$	194	196	197	1.00
$(EG)_5$	238	198	199	1.00
$(EG)_6$	282	221	222	1.00
PEG-200	200	205	209	1.02
PEG-400	400	341	368	1.08
PEG-600	600	538	578	1.07
PEG-1000	1000	976	1038	1.06
PEG-1500	1500	1461	1532	1.04
PEG-2000	2000	2148	2246	1.04
PEG-4000	4000	4439	4626	1.04

The preparation of the samples for NMR experiments have been described previously.[15] PVA was dissolved in D_2O containing 1 wt % solute probe. The concentration of PVA ranged from 0.03 to 0.38 g/mL. D_2O (99.9%) was purchased from C.I.L. (Andover, MA). The NMR tubes containing the samples were sealed to avoid evaporation of the solvent and then heated at 100−110 °C. The heating of the samples is necessary to help in the mixing of the sample and also to prevent gelation effects. The NMR measurements were made within the 3 following days.

The self-diffusion coefficients were measured by the use of the pulsed-gradient spin−echo (PGSE) NMR technique developed by Stejskal and Tanner ($90°_x-\tau-180°_y-\tau-$echo, with gradient pulses during the half-echo time τ)[24] on a Chemagnetics CMX-300 NMR spectrometer operating at 300 MHz for protons. A magnetic resonance imaging probe with actively shielded gradients coils (Doty Scientific, Columbia, SC) and a Techron gradient amplifier were used. The gradient was applied only in the z direction. The gradient strengths used in this study were between 0.3 and 0.6 T/m, calibrated with a sample of known self-diffusion coefficient, i.e., 1 vol % HDO in D_2O with $D_{HDO} = 1.9 \times 10^{-9}$ m²/s.[25] Variable temperature NMR experiments were performed at 23, 33, 43, and 53 °C. These temperatures were calibrated while the gradient pulses were applied with a thermocouple having a constantan copper−nickel extension (T), which is not sensitive to the magnetic field. Given the slight fluctuation of the temperature (±0.5 °C), no temperature gradient was detected along the sample position in the coil. The self-diffusion coefficient D can be extracted from the attenuation of the NMR signals due to the application of the gradient pulse of various durations[4] as given in the following expression:

$$A_{2\tau} = A^*_{2\tau} \exp[-(\gamma G\delta)^2(\Delta - \delta/3)D] \tag{3}$$

Here $A_{2\tau}$ is the echo amplitude, γ is the magnetogyric ratio of ^{1}H, G is the pulsed gradient strength, δ is the duration of the gradient pulse, and Δ is the interval between the gradient pulses. The effect of T_2 (spin−spin relaxation time) is constant when τ is kept constant and is contained in $A^*_{2\tau}$, the amplitude of the echo in the absence of gradient pulses. The self-diffusion coefficient can be obtained from the relationship between the amplitude of the NMR signal and the other NMR parameters as shown in eq 3. The error of the measured self-diffusion coefficients was estimated as less than 5%. In the NMR experiments, the gradient pulse duration δ varied from 0.1 to 60 ms, the other parameters were kept constant, and their values are those noted in parentheses: half spin−echo time τ (120−140 ms); gradient pulse interval Δ (the same as τ), recycle delay (8−60 s), number of acquisitions (4−8), 90° pulse length (22−35 μs), spectral width (10 kHz), and line broadening (5−10 Hz).

A nonlinear least-squares fitting method was used to fit the experimental data to the diffusion model (eq 1), and the errors

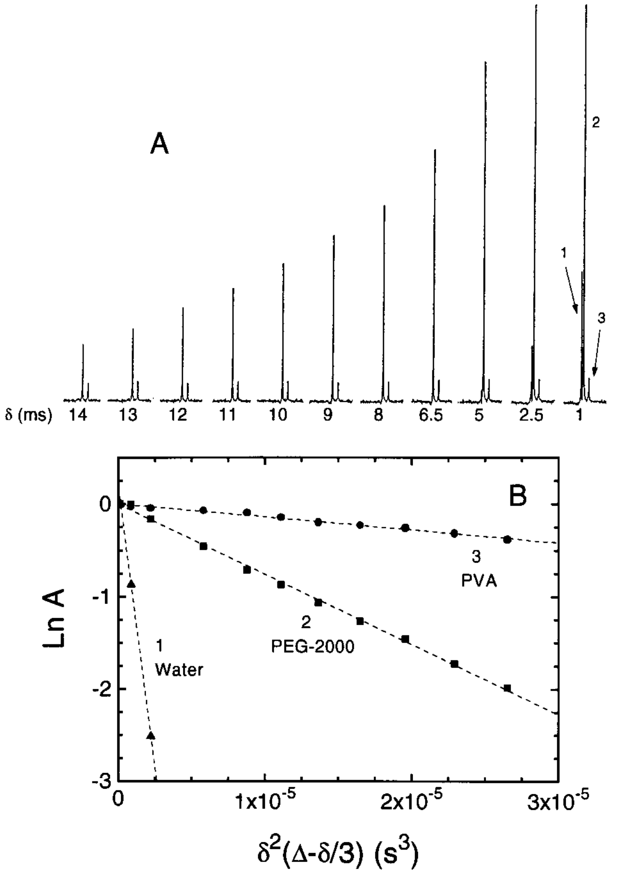

Figure 1. (A) ^{1}H PGSE-NMR spectra of the PVA–water–PEG-2000 system at 43 °C, showing proton signal attenuation with increasing gradient pulse durations (δ). [PVA] = 0.03 g/mL, $G = 0.491$ T/m, interval between gradient pulses $\Delta = 120$ ms, and the recycle delay was 12 s. (B) Semilogarithmic plot of the signal intensities as a function of $\delta^2(\Delta - \delta/3)$ (eq 3) for PVA, PEG-2000, and water proton signals. From the slope of these lines, the self-diffusion coefficients can be calculated. In this particular case, $D_{PVA} = 3.18 \times 10^{-11}$ m^2/s, $D_{PEG-2000} = 1.73 \times 10^{-10}$ m^2/s, and $D_{water} = 2.77 \times 10^{-9}$ m^2/s.

Table 2. Hydrodynamic Radii, Self-diffusion Coefficients, and Fitting Parameters $k\beta^2$ and ν Obtained for the Diffusants (EG, OEG, and PEG) in Aqueous PVA Systems

sample	R_H (Å)	D_0 (10^{-10} m^2/s) measd	calcd	$k\beta^2$ (10^{-10} m^2/s)	ν	rms error
EG	2.43	9.37	9.56	0.28	0.76	0.13
(EG)$_3$	3.91	5.95	5.95	0.23	0.60	0.08
(EG)$_4$	4.32	5.38	5.42	0.24	0.59	0.05
(EG)$_5$	5.08	4.58	4.85	0.25	0.60	0.04
(EG)$_6$	5.70	4.08	4.08	0.21	0.63	0.06
PEG-200	4.81	4.84	4.85	0.24	0.60	0.08
PEG-400	7.00	3.31	3.34	0.23	0.56	0.04
PEG-600	12.48	1.86	1.87	0.12	0.58	0.002
PEG-1000	13.99	1.66	1.66	0.12	0.49	0.02
PEG-1500	20.59	1.13	1.13	0.068	0.54	0.02
PEG-2000	22.69	1.07	1.02	0.053	0.53	0.001
PEG-4000	24.35	0.958	0.96	0.047	0.50	0.01

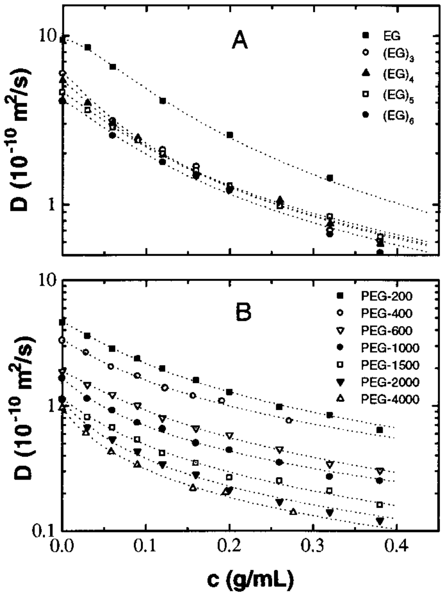

Figure 2. Self-diffusion coefficients of the solute probes, (A) EG and OEG and (B) OEG and PEG, plotted as a function of PVA concentration at 23 °C. Dashed lines are fittings to eq 1.

listed in Table 2 are expressed as the root-mean-square (RMS) fractional errors.

Results and Discussion

Figure 1A represents a series of typical ^{1}H NMR spectra of a PVA–water–PEG system from a PGSE experiment with varying gradient pulse duration δ and constant gradient strength. The NMR signals of all components in the system are very well resolved. Even though D_2O was used as the solvent, the peak of the residual water (resulted from exchange with the protons of the hydroxyl groups in the system) was observable only when shorter gradient pulses were used. This signal rapidly disappears as the duration of the gradient pulses increases, indicating a faster self-diffusion of the molecule. Only one proton signal was observed for PVA under the experimental conditions used. This signal is attributed to the CH_2 group on the main chain of PVA. It is little affected by the duration of the gradient pulses, indicating a much slower diffusion rate. The most intense signal in this case belongs to PEG-2000. It is of note that the signal intensities here are not indications of the abundance of the protons but rather the effects of the spin–spin relaxation times and diffusion rates of the individual molecules. Figure 1B shows the logarithms of the NMR signal intensities plotted as a function of the NMR parameter $\delta^2(\Delta - \delta/3)$. According to eq 3, this relationship is linear and the slope of the line equals $-\gamma^2G^2D$. When G is already known from calibration, D can be easily calculated from the slopes. For the diffusants investigated in this study, in general, monoexponential decays were observed, indicating that the samples were homogeneous and that the self-diffusion coefficients are monodisperse. We have also noticed some curvature of the line, particularly in the case of ethylene glycol, where the linear part with shorter gradient pulses were used for the calculation of the self-diffusion coefficients. The curvature might be due to the fact that ethylene glycol, being a small molecule with two hydroxyl groups, can form hydrogen bonds much more easily than the larger OEG and PEG molecules. However, further experimental evidences are needed to confirm such a hypothesis.

(1) Effect of Polymer Concentration. The measured self-diffusion coefficients of EG, OEG and PEG as a function of PVA concentration are shown in Figure 2. It is evident that there is a decrease of the values of D with increasing PVA concentration for each of the solute probes. The PVA concentration ranged from 0 to 0.38 g/mL, close to which the solutions became viscous gels. The difference of the self-diffusion coefficients of the solute probes at lower PVA concentrations are greater and it appears that all of the measured D values approach a common low value at high PVA concentrations.

In a recent work, Matsukuwa and Ando studied the diffusion of PEG in water and poly(N,N-dimethylacrylamide) gels by ^{1}H PGSE NMR spectroscopy.[26] The D value for PEG-4250 (ca. 1.2×10^{-10} m^2/s, for 1 wt % aqueous solution at 303 K) is comparable with the D_0 value determined for PEG-4000 (0.95×10^{-10} m^2/s) at 23 °C in this report. Their experimental temperature is about 7 °C higher, and their PEG samples seemed more polydisperse ($M_w/M_n < 1.19$) than the sample used in this study. They have also observed decreases in D values as the degree of swelling of the gels decreased, which corresponds to a higher concentration of the polymer matrix.[26]

(2) Effect of Molecular Size of the Diffusant. In Figure 2, we can observe the dependence of the measured D values of the solute probes on their molecular sizes. In general, the D values decrease as the molecular size of the diffusant increases for the entire PVA concentration range studied. The self-diffusion coefficients of EG measured at different concentrations of PVA are significantly higher than the oligomers and polymers (Figure 2A). As the molecular weight (MW) or the molecular size of the diffusant increases, the measured D value decreases. The difference in D values of PEGs with different MWs becomes less significant as the MW of PEG increases, especially at higher PVA concentrations (Figure 2B). The hydrodynamic radii of the diffusants, R_H, can be calculated from the D_0 value by the use of the Stokes–Einstein equation (Table 2) and give an indication of the relative size of the diffusants. The effect of the molecular size of the diffusant on self-diffusion observed here is similar to those observed in other types of gels and solutions by the radioactive tracer method[27] and the results of another study in cellulose gels and membranes.[28] It is to be noted that the D values measured by PGSE NMR methods here and in the study of Matsukuwa and Ando[26] are of the same order of magnitude with results obtained by other methods,[27,28] but they seem to be consistently lower in value. As shown in Table 2, R_H of the probes increases in a nonlinear fashion as a function of the molecular weight of the PEG samples. The use of R_H as an indication of the molecular size is justified in this case since all the probes used are linear oligo- and poly(ethylene glycol)s. However, the R_H value does not take into account the effect of molecular shape. The study by Won and Lodge showed that the diffusion behaviors of linear and star-shaped polystyrene probes in poly(vinyl methyl ether)–toluene systems are different since the freedom of motion of the linear polymer is much higher than that of the star-shaped molecules.[20] The same is true for the diffusion of polystyrene latex spheres.[29] Therefore, precautions should be taken when R_H is used to indicate the molecular size of the diffusant probes having various molecular shapes. The Stokes–Einstein equation may even fail at higher concentrations of polymers.[30] The hydrodynamic radius of the diffusants may also change as a function of polymer concentration since diffusion coefficient and viscosity are independent parameters.[29,30] R_H values in Table 2 are calculated from D_0 and are regarded as a molecular size parameter in our discussion.

(3) Effect of Temperature. We have studied the variable temperature effect on the self-diffusion coefficients of selected solute probes such as EG, PEG-600, and PEG-2000. As one may expect, the D values increase for a given diffusant as the temperature rises. An example of the plots of D values as a function of PVA concentration at different temperatures (PEG-600) is shown in Figure 3. The experimental data can be fitted very well to eq 1 for each of the temperatures studied and for all the probes used, including EG and PEG-2000.

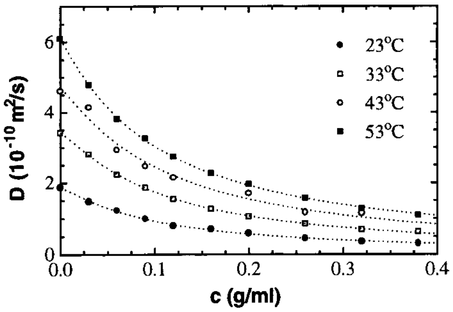

Figure 3. Self-diffusion coefficients of PEG-600 plotted as a function of PVA concentration at four different temperatures. Dashed lines are fittings to eq 1.

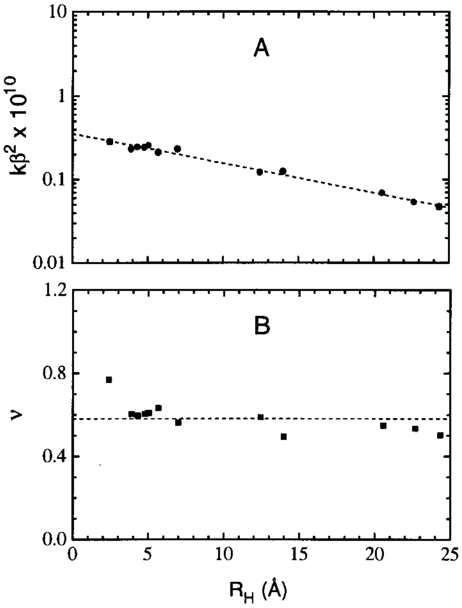

Figure 4. (A) Semilogarithmic plot of $k\beta^2$ and (B) plot of the parameter ν, as a function of the hydrodynamic radius, R_H, of this series of diffusants in PVA–water systems at 23 °C.

(4) Correspondence with the New Diffusion Model. As shown in Figure 2, the experimental data can be fitted very well with the new model of diffusion as expressed in eq 1. To use the model to estimate and eventually to predict the diffusion behavior in the polymer system, it is necessary to obtain values of fitting parameters in eqs 1 and 2. The quantity of $k\beta^2$ is related to the jump frequency k of the diffusant while β is a characteristic constant. Clearly, the jump frequency should be related inversely to the molecular size of the diffusant. Values of $k\beta^2$ can be obtained from fittings the experimental data to eq 1, but a separate value for k cannot be extracted since the value of the constant β is not known. They can be related to the hydrodynamic radii of the diffusants, R_H. The logarithm of the parameter $k\beta^2$ as a function of R_H has more or less a linear relationship (Figure 4A), which confirms that an increase in the molecular size of the diffusant leads to a lower jump frequency, k. The following empirical

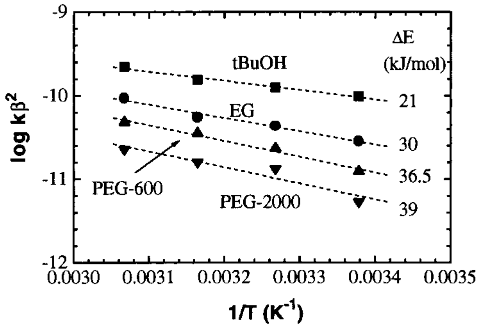

Figure 5. Logarithm of the parameter $k\beta^2$ plotted as a function of reciprocal temperature for selected diffusants. The potential energy barriers can be calculated from the slopes of these lines.

expression can be obtained for this series of probe molecules:

$$\log k\beta^2 = -0.0356R_{\mathrm{H}} - 10.45 \qquad (4)$$

This provides a rough estimate of the $k\beta^2$ value at 23 °C for a given OEG or PEG diffusant with a known R_{H}, which can be calculated from the D_0 value as shown above.

The second fitting parameter, ν, should remain more or less a constant for a given polymer system. Figure 4B shows that indeed ν can be regarded to be characteristic of the PVA−water system since the variation of ν is small for the series of OEG and PEG studied. The average value of ν obtained in this study (ca. 0.58) is similar to that obtained previously for the same system.[21] A certain deviation was observed for the very small molecules such as ethylene glycol itself ($\nu = 0.76$), probably as a result of the curvature in the measurement of the diffusion coefficient as discussed previously. In addition, we can also notice a slight decrease in ν as a function of the hydrodynamic size of the diffusants in this series. This decreasing trend, however, is very small and may be regarded as negligible when the RMS errors of the fittings (Table 2) are taken into account.

As shown in eq 2, the jump frequency k for a given diffusant is expected to be dependent on the temperature. The $k\beta^2$ values can be obtained from fittings to eq 1 at each temperature. Since we assume that β is a constant within the temperature range studied here, the relationships between $k\beta^2$ and T shown in Figure 5 can be regarded as the relationship between k and T. The Arrhenius plots (log $k\beta^2$ vs $1/T$, as in eq 2) in Figure 5 show excellent linear relationships. The energy barrier ΔE can be calculated from the slopes of the linear plots. We have obtained ΔE values of 30, 36.5, and 39 kJ/mol, respectively, for selected diffusants EG, PEG-600, and PEG-2000. Previously, we have calculated the energy barrier for *tert*-butyl alcohol (*t*BuOH) to be 21 kJ/mol in the same system over the same temperature range.[21] The data points are also plotted in Figure 5. The molecular weight of *t*BuOH is higher than that of EG, but the energy barrier for the diffusion of *t*BuOH is lower. The higher facility of EG in forming hydrogen bonds with the polymer matrix and with the aqueous environment is probably the reason for its higher energy barrier of diffusion than that of *t*BuOH. The effect of hydrogen bonds on diffusion of small molecules was also evidenced when trimethylamine was compared with tetramethylammonium cation.[15] Since PEG is a flexible linear polymer, the increase in molecular weight of PEG does not seem to increase the energy barrier of diffusion to a great extent. There is a clear trend that the energy barrier of diffusion increases with increasing molecular size of the diffusant, which leads to smaller self-diffusion coefficients.

Concluding Remarks

We have measured the self-diffusion coefficients of a series of diffusant probes based on ethylene glycol in PVA aqueous solutions and gels. These diffusants ranged from the monomer EG, to oligomers and to polymers with a molecular weight up to 4000, which enabled us to link the diffusion behavior of small to large molecules in the polymer system. The newly proposed physical model of diffusion is used successfully in the treatment of the self-diffusion data of these molecules. The effects of polymer concentration, molecular size of the diffusants and temperature can be described by the model. The jump frequency k, a physical parameter defined in the model, is shown to depend on the size of the diffusant as well as on temperature, while the parameter ν in the model remains more or less a constant of the given system. In this study, the hydrodynamic radii of the diffusants have been used to account for the changes of molecular size of the diffusants. The energy barriers of diffusion have been obtained from the variable temperature studies for selected diffusants of different sizes. Further studies are under way in an effort to elucidate the effect of molecular shape of the diffusant as well as the effects of hydrogen bonding and other interactions in the diffusion of solutes in polymer systems.

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References and Notes

(1) Kosmeyer, R. W.; von Meerwall, E. D.; Peppas, N. A. *J. Polym. Sci., Polym. Phys. Ed.* **1986**, *24*, 409.
(2) Waggoner, A.; Blum, F. D. *J. Coatings Technol.* **1989**, *61*, 768.
(3) Clericuzio, M.; Parker, W. O.; Soprani, M.; Andrei, M. *Solid State Ionic* **1995**, *77*, 685.
(4) Stilbs, P. *Prog. Nucl. Magn. Reson. Spectrosc.* **1987**, *19*, 1.
(5) Price, W. S. *Annu. Rep. NMR Spectrosc.* **1996**, *32*, 51.
(6) Fujita, H. *Adv. Polym. Sci.* **1961**, *3*, 1.
(7) Yasuda, H.; Lamaze, C. E.; Ikenberry, L. D. *Makromol. Chem.* **1968**, *118*, 19.
(8) Vrentas, J. S.; Duda, J. L. *J. Polym. Sci., Polym. Phys. Ed.* **1977**, *15*, 403.
(9) Vrentas, J. S.; Duda, J. L. *J. Polym. Sci., Polym. Phys. Ed.* **1977**, *15*, 417.
(10) Mackie, J. S.; Meares, P. *Proc. R. Soc. London, A* **1955**, *232*, 498.
(11) Ogston, A. G.; Preston, B. N.; Wells, J. D. *Proc. R. Soc. London, A* **1973**, *333*, 297.
(12) Cukier, R. I. *Macromolecules* **1984**, *17*, 252.
(13) Altenberger, A. R.; Tirrell, M. *J. Chem. Phys.* **1984**, *80*, 2208.
(14) Phillies, G. D. J. *Macromolecules* **1986**, *19*, 2367.
(15) Petit, J.-M.; Zhu, X. X.; Macdonald, P. M. *Macromolecules* **1996**, *29*, 70.
(16) Waggoner, R. A.; Blum, F. D.; MacElroy, J. M. D. *Macromolecules* **1993**, *26*, 6848.
(17) Vrentas, J. S.; Vrentas, C. M. *Macromolecules* **1994**, *27*, 5570.
(18) Su, H.; Benesi, A. J.; Duda, J. L. *Polym. Int.* **1996**, *39*, 243.
(19) Faldi, A.; Tirrell, M.; Lodge, T. P.; von Meerwall, E. *Macromolecules* **1994**, *27*, 4184.
(20) Won, J.; Lodge, T. P. *J. Polym. Sci. B: Polym. Phys.* **1993**, *31*, 1897.

(21) Petit, J.-M.; Roux, B.; Zhu, X. X.; Macdonald, P. M. *Macromolecules* **1996**, *29*, 6031.
(22) Zhu, X. X.; Macdonald, P. M. *Macromolecules* **1992**, *25*, 4345.
(23) Zhu, X. X.; Wang, F.; Nivaggioli, T.; Winnik, M. A.; Macdonald, P. M. *Macromolecules* **1993**, *26*, 6397.
(24) Stejskal, E. O.; Tanner, J. E. *J. Chem. Phys.* **1965**, *42*, 288.
(25) Mills, R. *J. Phys. Chem.* **1973**, *77*, 685.
(26) Matsukawa, S.; Ando, I. *Macromolecules* **1996**, *29*, 7136.
(27) Johansson, L.; Skantze, U.; Löfroth, J.-E. *Macromolecules* **1991**, *24*, 6019.
(28) Brown, W.; Honsen, R. M. *J. Appl. Polym. Sci.* **1981**, *26*, 4135.
(29) Won, J.; Onyenemezu, C.; Miller, W. G.; Lodge, T. P. *Macromolecules* **1994**, *27*, 7389.
(30) Phillies, G. D. J. *J. Phys. Chem.* **1989**, *93*, 5029.

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