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Self-Diffusion of End-Capped Oligo(ethylene glycol)s in Poly(vinyl alcohol) Aqueous Solutions and Gels

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ABSTRACT: We have studied the self-diffusion of a series of end-capped ethylene glycol and oligo(ethylene glycol)s in poly(vinyl alcohol) aqueous solutions and gels by pulsed-gradient spin echo NMR spectroscopy. The end groups of the diffusants include small flexible groups (methyl, ethyl, hexyl) and bulky rigid groups (*tert*-butyl and aromatic groups). The effect of the size and geometry of the end groups on the self-diffusion coefficients of the derivatives of ethylene glycol and of oligo(ethylene glycol)s is investigated. The diffusion data are analyzed with several physical models of diffusion based on different physical concepts to test their applicabilities. The variation of the parameters used in these diffusion models with the size and geometry of the diffusants is also discussed.

Introduction

The diffusion of small molecules in polymer solutions and gels has been a subject of increasing research interest in the past decade.[1−10] The understanding of the diffusion of small molecules in polymers is useful and important for the processes involving the devolatilization of monomer and solvent from polymer products,[11] controlled release of drugs,[12] membrane permeation,[13] transport in porous medium,[14,15] electrophoresis and gel filtration,[16,17] etc. With the development of more convenient experimental techniques such as pulsed field gradient NMR spectroscopy,[18,19] more diffusion data have become available.[1,2,4,12] The interpretation of the results has not been always easy[4,20−22] even with the availability of numerous physical models of diffusion in the literature.[23−34] In fact, there remains disagreement regarding the applicability of the models for various polymer systems. Due to the origin of the physical concepts considered, including the obstruction effect,[23,24] the free volume effect,[28−32] or hydrodynamic interactions,[25−27] limitations of the models to the different circumstances are bound to occur. It would be useful to verify the applicability of some pertinent diffusion models in the analysis of the diffusion results of relatively small molecules in polymer systems.

The diffusion in polymers may be influenced by various factors such as the concentration or the cross-linking of the polymer matrix, the temperature, and the size of the diffusants.[19−21,35,36] We have studied the effect of the size of the diffusant on its self-diffusion in poly(vinyl alcohol) (PVA) aqueous solutions and gels by using a series of linear diffusants based on ethylene glycol with increasing molecular weights.[36] It was found that at a given concentration of the polymer the size of the diffusant has the most significant effect on its diffusion.[36] However, the hydroxyl groups of ethylene glycol (EG) in these diffusants were found to interact strongly with the polymer system by the formation of hydrogen bonds. This was clearly shown in another report where the interaction of EG with PVA was studied by monitoring the changes in chemical shifts, self-diffusion coefficients, and relaxation times.[37] Therefore, we would like to examine the effect of molecular size and geometry of the diffusant by the use of end-capped ethylene glycol and derivatives. To do this, we have studied the self-diffusion coefficients of a series of ethylene glycol derivatives as well as a crown ether in PVA−aqueous systems by pulsed-gradient spin echo (PGSE) NMR spectroscopy. Several pertinent models of diffusion are used in the analysis of the diffusion data, and the physical significance of the parameters used in these models is evaluated as well. The results are also compared with those obtained with oligo- and poly(ethylene glycol) diffusants in the same system.

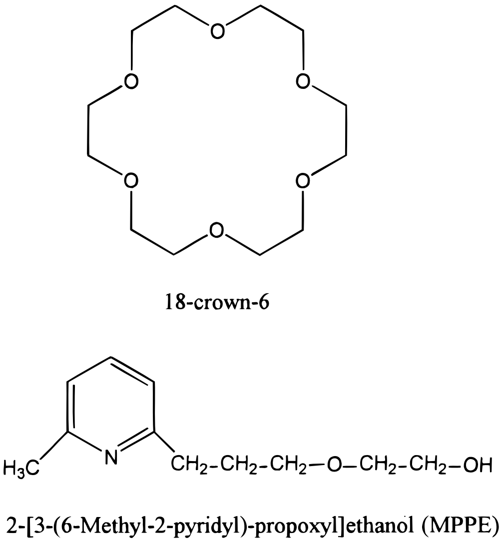

Figure 1. Chemical structure of the diffusants 18-crown-6 and 2-[3-(6-methyl-2-pyridyl)propoxyl]ethanol (MPPE) used in this study.

Experimental Section

Materials. The diffusants used in this study are shown in Table 1 and Figure 1. These diffusants include ethylene glycol, oligo(ethylene glycol)s and their end-capped derivatives, a crown ether (18-crown-6), and 2-[3-(6-methyl-2-pyridyl)pro-

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Table 1. Structure and Molecular Weight (*M*) of the End-Capped Oligo(ethylene glycol)s Used in This Study

$$R_1O\left[CH_2-CH_2-O\right]_n R_2$$

diffusant	abbreviation	*n*	R_1	R_2	*M* (g/mol)
ethylene glycol	EG	1	−H	−H	62
ethylene glycol methyl ether (2-methoxyethanol)	EG-Me	1	−H	$-CH_3$	76
ethylene glycol dimethyl ether	EG-Me_2	1	$-CH_3$	$-CH_3$	90
ethylene glycol *tert*-butyl methyl ether (1-*tert*-butoxy-2-methoxyethane)	EG-tBuMe	1	$-CH_3$	$-C(CH_3)_3$	132
di(ethylene glycol) methyl ether	DEG-Me	2	−H	$-CH_3$	120
di(ethylene glycol) ethyl ether	DEG-Et	2	−H	$-C_2H_5$	134
di(ethylene glycol) hexyl ether	DEG-He	2	−H	$-C_6H_{13}$	190
diethylene glycol *tert*-butyl methyl ether	DEG-tBuMe	2	$-CH_3$	$-C(CH_3)_3$	176
tri(ethylene glycol) methyl ether	TEG-Me	3	−H	$-CH_3$	164
tri(ethylene glycol) dimethyl ether	TEG-Me_2	3	$-CH_3$	$-CH_3$	178

Table 2. Measured D_0 Values and the D_0, $k\beta^2$, and ν Values Obtained as Free Parameters from Fits to Eq 1 and the D_0 and $k\beta^2$ Values Obtained from Fits to Eq 1 with ν Fixed to 0.58

diffusant	R_h (Å)	$D_0 \times 10^{-10}$ (m²/s)[a]	$D_0 \times 10^{-10}$ (m²/s)[b]	$k\beta^2 \times 10^{10}$ [b]	ν[b]	χ^2 [b]	$D_0 \times 10^{-10}$ (m²/s)[c]	$k\beta^2 \times 10^{10}$ [c]	χ^2 [c]
EG	2.79	8.59	8.48	0.93	0.65	0.020	8.68	1.16	0.033
EG-Me	3.07	7.88	7.83	1.16	0.60	0.004	7.89	1.24	0.005
EG-Me_2	3.24	7.56	7.55	1.27	0.55	0.008	7.49	1.18	0.009
EG-tBuMe	4.38	5.58	5.52	0.65	0.59	0.009	5.54	0.67	0.008
DEG-Me	3.83	6.46	6.32	0.87	0.59	0.025	6.33	0.89	0.022
DEG-Et	4.18	5.77	5.72	0.66	0.62	0.010	5.80	0.76	0.011
DEG-He	5.45	4.43	4.42	0.38	0.60	0.003	4.45	0.41	0.003
DEG-tBuMe	5.05	4.80	4.74	0.48	0.62	0.009	4.80	0.55	0.013
TEG-Me	4.65	5.23	5.21	0.65	0.58	0.003	5.21	0.65	0.002
TEG-Me_2	4.75	5.15	5.10	0.64	0.58	0.004	5.10	0.63	0.005
18-crown-6	5.54	4.37	4.37	0.36	0.58	0.005	4.37	0.35	0.004
MPPE	5.55	4.39	4.40	0.40	0.56	0.005	4.38	0.38	0.004

[a] Measured experimentally. [b] Obtained from fits to eq 1 with free parameters. [c] Obtained from fits to eq 1 with $\nu = 0.58$.

poxy]ethanol (MPPE). These compounds and poly(vinyl alcohol) ($M_w = 52\,000$, $M_w/M_n = 2.09$, degree of hydrolysis 99%) were all purchased from Aldrich (Milwaukee, WI) and used as received. D_2O (99.9%) was purchased from C.I.L. (Andover, MA).

NMR Measurements. The samples were prepared as described previously.[22,36] The measurements of the self-diffusion coefficients were carried out on a Bruker Avance AMX-300 NMR spectrometer operating at 300.13 MHz for protons. The temperature was set at 25 °C. The PGSE pulse sequence developed by Stejskal and Tanner[38] was used. A Bruker magnetic resonance imaging probe, Micro 2.5 Probe, was used in conjunction with a gradient amplifier (BAFPA-40). Gradient pulses were applied only in the *z* direction. The calibration of the gradient strength and the temperature was described elsewhere.[18,19,39] The gradient strengths, *G*, used in this study ranged between 0.1 and 1 T/m. The other parameters were kept constant, and their values are those noted in the parentheses depending on the experiments: gradient pulse duration (1−4 ms), gradient pulse interval (30−80 ms), recycle delay (10−25 s), number of acquisitions (1−8), 90° pulse (23−29 μs), spectral width (3−8 kHz), line broadening (5−10 Hz).

The fitting procedure of the experimental diffusion data to the physical models of diffusion was the chi-square (χ^2) minimization procedure available with Microcal Origin 3.5 (Northampton, MA), and the χ^2 values are listed in the tables.

Rheological Measurements. Rheological experiments were carried out in order to characterize the PVA solutions and gels. A Bohlin VOR rheometer equipped with a couette for dilute solutions and with a cone for more concentrated solutions was used. Calibration of the rheometer was achieved with poly(dimethylsiloxane) standards. PVA concentrations were similar to those of the samples used for NMR measurements ([PVA] = 0−0.38 g/mL) but without the diffusant.

Results and Discussion

The rheological experiments of the PVA samples have shown that the PVA−water systems are Newtonian solutions for a PVA concentration between 0 and 0.12 g/mL. But for samples with PVA concentrations above 0.26 g/mL, the elastic modulus (G') was higher than the viscous modulus (G''), which is characteristic of a gel. The samples of intermediate PVA concentrations lie between these two cases.

The measured self-diffusion coefficients of the solutes molecules in the PVA systems have been analyzed with several physical models with varying degree of success. The self-diffusion coefficient values, *D*, are those of the free diffusant (especially in the case of EG).

The Model of Petit et al.[35] In this model, the polymer network is considered as a transient statistical network characterized by a mesh size, ξ. The diffusant is considered to reside temporarily inside a cavity until it has enough energy to diffuse to the next one. Therefore, the diffusion process is a succession of jumps over equal potential barrier.[35] The self-diffusion coefficient *D* is given as

$$D = \frac{D_0}{1 + ac^{2\nu}} \qquad (1)$$

where *D* is the self-diffusion coefficient, D_0 is the self-diffusion coefficient without the matrix polymer, *a* and ν are the parameters of the model. The parameter ν depends on the solvent quality and should be a constant for a given system. In a previous study,[36] ν was found to be equal to 0.58 in PVA aqueous systems. The parameter a is given by

$$a = \frac{D_0}{k\beta^2} \tag{2}$$

where k is the jump frequency of the diffusant and β can be regarded as a constant for a given system. The parameter $k\beta^2$ depends on the size of the diffusant, such as the hydrodynamic radius (R_h), and on the temperature.[36] R_h can be calculated with the Stokes–Einstein equation from the D_0 values listed in Table 2:

$$R_h = \frac{k_B T}{6\pi\eta_0 D_0} \tag{3}$$

where k_B is the Boltzmann constant, T the temperature, and η_0 is approximated as the viscosity of the solvent without the polymer. The Stokes–Einstein equation is applicable to spherical diffusants. R_h is used as an indication of the relative size of the diffusants, but the R_h value calculated from eq 3 does not necessarily take into account the effect of the molecular shape. Therefore, precautions should be taken when R_h is used to indicate the molecular size of the diffusants, as discussed previously.[36]

Figure 2 shows the self-diffusion coefficients of EG and its end-capped derivatives as a function of PVA concentration with fits to eq 1. The modification of the hydroxyl groups of EG by the addition of one or two methyl group(s) does not change to any significant extent the self-diffusion coefficients at a given PVA concentration (Figure 2A). The most important difference is that for the end-capped EG derivatives monoexponential decrease of the spin echo attenuation was observed, unlike in the case of EG, where both free and bond molecules were clearly evidenced.[37] This indicates that the methyl groups reduced or prevented the binding of EG to PVA. A bulky *tert*-butyl end group, however, affects much more the diffusion behavior of EG over the entire range of polymer concentrations. For the end-capped di(ethylene glycol) derivatives, the data are shown in Figure 2B. At a given PVA concentration D decreases with increasing size of the end alkyl group ($D_{\text{methyl}} > D_{\text{ethyl}} > D_{\text{hexyl}}$). A large linear hydrophobic end group such as a hexyl group seems to have a greater effect than a more spherical end group such as a *tert*-butyl. For the derivatives of tri(ethylene glycol), D values for TEG-Me and TEG-Me$_2$ are quite the same over the entire range of PVA concentrations, which is similar to the results observed for EG, EG-Me, and EG-Me$_2$ in concentrated PVA solutions. If the self-diffusion coefficients of EG-tBuMe (M = 132 g/mol) and DEG-Et (M = 134 g/mol) are compared, we notice that the diffusant with a bulkier end group (*tert*-butyl) diffuses less rapidly than the diffusant with a linear end group (ethyl) over the entire range of polymer concentrations. Similar differences can also be observed between DEG-tBuMe and TEG-Me$_2$. Obviously, the geometry of the diffusant seems to be quite important in the diffusion process. Similarly, the self-diffusion coefficient of TEG-Me$_2$ is always higher than that of MPPE (Figure 2C). The difference can be explained by the fact that MPPE has a bulky aromatic end group. The cyclic molecule 18-crown-6 behaves similarly as MPPE in the concentration range studied (Figure 2C).

Good fits are obtained for all the diffusants in Figure 2 over the entire range of polymer concentrations. The fitting parameters are listed in Table 2. When the data are fitted with free parameters of D_0, $k\beta^2$, and ν, the average value obtained for ν is equal to 0.59 (Table 2), which is almost identical to the average value of 0.58 reported previously for the same polymer–water system.[36] This confirms that the parameter ν is an indication of the quality of the solvent.[35] Table 2 also lists the values obtained for the parameters D_0 and $k\beta^2$ when ν is fixed to 0.58. D_0 is found in good agreement with the experimental values. The $k\beta^2$ values are similar to those obtained with free ν values.

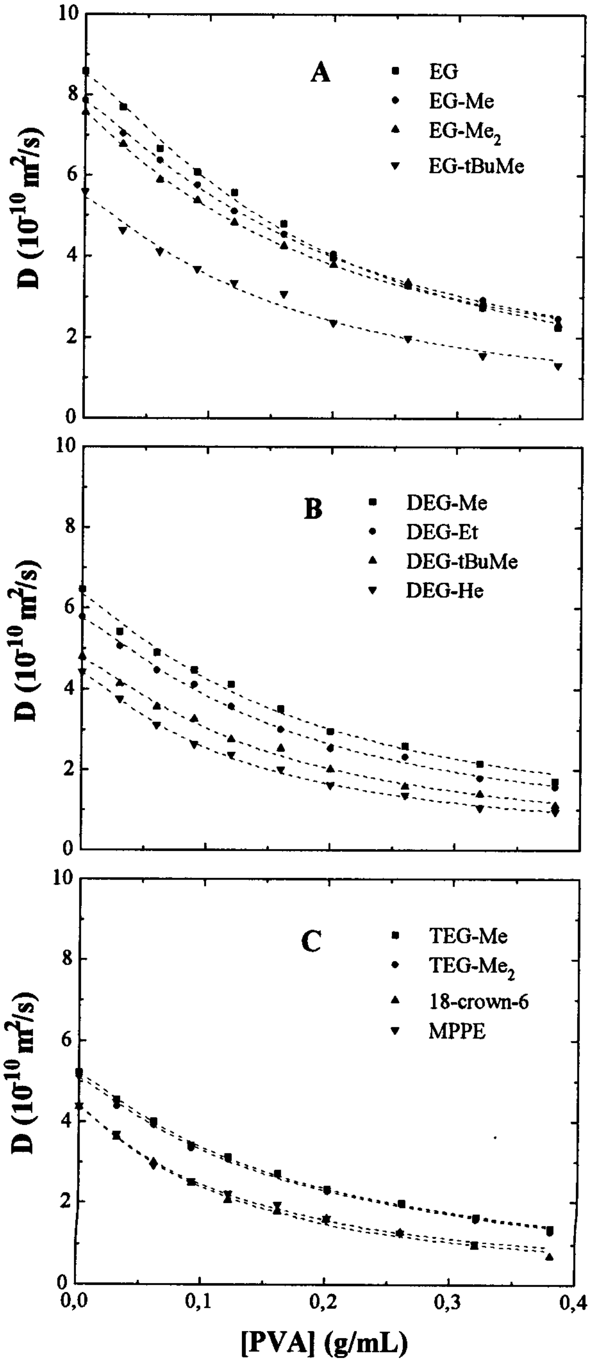

Figure 2. Plot of the self-diffusion coefficient of (A) ethylene glycol and its end-capped derivatives, (B) end-capped di(ethylene glycol)s, and (C) other end-capped oligo(ethylene glycol)s as a function of the PVA concentration at 25 °C. Dashed lines are fit to eq 1.

In Figure 3A, the logarithm of the parameter $k\beta^2$ (obtained with floating ν) is plotted as a function of R_h

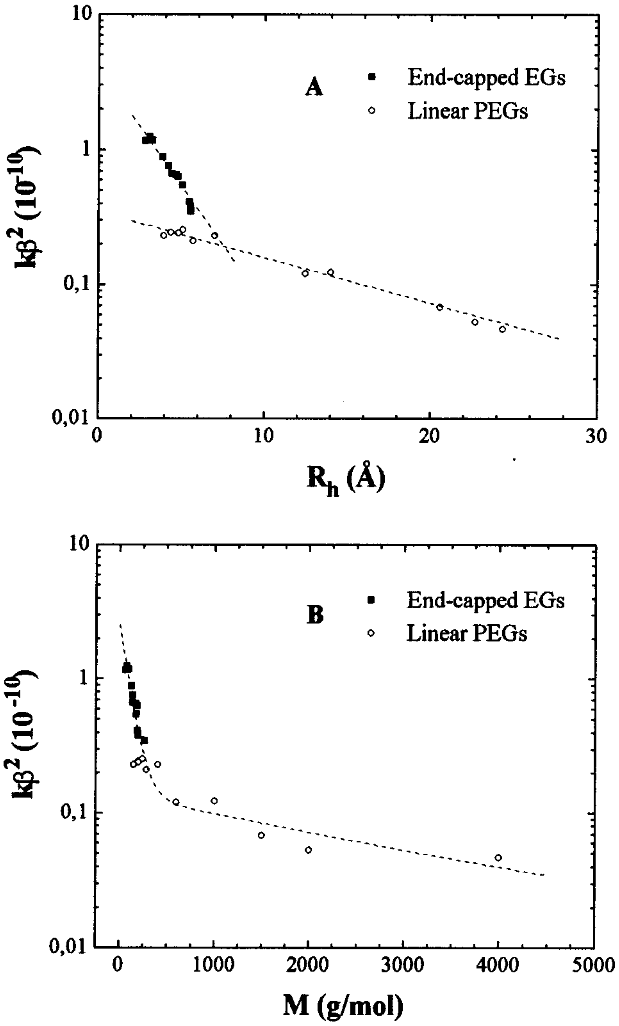

Figure 3. Semilogarithmic plot of the parameter $k\beta^2$ as a function of (A) the hydrodynamic radius and (B) the molecular weight of the diffusants.

of the diffusants. The data are combined with the data obtained previously with a series of linear poly(ethylene glycol)s.[36] For both series, the jump frequency k decreases when the size of the diffusant is increased. Some of the linear PEG diffusants, especially the oligomers, were found to interact strongly with PVA via hydrogen bonding as mentioned previously. In the presence of hydrogen bonds in the PEG series, the jump frequency k is lower because of the hindrance caused by the interaction, and the decrease of the jump frequency with R_h is also more gradual as shown by the slope of the line ($k\beta^2 \sim R_h^{-0.036}$). With end-capped EG derivatives, even when the molecular size are similar to the PEGs, the jump frequency is still higher since the interactions are not as strong because of the capped ends that screen the interaction with PVA. The decrease of the jump frequency with R_h is also more abrupt as shown by the steeper slope ($k\beta^2 \sim R_h^{-0.19}$). When the PEG chain is sufficiently long, the effect of the end group is no longer as significant and may even be negligible. In Figure 3B, the parameter $k\beta^2$ is plotted as a function of the molecular weight (M) of the diffusants. The general trend of the data is similar; i.e., the jump frequency decreases when the size of the diffusant is increased. Two distinct regions can also be identified, corresponding to low molecular weight diffusant and high molecular weight diffusant, with an inflection point approximately around $M = 500$. The first part of the line seems quite linear; the decrease becomes much less abrupt in the second part.

Table 3. Measured D_0 Values, Calculated Hydrodynamic Radius (R_h), and D_0, α, and ν Obtained as Free Parameters from Fits to Eq 4

diffusant	$D_0 \times 10^{10}$ (m^2/s) exptl	$D_0 \times 10^{10}$ (m^2/s) fitted	α	ν	χ^2
EG	8.59	8.60	3.40	0.95	0.010
EG-Me	7.88	7.92	2.83	0.90	0.006
EG-Me$_2$	7.56	7.61	2.60	0.83	0.009
EG-tBuMe	5.58	5.52	3.32	0.88	0.013
DEG-Me	6.46	6.40	2.94	0.86	0.010
DEG-Et	5.77	5.80	3.22	0.90	0.010
DEG-He	4.43	4.81	3.53	0.89	0.006
DEG-tBuMe	4.80	4.47	3.67	0.83	0.005
TEG-Me	5.23	5.27	3.06	0.84	0.004
TEG-Me$_2$	5.15	5.16	3.06	0.84	0.003
18-crown-6	4.37	4.41	3.84	0.80	0.088
MPPE	4.39	4.42	3.69	0.80	0.007

The Model of Phillies.[27] Phillies proposed a universal equation to describe the self-diffusion of one macromolecule in another over a wide range of concentrations.[27] In this model, the hydrodynamic interactions between the diffusants (solvent or solute) and the polymer are taken into account, and the polymer chains are considered to be mobile. This approach provided good fits to the experimental data in many polymer systems.[40-42] It also provided good results in the treatment of the diffusion data of small molecules.[22,43,44] The equation is given as

$$D = D_0 \exp(-\alpha c^{\nu}) \tag{4}$$

where α and ν are scaling parameters. The scaling parameter α is predicted to depend strongly on the hydrodynamic radius ($\alpha \sim R_h$) for small diffusants,[45] as proposed by Mustafa et al.[46]

Equation 4 was used to fit the diffusion data of EG and its end-capped derivatives as a function of PVA concentration in Figure 4. The fitting parameters are listed in Table 3. A very good correlation is observed between the fits and the experimental data for all the diffusants over the entire range of polymer concentrations.

Park et al.[47] and Gibbs and Johnson[48] reported $\alpha = 3.03R_H^{0.59}$ and $\alpha = 3.2R_H^{0.53}$, respectively, for small probes (water, tetramethylammonium iodide, tetramethylethylenediamine, tetrahexylammonium, benzospiropyran, and bovine serum albumin) in polyacrylamide gels. In the present study, the estimates obtained from these empirical relationships tend to be higher than the α values obtained from the fits. However, the parameter α listed in Table 3 seems to depend somewhat on the hydrodynamic radius of the diffusant as shown in Figure 5A. A more or less linear relationship is observed ($\alpha \sim 0.28R_h$).

According to Phillies, ν should scale between 1 for low molecular weight diffusants and 0.5 for high molecular weight diffusants.[40-42] Inside these limits the scaling follows $\nu \sim M^{-1/4}$. The ν values listed in Table 3 are found to be more or less a constant and always less than 1. These values are plotted as a function of the hydrodynamic radius of the diffusants (Figure 5B). An average value of 0.86 is found. Gibbs and Johnson[48] reported values for the parameter ν between 0.89 and 1.13, slightly higher than the values obtained here.

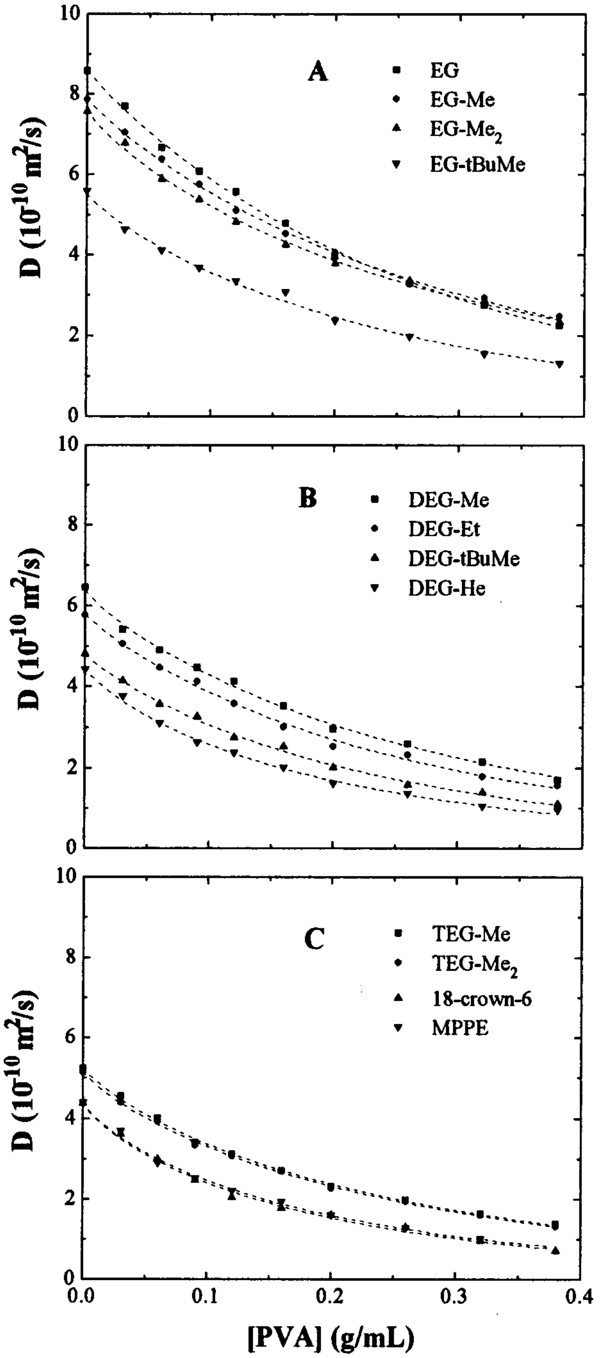

Figure 4. Plot of the self-diffusion coefficient of (A) ethylene glycol and its end-capped derivatives, (B) end-capped di(ethylene glycol), and (C) other end-capped oligo(ethylene glycol)s as a function of the PVA concentration at 25 °C. Dashed lines are fits to eq 4.

The Model of Yasuda et al.[29] The free volume models consider the diffusion process as a succession of jumps into voids created by the thermal motion of the molecules. The diffusion of a solute is a function of the probability to find a void large enough to allow the diffusion of the solute. The free volume model of Fujita[28] is not suitable to describe diffusion in aqueous systems. The model of Vrentas–Duda[30,31] can be used for the diffusion in binary polymer–solvent systems. Because of the numerous physical parameters needed, it is difficult to use it in the more complicated ternary systems. Yasuda et al.[29] assumed that the contribution to the free volume is mainly contributed by the solvent in binary and ternary systems when the solute probe is present in low concentration (pseudobinary system). The following expression was obtained:

$$\ln D = \ln D_0 - \frac{B_f}{f_w}\left(\frac{\varphi}{1-\varphi}\right) \quad (5)$$

where B_s is the minimum hole size required for the diffusant displacement and f_w is the free volume of water in the polymer–water system.

The semilogarithmic of the normalized self-diffusion coefficient of selected solutes as a function of $\varphi/(1-\varphi)$ is shown in Figure 6A. The dashed lines are fits to eq 5, which seems to be linear for EG-Me and DEG-tBuMe at lower PVA concentrations, but deviations are observed at higher PVA concentrations, where the free volume contribution by the polymer may no longer be negligible. The deviation of the diffusion data of a larger diffusant such as MPPE from linearity is much more significant, which clearly shows that the use of the model is limited to relatively small diffusants in relatively dilute solutions. This is consistent with the previous studies with similar systems.[22,34,49] We tried to use D_0 and B_s/f_w as free parameters in the fitting to eq 5. The D_0 values obtained for the diffusants from the fits are similar to the measured D_0. If the parameter f_w is a constant as assumed by Yasuda et al.,[30] B_s/f_w should reflect the variation of the minimum hole size (B_s) required for diffusant displacement to take place. The values obtained for B_s/f_w from the fits of the linear part of the curves are plotted as a function of the hydrody-

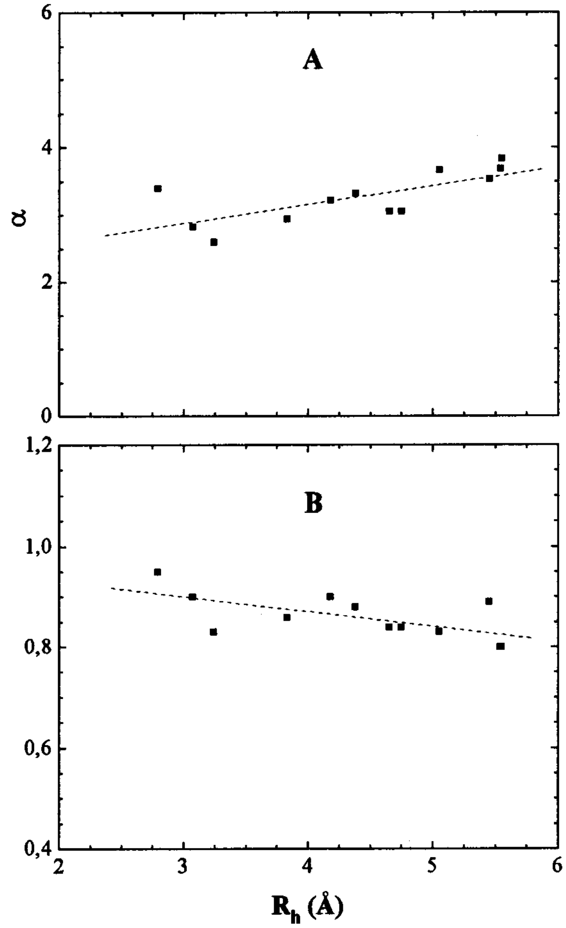

Figure 5. (A) Plot of the parameter α as a function of the hydrodynamic radius of the diffusants. (B) Plot of ν as a function of the molecular weight of the diffusants.

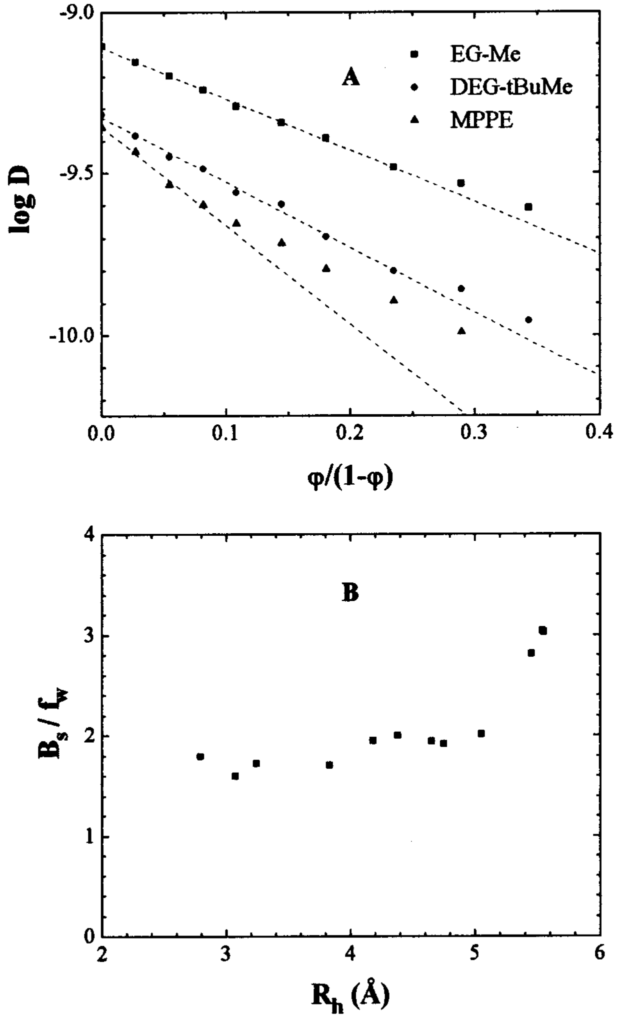

Figure 6. (A) Plot of the logarithmic self-diffusion coefficient of selected diffusants as a function of $\varphi/(1 - \varphi)$ at 25 °C. (B) Plot of the parameter B_s/f_w as a function of the hydrodynamic radius of the diffusants. Dashed lines are fits to eq 5.

namic radii of the diffusants in Figure 6B. B_s/f_w is found to be quite constant for the smaller diffusants and increases for the large ones in this series. The minimum hole size required for diffusant displacement should increase with increasing size of the diffusant.

The Model of Mackie and Meares.[23] In this model, the polymer chains are regarded as motionless relative to the diffusing molecules. Therefore, they impose a tortuosity or an increase in the path length for the molecules in motion. The self-diffusion coefficient of the diffusants is related to the volume fraction of the polymer according to the following equation

$$\frac{D}{D_0} = \left[\frac{1 - \varphi}{1 + \varphi}\right]^2 \tag{6}$$

where φ the volume fraction of the matrix polymer.

Figure 7 shows the normalized self-diffusion coefficient of selected diffusants (EG-Me, EG-Me$_2$, EG-tBuMe, and 18-crown-6) as a function of the volume faction of the polymer matrix. The self-diffusion coefficient decreases with increasing volume fraction of the polymer and with increasing size of the diffusant. This is consistent with the results reported in previous studies.[22,36] The dotted line in Figure 7 represents the fit to eq 6. The fit can be regarded as acceptable for the diffusion data of EG-Me and EG-Me$_2$ especially at low PVA concentrations, but the deviation becomes obvious for higher polymer concentrations. The deviation between eq 6 and the data is more pronounced for the larger diffusants such as EG-tBuMe and 18-crown-6. Petit et al.[22] studied the self-diffusion of solvents and solute probes in PVA−water systems and found that this model can only be used for the description of the diffusion data of water and methanol, whereas the fits for larger diffusants significantly deviate from the experimental data. Waggoner et al.[4] also studied the self-diffusion coefficients of different solvents (toluene, ethylbenzene, cumene, *tert*-butyl acetate, chloroform, and methyl ethyl ketone) in polystyrene (PS) and in poly(methyl methacrylate). They found that the model of Mackie−Meares described fairly well the data, but they noticed that the subtle differences between the various systems were not taken into account by the model.

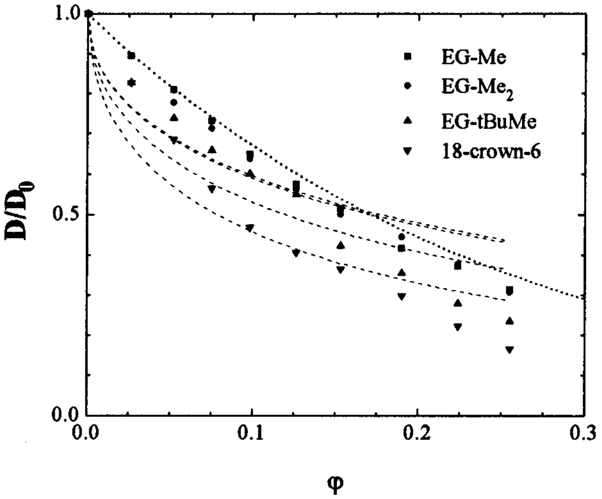

Figure 7. Plot of the normalized self-diffusion coefficient of selected diffusants as a function of the volume fraction of PVA at 25 °C. Dotted line and dashed lines are fits to eq 6 and eq 7, respectively.

The Model of Ogston et al.[24] In this model the diffusing particle is considered as a hard sphere and the polymer as randomly oriented fibers. The diffusion process is assumed to correspond to the average displacement of a hard sphere in a lattice of long fibers of negligible width according to

$$\frac{D}{D_0} = \exp\left[-\frac{r_s + r_f}{r_f}\varphi^{1/2}\right] \tag{7}$$

where r_s is the hydrodynamic radius of the diffusant and r_f the hydrodynamic radius of the fiber.

Dashed lines in Figure 7 are fits to eq 7. The model of Ogston et al.[24] takes into account the volume fraction of the polymer matrix, the hydrodynamic radius of the polymer fiber, and the hydrodynamic radius of the diffusant. Therefore, the model provides different fits for each diffusant, which seems to be an improvement compared with the model of Mackie and Meares.[24] However, the fits to eq 7 still deviate significantly from the experimental data, indicating the limitation of this model in handling the diffusion data in such a system.

The Model of Amsden.[34] This diffusion model combines the free volume theory with the obstruction and scaling concepts. It takes into account several structural properties of the polymer such as the polymer

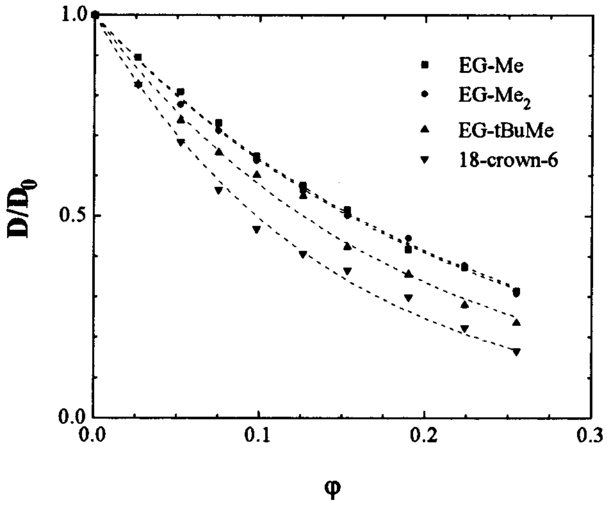

Figure 8. Plot of the normalized self-diffusion coefficient of selected diffusants as a function of the volume fraction of PVA at 25 °C. Dashed lines are fits to eq 8.

Table 4. Parameters D_0, r_f, and k_1 Obtained by Fitting the Diffusion Data to Eq 8 While Fixing r_s to the R_h Values Reported in Table 2

diffusant	$D_0 \times 10^{-10}$ (m^2/s)	r_f (Å)	k_1	χ^2
EG	8.56	0.404	−7.14	0.015
EG-Me	7.93	0.051	−51.68	0.013
EG-Me_2	7.53	0.019	−137.95	0.013
EG-tBuMe	5.46	0.264	−14.35	0.007
DEG-Me	6.32	0.160	−21.00	0.009
DEG-Et	5.77	0.225	−16.26	0.006
DEG-He	4.39	0.017	−217.67	0.008
DEG-tBuMe	4.77	0.269	−15.73	0.007
TEG-Me	5.20	0.020	−178.82	0.004
TEG-Me_2	5.09	0.026	−144.53	0.007
MPPE	4.30	0.010	−196.17	0.004
18-crown-6	4.31	0.019	−367.43	0.005

chain stiffness, the chain radius, the volume fraction, and the size of the diffusant.[34] The motion of a molecule through a hydrogel matrix depends on the probability of finding holes larger than the diffusant diameter. The distribution of the holes is described by the expression given by Ogston et al.[24] Amsden evaluated the distance between polymer chains with the help of scaling concepts, and the following equation was given

$$\frac{D}{D_0} = \exp\left[-\pi\left(\frac{r_s + r_f}{r_f}\right)^2 \frac{\varphi}{(k_1 + 2\varphi^{1/2})^2}\right] \qquad (8)$$

where r_s and r_f are the same as in eq 7, and k_1 is a constant for a given polymer−solvent system.

The normalized self-diffusion coefficient D/D_0 of selected diffusants is plotted as a function of the volume fraction of the PVA in Figure 8. Dashed lines are fits to eq 8 with floating parameters, including r_s, r_f, and k_1. Equation 8 provides relatively good fits to the data. Similar results are observed with the other diffusants. The fits provided values of r_s of 3.99, 5.42, 3.02, 284.0 and values of r_f of 0.033, 0.050, 0.031, 2.29 for EG-Me_2, EG-tBuMe, and 18-crown-6, respectively, which does not seem to be coherent. Therefore, we have fixed r_s to the R_h values listed in Table 2 during the fittings, but systematically lower values of r_f were obtained for each diffusant, while k_1 was found negative as shown in Table 4. The various r_f values obtained can be hardly related to the hydrodynamic radius of the polymer chain. The physical significance of k_1 remains unclear.

Conclusion

This study confirms that the self-diffusion coefficient depends on the size and geometry of the diffusant, evidenced by the effect of bulky end groups. Diffusants with a bulkier end group diffuse less rapidly than those with a smaller linear end group even though the molecular weights of the molecules are comparable. A hydrophobic hexyl group also restrains the diffusion more than the shorter alkyl groups.

The diffusion model of Mackie−Meares is strictly limited to very small diffusants since it does not take into account the differences of the diffusants. The diffusion model of Ogston et al. improved in this regard but still deviates significantly from the experimental data. The model of Amsden solved this problem by combining this obstruction model with other concepts such as the free volume concept, but the numerical values of the parameters are inconsistent with their original physical significance. The free volume model of Yasuda et al. is limited to the diffusion of small-sized diffusants and in dilute polymer solutions. The experimental data for this group of relatively small diffusants all fitted very well to the diffusion model of Phillies. The parameter α was found to increase as a function of the hydrodynamic radius of the diffusants, while a slight decrease is observed for the parameter ν.

The model of Petit et al. was used successfully in the fitting of the experimental data of all the diffusants over the entire range of polymer concentrations. As predicted, the parameter ν was found related to the solvent quality and remained a constant for the PVA−water system. The parameter $k\beta^2$ reflects the jump frequency of the diffusants and was found to decrease with increasing size of the diffusing molecules. By comparing these parameters with those obtained for oligo- and poly(ethylene glycol) diffusants, we are able to confirm the usefulness of this model in the analysis of both small and large diffusants in the PVA−water systems.

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