Solute Probe Diffusion in Aqueous Solutions of Poly(vinyl alcohol) As Studied by Pulsed-Gradient Spin-Echo NMR Spectroscopy

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ABSTRACT: A pulsed-gradient spin-echo NMR technique was used to measure the self-diffusion coefficients (D) of water and several different solute probe molecules in ternary poly(vinyl alcohol) (PVA)−water−solute systems, as a function of PVA concentration (up to 0.35 g/mL). The self-diffusion coefficient of water decreased with increasing PVA concentration, in a manner consistent with the Mackie−Meares obstruction effect model, and was independent of the polymer molecular weight, degree of hydrolysis, or the presence of the solute probes. The self-diffusion coefficients of the solute probes (methanol, *tert*-butanol, formamide, acetic acid, trimethylamine, tetramethylammonium cation, and poly(ethylene glycol) of molecular weight 400 and 4000) decreased with increasing PVA concentration and increasing probe size. The free volume theory could be used to describe the self-diffusion of solute probes only. The dependence of all the probe self-diffusion coefficients on polymer concentration could also be described using a stretched exponential function of the form $D = D_0 \exp(-\alpha c^{\nu})$ proposed by Phillies. With increasing PVA molecular weight, the scaling parameter ν generally decreased while the scaling parameter α generally increased. The analysis permitted an estimate of the correlation length (ξ), corresponding to the mesh size of the polymer network, which is found to decrease from 20−30 Å in the semidilute regime to 4−6 Å in the moderately concentrated regime and was independent of PVA molecular weight.

Introduction

Hydrogels are water-swollen cross-linked polymer networks. They are widely used in the biomedical, pharmaceutical, and other fields.[1] A particularly important application involves the use of hydrogels as vehicles for the controlled release of drugs. The drug-release process entails the diffusion of molecules from the interior of the polymer network to its exterior. One anticipates that diffusion in such systems will be influenced by a host of factors, including those specific to the diffusant, such as molecular size and shape, and those specific to the matrix, such as polymer molecular weight, flexibility, and concentration, as well as any specific interactions between the diffusant and the matrix, such as ionic or hydrogen bonding.

Theoretical descriptions of diffusion in polymer systems abound.[2] They include approaches based on free-volume concepts in polymers,[3,4] obstruction effects,[5−7] monomer friction coefficients,[8] and hydrodynamic interactions.[9−11] However, systematic experimental diffusion studies, particularly in hydrogels, are still few in number, largely because, until recently, diffusion measurements were tedious and time-consuming. The advent of the pulse-gradient spin-echo (PGSE) nuclear magnetic resonance (NMR) spectroscopy technique for measuring diffusion coefficients[12,13] has made systematic diffusion studies feasible and permits one to test the wider validity of the various theoretical descriptions of diffusion.

In this report we describe PGSE NMR measurements of the diffusion of water and of a series of different solute probe molecules in ternary mixtures of poly(vinyl alcohol) (PVA)−water−solute. PVA is commonly used in the preparation of hydrogels. Its gel-forming propensity derives from its ability to hydrogen-bond both with water, thereby ensuring polymer solvent compatability, and with itself, thereby providing the cross-links needed for gel-formation. The various solute probes (methanol, *tert*-butanol, formamide, acetic acid, trimethylamine, tetramethylammonium cation, and poly(ethylene glycol) of molecular weight 400 and 4000) were chosen to span a range of molecular weights. Measuring the diffusion of the water and the probe molecules as a function of PVA concentration then permits us to evaluate which theoretical model of diffusion in polymer systems is most appropriate to describe small molecule diffusion in the PVA−water−solute probe systems.

Theory of Molecular Diffusion in Polymer Systems

A number of different approaches have been proposed to describe molecular diffusion in polymers, each having its particular advantages and limitations. In obstructions theories, the polymer chains are viewed as slow moving and impenetrable, so the path length for diffusion of a small molecule increases and its diffusion slows. Mackie and Meares[5] used the lattice model for liquids and assumed that the polymer blocks a fraction of the sites, so the diffusion coefficient of a small molecule, equal in size to the polymer segment, is predicted to decrease according to the volume fraction of the polymer, φ_p, as per eq 1.

$$\frac{D}{D_0} = \left[\frac{1-\varphi_p}{1+\varphi_p}\right]^2 \qquad (1)$$

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The theory provides a good approximation of solvent diffusion over a large range of polymer concentrations.[2,14] However, the approach is strictly limited to very small molecules only, and no solvent-specific effects are considered.[14] For larger molecules, Ogston *et al.*[6] treated the polymers as randomly oriented straight fibers and defined the probability distribution, $g(R)$, of spaces of size R in order to estimate the diffusion coefficient of the diffusing molecule. The concept of "spaces in a uniform random suspension of fibers" was used by Johansson *et al.*[7] to describe the diffusion of a molecule in a flexible polymer. This model is quite successful for a dilute solution, but fails at higher concentrations, where hydrodynamic interactions are non-negligible.

The free volume theory of Fujita[3] considers diffusion to be a process in which molecules jump into voids created by the thermal motion of the molecules. Consequently, solvent diffusion decreases with increasing polymer concentration because the free volume intrinsic to the polymer is much less than that of the solvent. The approach successfully reproduces the polymer concentration dependence of solvent diffusion for a variety of solvent−polymer pairs over the full range of polymer concentrations.[4] Lodge et al. also used the free volume theories of Fujita[3] and Vrentas and Duda[4] to explain probe diffusion in a probe/poly(vinyl acetate)/toluene ternary system,[15] where the solvent is organic, but these theories do not apply to aqueous systems.[3] The free volume theory adapted by Yasuda for electrolyte diffusion in polymer systems can be used for pseudo-binary systems (polymer−solvent−solute probe) and explains the diffusion of the solute probe at low probe concentrations, assuming there are no interactions between the solute probe and the polymer.[16] The effective free volume, f_v, available to the probe molecule is approximately equal to the free volume contributed by the water, f_w, according to eq 2,

$$f_v = \varphi_w f w = (1 - \varphi_p) f_w \tag{2}$$

where φ_w is the volume fraction of water and φ_p is the volume fraction of the polymer. Consequently, the diffusion coefficient of a small solute molecule becomes a function of the probability of encountering a void commensurate in size with the cross section of the diffusing molecule, according to eq 3,

$$D = D_0 \exp\left[\frac{B_g}{f_w}\left(1 - \frac{1}{1 - \varphi_p}\right)\right] \tag{3}$$

where B_s is a measure of the size of the diffusing molecule.

Unlike obstruction and free volume theories, hydrodynamic models of diffusion explicitly consider the hydrodynamic interactions between small molecules and polymer. Cukier,[9] for example, described the diffusion of a spherical probe in the presence of randomly distributed fixed spheres as being equal to

$$D = D_0 \exp(-\kappa R) \tag{4}$$

where R is the radius of the diffusing species and κ describes the screening of the hydrodynamic interactions between the polymer and the solute. For an ideal chain, κ is predicted to depend on the polymer concentration according to $\kappa \propto c$,[17] while for a swollen chain it is predicted that $\kappa \propto c^{0.75}$.[18]

A more phenomenological approach is to employ a "universal" diffusion equation using a stretched exponential form as introduced by Phillies,[10,11]

$$D = D_0 \exp(-\alpha c^{\nu}) \tag{5}$$

where α is related to the size of the diffusant and ν is characteristic of the system at hand. Although, extensively used to describe the diffusion of spherical probes in polymer solutions,[19−21] there is still no definitive agreement regarding the physical significance of the parameters α and ν. Phillies suggests that α varies according to R/a_0 for polymers where a_0 is the distance of closest approach between the solute probe and the polymer bead.[22]

In nondilute polymer solutions, diffusion reflects chain dynamics, so scaling concepts are helpful in understanding the behavior. The "blob" model of de Gennes[23] treats the polymer solution as a succession of units (blobs) of size ξ, corresponding to the correlation length or the average distance between the junctions of entangled chains. For neutral polymers, ξ is proportional to $c^{-3/4}$ and is independent of the molecular weight. Langevin and Rondelez[24] proposed a scaling law for the friction coefficient, f, of a particle of diameter d in a semidilute polymer solution,

$$\frac{f_0}{f} = \exp\left(-\frac{d}{\xi}\right) + \frac{\eta_0}{\eta_m} \tag{6}$$

where η_0 and η_m are viscosities of the pure solvent and the macroscopic solvent−polymer mixture, respectively. For small molecules ($d \ll \xi$) the diffusion coefficient can be written as

$$D = D_0 \exp(-d/\xi) \tag{7}$$

Since de Gennes[23] has shown that ξ can be expressed as function of the polymer concentration according to

$$\xi = R_g(c^*/c)^{\nu} = \beta c^{-\nu} \tag{8}$$

where c^* is the overlap concentration between the dilute and semidilute regimes, it follows that

$$D = D_0 \exp\left(-\frac{d}{\beta} c^{\nu}\right) \tag{9}$$

which is identical to eq 5 with α equal to d/β. Equation 9 is in accordance with the predictions of hydrodynamic models that $\alpha \propto R$.[9]

von Meerwall[8] applied de Gennes' scaling concepts to model the diffusion of solute probes in polymers solutions using the monomer friction coefficient. This treatment requires values for the diffusion coefficients of both the probe molecule and the polymer, the latter being more difficult to obtain in many cases.

Table 1 summarizes the predictions of the various hydrodynamic models regarding the dependence of the scaling parameters α and β on solute probe size and polymer molecular weight.

Experimental

Materials. PVA samples of different degrees of hydrolysis (DH) and molecular weights (M) were purchased from Aldrich (Milwaukee, WI). These include the following samples: PVA1 (DH = 99% and M = 50 000), PVA2 (DH = 99% and M = 115 000) and PVA3 (DH = 87−89% and M = 115 000). D_2O (99.9% D) was purchased from C.I.L. (Woburn, MA) and the

Table 1. Hydrodynamic Diffusion Theories: Polymer Molecular Weight and Diffusant Size Dependence of Scaling Parameters[a]

models	α	ν
Cukier[9]	$\propto R_H$	Cukier:[9] 0.5 Freed and Edwards:[17] 1.0 de Gennes:[18] 0.75
Phillies[10]	$\propto R_H/a_0$	small M: 0.6 large M: 1.0 intermediate M: $\propto M^{-1/4}$

[a] R_H is the radius of the diffusing probe, a_0 is the distance of closest approach between the probe and the polymer bead, and M is the molecular weight of the polymer.

third component of the solution was one of the following: methanol (MeOH, from A.C.P., Montreal, Canada), *tert*-butanol (tBuOH, from Anachemia,Toronto, Canada), acetic acid (HAc, from B.D.H., Toronto, Canada), tetramethylammonium chloride (TMACl), trimethylamine (TMA), formamide, PEG 400, and PEG 4000 (all from Aldrich).

Sample Preparation. A mixture of D_2O and the desired solute probe (weight ratio fixed at 99:1) was prepared and weighed directly into a 5-mm NMR tube containing a known weight of polymer. The NMR tube was then sealed to prevent the loss of volatile components. The samples were heated for 5 hours at 100−110 °C. PGSE NMR measurements were made within 2 days to avoid gelation effects. Otherwise, the samples were heated for 1 h at 100 °C just prior to diffusion measurements. Diffusion coefficients were unchanged upon prolonged storage and treatment as described above. The concentration of PVA ranged from 0.028 to 0.35 g/mL.

PGSE NMR Diffusion Measurements. The diffusion measurements were performed using the PGSE NMR technique, using a standard Stejskal−Tanner PGSE sequence ($90°_x - \tau - 180°_y - \tau$ with gradient pulses during τ).[12] An MRI (magnetic resonance imaging) probe with actively shielded gradients coils (Doty Scientific, Columbia, SC) was installed in a Chemagnetics CMX 300 NMR spectrometer operating at 300 MHz for protons. Experiments were performed at 23 °C. A Techron gradient-coil driver was used to amplify the gradient pulse, which was applied to the z-direction only. We used two levels of gradient strength (G = 0.025 and 0.2 T/m) calibrated with a sample of 2 vol % H_2O in D_2O ($D = 1.9 \times 10^{-9}$ m^2 s^{-1}).[25,26] The error of the measured self-diffusion coefficients was estimated as less than 5%. Particulars regarding to the 90° pulse lengths (25 μs), interpulse delays (τ = 80 - 140 ms), recycle delays (10 − 60 s), spectral widths (10 kHz), data size (8 K), line broadening (5 Hz), number of acquisition (8), and gradient pulse widths (δ, variable parameter of the experiment from 0 up to 100 ms) are those indicated in parentheses unless otherwise mentioned.

The magnetic field gradient pulses result in an attenuation of the echo amplitude according to

$$A_{2\tau} = A^*_{2\tau} \exp[-(\gamma G\delta)^2(\Delta - \delta/3)D] \qquad (10)$$

where $A_{2\tau}$ is the echo amplitude, γ is the magnetogyric ratio of the nucleus (for ^{1}H, $\gamma = 2.675 \times 10^{11}$ rad G^{-1} s^{-1}), G is the pulsed-gradient strength, D is the self-diffusion coefficient, and Δ is the interval between the two gradient pulses. The effect of T_2 (spin−spin relaxation time) is constant when τ is kept constant and is contained in the term $A^*_{2\tau}$, the amplitude in the absence of gradient pulses. To determine the self-diffusion coefficient, the logarithm of the amplitude is plotted as a function of δ^2 ($\Delta - \delta/3$), and from the slope of the resulting line, D can be calculated once G is known.

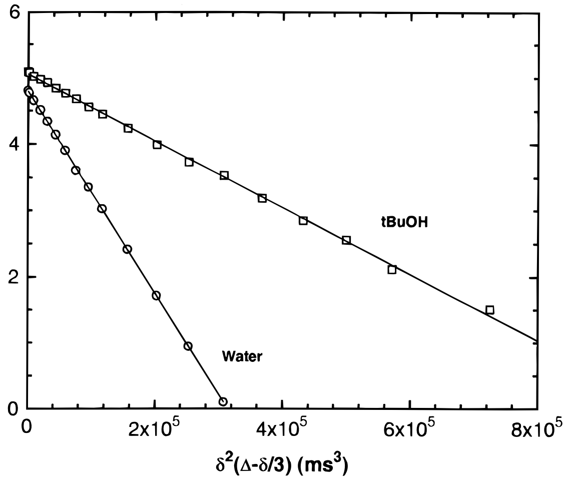

Figure 1. The logarithm of the intensities of the NMR signals as a function of δ^2 ($\Delta - \delta/3$) according to eq 10 for a PVA−water−tBuOH ternary system (PVA concentration 0.123 g/mL): circles, water; and squares, tBuOH. From the slope of the lines, self-diffusion coefficients of water are calculated to be 1.29×10^{-9} and 4.24×10^{-10} m^2 s^{-1}, respectively. Experimental parameters: G = 0.0256 T/m, $\Delta = \tau$ = 140 ms, recycle delay = 30 s.

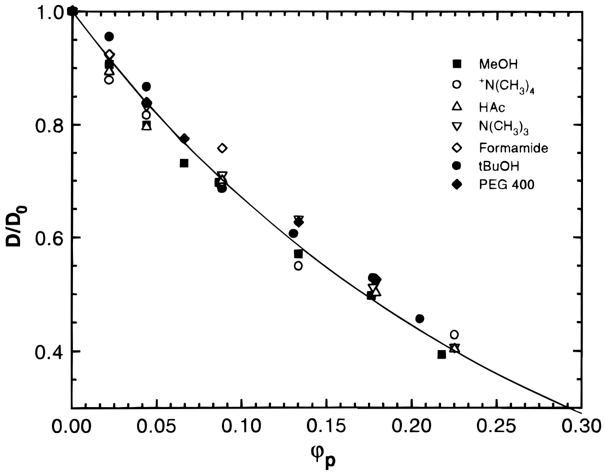

Figure 2. Reduced self-diffusion coefficients of water for each of the ternary systems in PVA1 (DH = 99% and M = 50 000) as a function of the volume fraction of the polymer. The solid line shows the prediction of the Mackie−Meares model (eq 1). The probe concentration is 1 wt% of the solvent (D_2O)−solute probe mixture.

Results and Discussion

In the PGSE NMR spectra of the PVA−water−solute ternary mixtures only two well-resolved proton signals are evident, corresponding to the water protons and the solute probe protons. The protons of the large PVA molecules exhibit a short T_2, so with the τ values employed here in the PGSE sequence, their intensities have decayed to zero prior to detection. Figure 1 illustrates typical intensity decays with increasing gradient pulse duration, in this instance for water and tBuOH in the presence of 0.123 g/mL PVA. From the slope of such intensity decays one extracts the diffusion coefficient as described in the Experimental Section. It is important to point out that, in each and every case investigated here, monoexponential decays are observed, indicating that the diffusion coefficients are monodisperse, the solutions are homogeneous, and the diffusion is nonrestricted.

Water Diffusion. The self-diffusion coefficients of water were measured for PVA1−water−solute ternary systems in the presence of each of the different solute probes. Figure 2 shows the reduced diffusion coefficient of water, D/D_0, as a function of the polymer volume fraction. It is evident that water diffusion in such systems is not influenced by the presence of a mere 1 wt % of the solute probes, regardless of the chemical differences between the probe molecules. With increas-

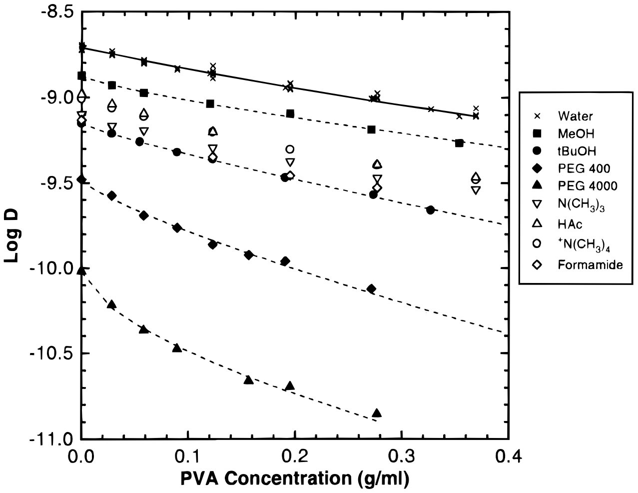

Figure 3. Semilogarithmic plot of solute probe self-diffusion coefficients in PVA1 ternary solutions as a function of polymer concentration. The water diffusion is also shown, along with the prediction of the Mackie–Meares model (eq 1). The dashed lines correspond to the "universal" equation of Phillies (eq 5) using the scaling parameters listed in Table 3. *D* is expressed in units of m^2 s^{-1}. The D_2O and solute probe ratio was fixed at 99:1.

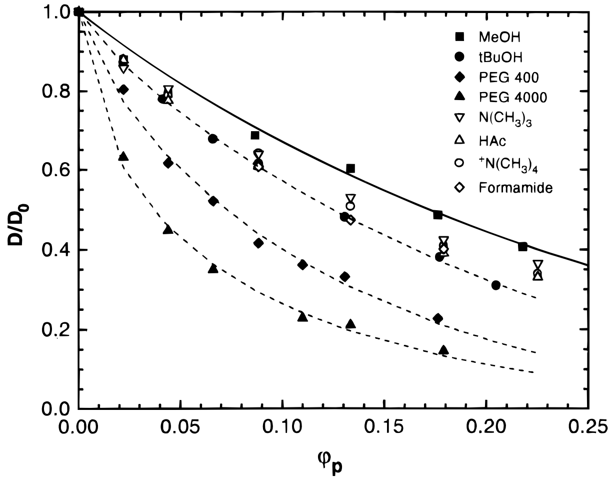

Figure 4. The reduced diffusion coefficient of water and the solute probes in PVA1 as a function of PVA volume fraction. The solid line show Mackie–Meares' prediction, while the dashed lines correspond to eq 5 with the scaling parameters listed in Table 3. The D_2O and solute probe ratio was fixed at 99:1.

ing PVA weight fraction, water diffusion decreases in a manner readily described by the Mackie–Meares obstruction model, as indicated by the solid line derived from eq 1. The molecular weight or degree of hydrolysis of PVA had no noticeable effect on the water diffusion.

Probe Diffusion. The diffusion coefficients for all solute probes investigated here are plotted as a function of PVA concentration in Figure 3. The self-diffusion coefficients decrease in strict order of increasing molecular size regardless of the PVA concentration. Note that the effective molecular size for this purpose is the hydrodynamic radius, which includes any waters of hydration. For example, the tetramethylammonium cation diffuses more rapidly than *tert*-butanol, indicating that its hydrodynamic radius, as calculated from the Stokes–Einstein equation [$D_0 = kT/(6\pi\eta R_H)$, where η is the viscosity of pure water] is smaller than that of *tert*-butanol. However, molecular radii obtained from lattice parameters of the corresponding crystals indicate that the reverse is true. The volume compression for the tetramethylammonium cation in aqueous solution is due to the electrostriction effect and to a reduced hydration of the cation.[27] One concludes that the occurrence of specific solute–water interactions and their consequences for the hydrodynamic radii are sufficient to explain in large part the differences in the diffusion of the solutes investigated here.

To focus on the polymer effects and to eliminate any differences due solely to solute–water interactions, it is useful to employ a reduced diffusion coefficient, D/D_0, where D_0 is the diffusion coefficient measured in the absence of polymer. In general, the solute diffusion coefficient can be considered to be a function of solute–solute, water–solute, and polymer–solute interactions.[28] Therefore, the diffusion coefficient measured in the absence of polymer reflects solute–solute plus water–solute interactions, while the reduced diffusion coefficient reflects primarily polymer–solute interactions. When plotted in this fashion, as shown in Figure 4, the reduced diffusion coefficients are quite evidently a function of the molecular size of the particular solute probe.

Obstruction Models. The Mackie–Meares model is intended to describe the diffusion of small molecules of a size similar to that of the polymer unit. The solid lines in Figures 2 and 4 are plots of eq 1, showing that the diffusion of water and methanol as a function of PVA concentration is adequately described in terms of obstruction effects. The diffusion behavior of the larger solute probes, however, deviates progressively with increasing molecular size from the predictions of Mackie–Meares' model. Obstruction theories for larger molecules, such as that of Ogston *et al.*,[6] likewise fail to reproduce the experimental observations, particularly at high PVA concentrations, where hydrodynamic considerations come to bear.

Free Volume Models. Equation 3 can be rewritten as

$$\ln \frac{D}{D_0} = A - B\left(\frac{1}{1 - \varphi_p}\right) \qquad (11)$$

where *A* and *B* are identical and equal to B_s/f_w. These free volume parameters can be measured by linear regression of $\ln(D/D_0)$ as a function of $(1 - \varphi_p)^{-1}$. Figure 5 shows the results of expressing the PVA concentration dependence of the diffusion coefficients in this fashion for selected solute probes. The dashed lines show the best fit, as determined using linear regression analysis, with the corresponding free volume parameter B_s/f_w listed in Table 2. For the smaller molecules, a very reasonable fit is obtained using free volume theory (linear correlation coefficients between 0.990 and 0.998). The PVA concentration dependence of the diffusion of larger molecules such as PEG 400 and PEG 4000 is rather poorly described by free volume theory (linear correlation coefficients of 0.986 for PEG 400 and even lower for PEG 4000). In fact, a gradual deterioration of the fitting can be observed as the probe molecules become larger. This derivation is likely due to neglecting the flexibility of such random-coil polymers.

In the version of free volume theory applied here,[16] it is assumed that the solute probes do not affect the properties of the solvent, so f_w should remain constant. Consequently, B_s/f_w should reflect the hydrodynamic radius of the solute probes. As shown in Figure 6, this is found to be the case for the smaller solute probes, so

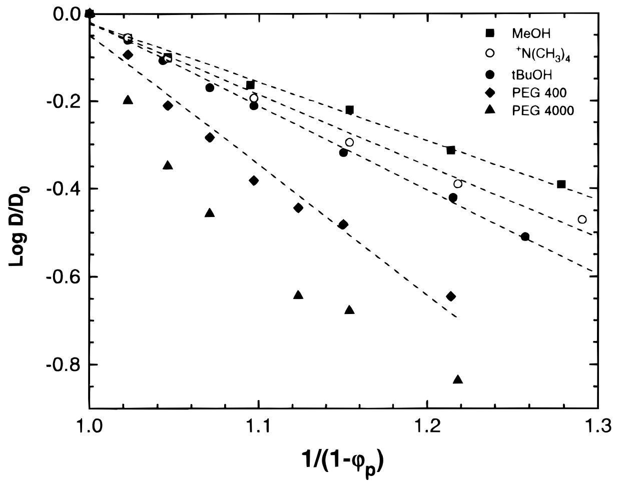

Figure 5. Application of free volume theory to solute probe diffusion in PVA ternary systems. The reduced diffusion coefficients are plotted as a function of $(1 - \varphi)^{-1}$ for PVA1. The dashed lines show the best fits using eq 11 with the free volume parameters listed in Table 2. The D_2O and solute probe ratio was fixed at 99:1.

Table 2. Free Volume Parameters for Solute Probe Diffusion in PVA[a]

PVA	Probes	R_H (Å)	A	B	B_s/f_w
$M = 50\ 000$	MeOH	1.75	3.04	3.09	3.07
DH = 99%	tBuOH	3.30	4.37	4.41	4.39
	PEG 400	7.00	6.71	6.82	6.77
	$N(CH_3)_3$	2.93	3.40	3.47	3.44
	$^+N(CH_3)_4$	2.38	3.70	3.75	3.73
	HAc	2.25	3.76	3.82	3.79
	$HCONH_2$	3.16	4.23	4.27	4.25
$M = 115\ 000$	MeOH	1.75	3.48	3.54	3.51
DH = 99%	tBuOH	3.30	4.42	4.51	4.46
$M = 115\ 000$	MeOH	1.75	3.04	3.13	3.09
DH = 87−89%	tBuOH	3.30	3.73	3.83	3.78

[a] *A* and *B* correspond to the slope and intercept in eq 11, as derived according to Yasuda[16] and detailed in the text. The free volume parameter B_s/f_w is the average of *A* and *B*.

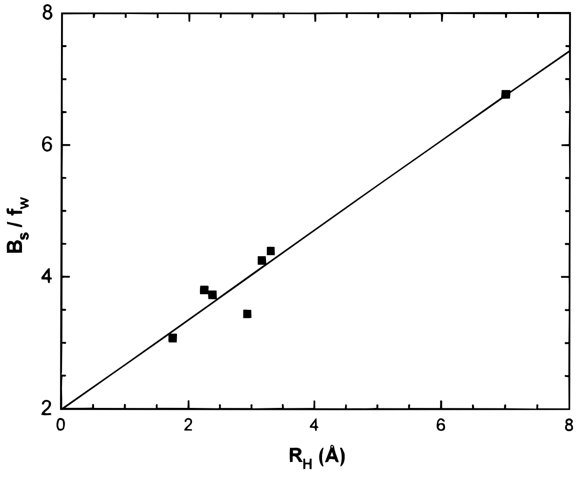

Figure 6. Correlation of free volume parameters with probe hydrodynamic radius for the case of solute probe diffusion in ternary PVA systems. Free volume parameters are listed in Table 2. Hydrodynamic radii were calculated using the Stokes−Einstein equation as detailed in the text.

the application of Yasuda's version of the free volume theory[16] to these pseudo-binary systems seems justified.

The free volume contributed by the polymer is considered to be much smaller than that of the water in Yasuda's theory. Since the additional free volume contributed by chain ends will be, likewise, minimal,

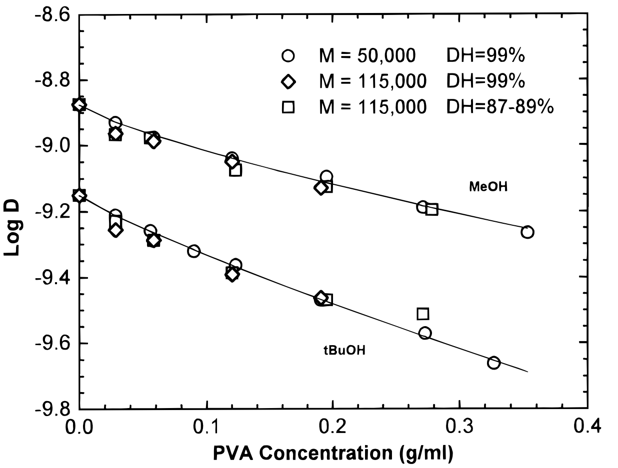

Figure 7. A comparison of the PVA concentration dependence of the self-diffusion coefficients of MeOH and tBuOH for two different PVA molecular weights and degrees of hydrolysis. PVA1 (circles), PVA2 (squares), and PVA3 (diamonds) systems. Solid lines are fits to eq 5 with the scaling parameters listed in Table 3. The D_2O and solute probe ratio was fixed at 99:1.

one expects that solute probe diffusion will be independent of the molecular weight of the polymer. The experimental data for the diffusion of MeOH and tBuOH in PVA2 and PVA3 confirm the validity of this assumption, as illustrated in Figure 7, while the values of B_s/f_w extracted for these systems (see Table 2) lend further support to this conclusion.

Hydrodynamic Models. The various hydrodynamic theories discussed earlier yield different expectations for the dependence of the fitting parameters α and *ν* on solute probe size and polymer molecular weight, as summarized in Table 1. The diffusion data for the solute probes were fitted to the stretched exponential, eq 5, using a nonlinear least-squares protocol, with α, *ν*, and D_0 as free parameters. The results are listed in Table 3. The dashed lines in Figure 4 were drawn using the parameters listed in Table 3 in conjunction with eq 5, and the success of this approach in reproducing the diffusion behavior is evident. Such treatments of the diffusion of solute probes in polymer systems have been reported previously in the literature.[19,20]

The parameter α generally increases as the molecular size of the solute probes increases, as shown in Figure 8, where α is plotted as a function of the hydrodynamic radius, R_H, of the solute molecules calculated using the Stokes−Einstein equation. The exception, again, is PEG 4000. So, for smaller solute probes, α depends directly on R_H, as predicted by Cukier's theory.[9] This is not necessarily at odds with Phillies' predictions[22] that α should vary with R_H/a_0, where a_0 is the distance of closest approach between the solute probe and the polymer bead. For instance, as a first approximation, $a_0 = R_H + \rho$, where ρ is the monomer radius. One calculates $\rho = 2.7$ Å for PVA, using $v = \pi\rho^2 L N_A/M_0$, where *v* is the partial specific volume (0.781 mL g^{-1}), *L* is the mean residue length (2.5 Å), N_A is Avogadro's number, and M_0 is the molar mass of the monomer unit (44 g mol^{-1}). For all the solute probes used in this study, fitting of the results in Figure 8 yields $\alpha = 5.19R_H/(R_H + \rho)$. In contrast, other hydrodynamic theories predict a power law dependence of α on R_H for spherical probes,[9,19] and Park *et al.*[21] reported that for probe diffusion in polyacrylamide gels $\alpha \propto R^{0.59}$.

The scaling exponent *ν* falls in the region of 0.8 for all solute probes in the presence of PVA1, with the

Table 3. Hydrodynamic Scaling Parameters for Diffusion of Solute Probes in PVA[a]

PVA	Probes	R_H (Å)	D_0 (10^{-10} m^2 s^{-1}) expl	D_0 (10^{-10} m^2 s^{-1}) calcd	α	ν	error	x
M = 50 000	MeOH	1.75	13.3	13.3	1.96	0.78	0.17	0.58
DH = 99%	tBuOH	3.30	7.07	7.06	3.03	0.86	0.04	0.61
	PEG 400	7.00	3.31	3.34	4.32	0.79	0.06	0.58
	PEG 4000	24.35	0.958	0.960	4.42	0.61	0.02	0.73
	$N(CH_3)_3$	2.93	7.96	7.96	2.28	0.79	0.10	0.58
	$^+N(CH_3)_4$	2.38	9.79	9.81	2.56	0.83	0.07	0.56
	HAc	2.25	10.35	10.41	2.58	0.80	0.13	0.57
	$HCONH_2$	3.16	7.37	7.37	2.42	0.74	0.07	0.54
M = 115 000	MeOH	1.75	13.3	13.3	1.50	0.60	0.21	0.75
DH = 99%	tBuOH	3.30	7.07	7.05	1.99	0.62	0.10	0.72
M = 115 000	MeOH	1.75	13.3	13.3	1.60	0.60	0.16	0.65
DH = 87–89%	tBuOH	3.30	7.07	7.09	2.06	0.65	0.10	0.68

[a] Scaling parameters α and ν are obtained by fitting diffusion data to eq 5. The error has a unit of 10^{-10} m^2 s^{-1} and is estimated by calculation the variance of the residuals from the measured and calculated self-diffusion coefficients. The hydrodynamic radius, R_H, is calculated using the Stokes–Einstein equation as described in the text. As per eq 13, $\nu = x/(3x - 1)$.

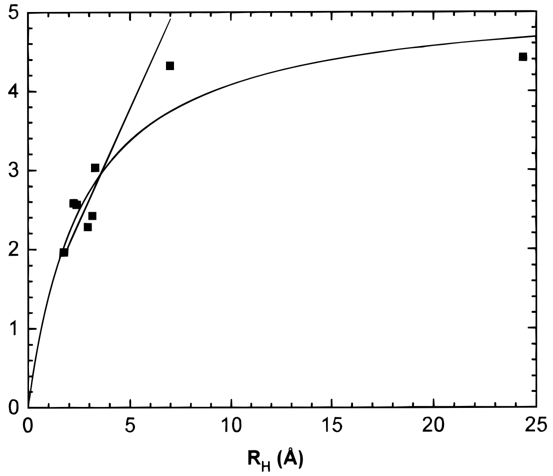

Figure 8. The correlation of scaling parameter α with probe hydrodynamic radius for the case of solute probe diffusion in ternary PVA systems. Scaling parameters are listed in Table 3. Hydrodynamic radii were calculated using the Stokes–Einstein equation as detailed in the text. The curved line corresponds to $\alpha = 5.19\ R_H / (R_H + \rho)$ as described in the text. The straight line shows the linear relation $\alpha \propto R_H$ as in Cukier's theory.[9]

exception of PEG 4000. For the two solute probes MeOH and tBuOH investigated in PVA2 and PVA3, values of ν decrease to approximately 0.60. Although these values of ν agree broadly with the predictions of Cukier[9] and de Gennes,[18] only Phillies[10,11] predicts that ν depends on the polymer molecular weight. According to Phillies,[10] ν takes a value of 0.60 for long polymer chains and 1 for short ones and between these limits, ν varies as a function of $M^{-1/4}$ [11] (see Table 1). Therefore, for polymers of intermediate size, one may write $(\nu_1/\nu_2) = (M_1/M_2)^{-1/4}$, where the subscripts 1 and 2 designate PVA1 and PVA2, respectively. For ν_1 equal to 0.8, one predicts a value of ν_2 equal to approximately 0.65, in good agreement with the experimental observations.

It is interesting that the values of both α and ν depend on polymer molecular weight for the two solute probes MeOH and tBuOH, but the self-diffusion coefficients themselves show no such polymer molecular weight dependence, as shown in Figure 7. This must be considered a consequence of the fact that, for small molecules, whole body diffusive motions occur on distance and time scales comparable to those of the internal deformations of the polymer. Whole body motions of the polymer, occurring on much longer distance and time scales, are not an influence.

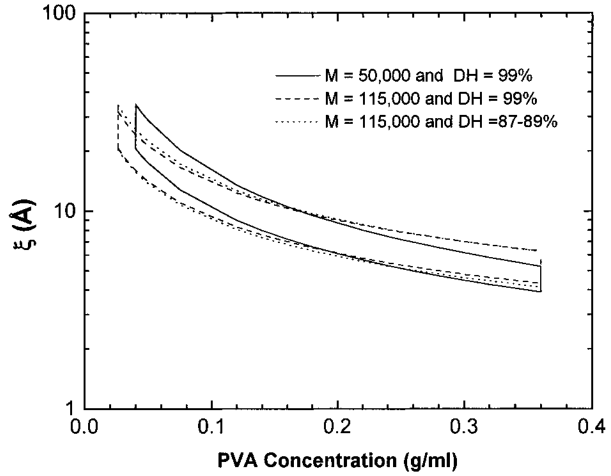

Figure 9. Correlation length (ξ) as a function of PVA concentration for different PVA molecular weights and degrees of hydrolysis. The distribution of ξ values from individual solute probes are indicated. For details of the calculation see the text.

Polymer Correlation Lengths from Probe Diffusion. De Smedt *et al.*[29] demonstrated how one may use diffusion data to obtain structural information on the transient network structure in hyaluronic acid solutions. From eqs 8 and 9, one may obtain

$$\xi = (2R_H/\alpha)c^{-\nu} \tag{12}$$

where α and ν are the scaling parameters listed in Table 3. Equation 12 is valid only for small molecules ($2R_H \ll \xi$). Using the diffusion data for all solute probes except PEG 4000, one derives the concentration dependence of ξ illustrated in Figure 9. At low PVA concentrations ξ falls in the region of 20–30 Å, decreasing to about 4–6 Å at high PVA concentrations. The PVA molecular weight or degree of hydrolysis seems to have little impact, in accordance with the prediction of de Gennes that ξ does not depend on M.[23] The values of ξ reported here are similar or somewhat lower than those obtained for PVA from dynamic light scattering experiments (38[30] and 82 Å[31]), but are comparable to values reported using small-angle X-ray scattering measurements (34 Å[32]). The estimates of ξ are valid provided that, as described by De Smedt *et al.*,[29] ν fulfills the following condition:

$$\nu = x/(3x - 1) \tag{13}$$

where x is the exponent describing the dependence of R_g on the degree of polymerization, N, $R_g \propto N^x$. Typically, for flexible polymers x falls in the range 0.5 to 0.6, as do the values calculated for the individual diffusants investigated here and listed in Table 3.

These correlation length calculations immediately explain the apparent anomalous behavior of PEG 4000 diffusion in PVA. The hydrodynamic diameter of PEG 4000 ($2R_H = 48.8$ Å) is comparable to the correlation length of PVA at low PVA concentrations and greater than ξ at higher PVA concentrations. Consequently, one expects that PEG 4000 diffusion should decrease with increasing PVA concentration in proportion to the change in the viscosity ratio η_0/η_M and should rapidly attain a diffusion rate too slow to measure with the particular combination of gradient strengths and pulse sequence employed here. However, the decrease in the PEG 4000 self-diffusion coefficient levels out at higher PVA concentrations. Two points are germane to the issue. First, PEG is a highly flexible molecule, able to accommodate its size and shape to the details of the network in which it is enmeshed. Second, the correlation length ξ represents the mean value of a statistical distribution of correlation lengths, each of which arises from a transient association between polymers. Thus, the whole body diffusion of PEG 4000 depends on the distance and time scales of the internal motions of both the PEG and the PVA, as well as the whole body motions of the PVA. As a consequence, diffusion theories which treat diffusants as hard spheres and ignore the mobility of the polymer network cannot be expected to describe the diffusion behavior of PEG 4000 in PVA.

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