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Polymer/Probe Interaction in Probe Diffusion through a Polymer Matrix: Methyl Red Diffusion in Poly(vinyl acetate)/Toluene Solutions

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ABSTRACT: The effect of hydrogen-bonding interaction on the probe diffusion was studied by forced Rayleigh scattering for the diffusion of methyl red derivatives through poly(vinyl acetate) (PVAc) solutions. In semidilute toluene solutions of PVAc, the effect of hydrogen bonding on the probe diffusion was confirmed from the different diffusion behavior of four methyl red derivatives. It was found that the dependence of reduced tracer diffusion coefficients D/D_0 of probes of polymer concentration C are well represented by the relation $D/D_0 = \exp(-aC^\nu)$ where D_0 is the diffusion coefficient of the probe in the pure solvent. The effect of hydrogen-bonding interaction on D is reflected both in ν and a; ν decreases while a increases relative to the system without hydrogen-bonding interaction.

Introduction

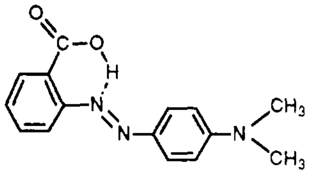
Diffusion of a material in a polymer matrix is retarded by the molecular sieving process, which is utilized in various separation techniques such as gel filtration and gel electrophoresis. Transport phenomena of this kind have received considerable attention in recent years. It is generally accepted, on theoretical[1–6] as well as on empirical grounds,[2,3,7–14] that diffusion coefficients of probes follow the relation

$$D/D_0 = \exp(-aC^\nu) \tag{1}$$

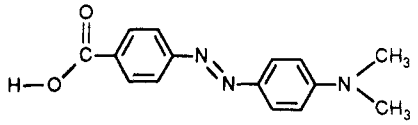
where D_0 is the diffusion coefficient in the pure solvent, C is the concentration of the polymer, and a is the parameter related to the size of the diffusant. Beyond the general form of eq 1, there are conflicts in detailed values of a and ν. Also, most of theoretical as well as experimental work has been concerned with the effect of excluded volume and hydrodynamic interaction without considering matrix–probe interactions such as Coulombic interaction, hydrogen bonding, etc. When such a specific interaction exists, the probe diffusion coefficients should be affected significantly.[11,15] For example, it was reported that the diffusion of methyl red (MR) was substantially more retarded in a toluene solution of poly(vinyl acetate) (PVAc) than that of polystyrene (PS).[15] The slower diffusion of MR in the presence of a PVAc matrix was ascribed to the hydrogen bonding between the probe and the polymer. Recently we have also found a similar behavior of methyl red diffusion in a poly(methyl methacrylate) (PMMA)/toluene solution.[16] This observation fully supports the view that a specific interaction between MR and the carbonyl group in these polymers is responsible for the retarded diffusion. The question that then arises is how the probe diffusion coefficient depends on the polymer concentration in the presence of such a specific interaction. In this paper, we present the results obtained from a forced Rayleigh scattering (FRS) study of the probe diffusion in polymer solutions in which specific interactions between the probe and polymer backbone exist.

Experimental Section

Materials. Four different azo dyes, 2-[[4-(dimethylamino)phenyl]azo]benzoic acid (methyl red, *o*-MR) (I), 4-[[4-(dimethylamino)phenyl]azo]benzoic acid (*p*-MR) (II), the methyl ester of methyl red (CH_3-*o*-MR), and the methyl ester of *p*-MR (CH_3-*p*-MR), were used in this study.



I



II

The free acid form of *o*-MR (I) was used as received from Aldrich. The sodium salt form of *p*-MR was acquired from Kodak, and its free acid form (II) was obtained by lowering the pH of an aqueous solution of the dye to 6 and extracting with dichloromethane. CH_3-*o*-MR and CH_3-*p*-MR were prepared from I and II, respectively. Esterification by methanol was carried out by use of dicyclohexylcarbodiimide as the coupling agent. PVAc was from Aldrich, and their molecular characteristics were determined by gel permeation chromatography with THF as an eluent. Its M_w and M_w/M_n were found to be 85.6K and 1.13 relative to polystyrene standards, respectively. Toluene solutions of the polymer and the dyes were prepared gravimetrically and converted to volume fractions from the density of the materials. The sample solutions were filtered through 0.2-μm-pore PTFE membrane filters (Gelman) directly to spectroscopic cuvettes for FRS measurements.

FRS Measurements. The instrumentation and analysis scheme of FRS experiments described elsewhere[16] is similar to others found in the literature.[17–22] The 488-nm line of an Ar ion laser (Coherent, Model 90-3) was used for the writing beam and the 632.8-nm line of a He/Ne laser (Melles Griot, 5 mW) for the reading beam. Spectroscopic cuvettes (5-mm path length) were used as sample cells, and the temperature of the cell was controlled at 25.0 ± 0.1 °C. The dye concentration was kept low, ~0.1 mg/mL, so that the measured diffusion coefficients are independent of concentration.

For simple decay prolifes, the decay time constants were determined by a nonlinear regression fit to the typical single-exponential model function. For decay-growth-decay type profiles, the double-exponential model function, $I_d(t) = [A_1 \exp(-t/\tau_1) - A_2 \exp(-t/\tau_2)]^2 + B$, was employed and the mean decay constants are determined by Δt, the time lapse between the dip

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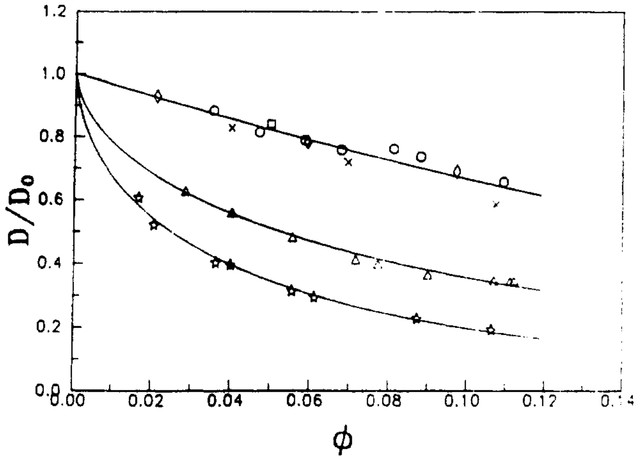

Figure 1. Dependence of reduced tracer diffusion coefficient D/D_0 on polymer volume fraction ϕ, where D_0 is the diffusion coefficient of the respective dyes in pure toluene: (○) *o*-MR/PS; (□) *p*-MR/PS; (◇) CH_3-*o*-MR/PVAc; (×) CH_3-*p*-MR/PVAc; (△) *o*-MR/PVAc; (☆) *p*-MR/PVAc. Solid lines are drawn according to eq 1 with the parameters shown in Table I.

Table I
Values of D_0, R_h, a, and ν for Four Different Dyes in a PVAc/Toluene Solution at 25 °C[a]

dye	D_0 ($\times 10^{-6}$ cm^2/s)	R_h (Å)	ν	a
o-MR	12.6 ± 0.9	3.1 ± 0.2	0.62 ± 0.06	$4._{4} \pm 1.2$
p-MR	11.9 ± 0.3	3.3 ± 0.1	0.62 ± 0.06	$6._{7} \pm 1.2$
CH_3-*o*-MR	12.4 ± 0.4	3.2 ± 0.1	1.0 ± 0.1[b]	$4._{2} \pm 1.4$[b]
CH_3-*p*-MR	12.9 ± 0.4	3.1 ± 0.1	1.0 ± 0.1[b]	$4._{2} \pm 1.4$[b]

[a] Uncertainties represent the 95% confidence limit. [b] Mean values for *o*-MR/PS, *p*-MR/PS, CH_3-*o*-MR/PVAc, and CH_3-*p*-MR/PVAc systems.

and maximum position, which is approximated to the mean of τ_1 and τ_2 when two decay constants do not differ much.[23] These diffusion coefficients are obtained from the q^2 dependence of τ or Δt, where $q = 2\pi/d$ and d is the spacing of the concentration fringe.

Results and Discussion

The FRS decay profiles of four different probes showed different shapes. A decay-growth-decay type signal was observed for *o*-MR in a PVAc/toluene solution as reported previously,[15] while *p*-MR, CH_3-*o*-MR, and CH_3-*p*-MR exhibit single-exponential decays. In pure toluene, all four dyes show clean single-exponential decay profiles. Therefore, the system of *o*-MR in a PVAc/toluene solution displays a characteristic complementary grating effect,[24] which needs a further study to elucidate the origin of the observation. For the present study, we restrict the discussion on the concentration dependence of diffusion coefficients.

Tracer diffusion coefficients of probe dyes measured by FRS are plotted in Figure 1 as a function of polymer volume fraction, ϕ. The diffusion coefficients are normalized to D_0 which is the diffusion coefficient of the respective dyes in pure toluene. In Table I are summarized the D_0 values and the hydrodynamic radii of the dyes obtained by the Stokes–Einstein relation, $R_h = kT/6\pi\eta D_0$. As expected from the similar structure of the dyes, R_h's of the dyes in the pure solvent are practically the same. Also the R_h values near 3 Å seem quite reasonable considering the molecular dimension of the dyes. In Figure 1, we observe three separate groups in terms of the extent of retardation due to the presence of the polymer matrix. The solid lines are the best fit results according to eq 1, which describe the variation of the diffusion coefficients with polymer concentration very well. This will be further discussed later.

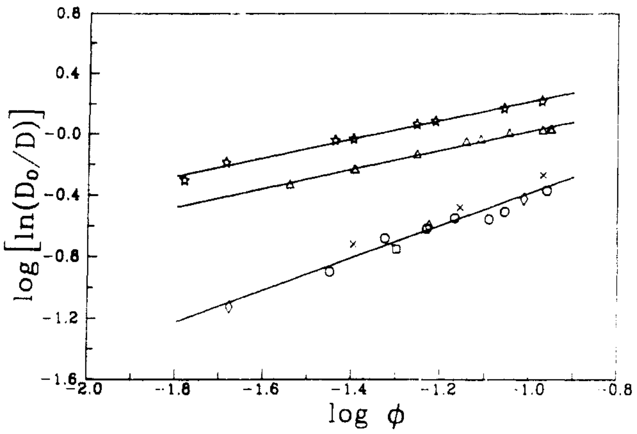

Figure 2. log–log plot of ln (D_0/D) vs polymer volume fraction, ϕ. Solid lines are the results of least-square analyses. Good linearity of the plot indicates the data points follow the relation of eq 1 and the slopes represent ν: (○) *o*-MR/PS; (□) *p*-MR/PS; (◇) CH_3-*o*-MR/PVAc; (×) CH_3-*p*-MR/PVAc; (△) *o*-MR/PVAc; (☆) *p*-MR/PVAc.

Within experimental uncertainty, all four dyes showed identical retardation in a PS/toluene solution where no specific interaction is expected other than hydrodynamic interaction between the probe and the polymer. In PVAc/toluene solutions, the two esterified dyes, CH_3-*o*-MR and CH_3-*p*-MR, behave similarly as in a PS/toluene solution, while the diffusion of *o*-MR and *p*-MR is far more retarded. This unambiguously confirms that the retarded diffusion found with *o*-MR and *p*-MR is caused by the hydrogen-bonding interaction with PVAc since the hydrogen-bonding capability is eliminated by the esterification.

The larger retardation found with *p*-MR as compared to *o*-MR manifests a stronger interaction of *p*-MR with PVAc provided there is no self-association of *p*-MR.[17] We confirmed experimentally the independence of D on dye concentration and on laser power, which allows us to assume that the carboxylic hydrogen in the 4′ position can form a more effective hydrogen bond than that in the 2′ position. This is due to the internal hydrogen bonding in *o*-MR between the carboxyl and the azo groups through a 6-membered ring structure as shown in I, which weakens the interaction with the polymer. This internal hydrogen-bonding effect can be clearly seen by NMR measurements. The proton resonance peak of carboxylic hydrogen of *o*-MR appears further downfield, 13.9 ppm, than that of *p*-MR (12.3 ppm) in a 3:1 (v/v) mixture of $CDCl_3$/DMSO-d_6. Also the resonance peak is much sharper for *o*-MR, indicating a more confined environment than in *p*-MR.

For the diffusion of a small diffusant in a polymer matrix where no specific interaction other than hydrodynamic interaction exists, it has been reasonably well established that D depends on polymer concentration as given in eq 1. The linear plots in Figure 2 confirm the dependences of D/D_0 on the polymer concentration given by eq 1 for the systems with specific interaction as well. The slope represents the exponent ν, and we found 1.0 for the system without specific interaction. This value can be favorably compared with other results available from the literature. Johnson and co-workers reported $\nu \simeq 1$ by FRS and pulsed field gradient methods for various probes in a polyacrylamide aqueous gel,[13] and about the same exponents are reported by Furukawa et al.[14] and Carlfors and Rymden[9] for the diffusion of small molecules in polymer solutions. As for the a value, we obtained 4.2 while one would obtain ~6 by use of the empirical equation reported by Park et al.,[13] $a = 3.03R_h^{0.59}$. This deviation should arise from the different R_h in two solvents: in water, R_h of *o*-MR was found to be 5.5. Å, which is much larger than the value found in toluene, 3.1 Å. This is more likely due to the ionization of *o*-MR in an aqueous media which leads to a stronger solvation by water molecules. Also the hydration of *o*-MR would effectively block the interaction of *o*-MR with polyacrylamide, resulting in an exponent ν similar to that in the noninteracting system. A similar trend was reported for the system of *o*-MR diffusion in a PVAc/ethyl acetate solution relative to a PVAc/toluene solution,[15] where ethyl acetate interacts with the dye whereby blocking the interaction with PVAc. Therefore, small probe diffusion in a noninteracting polymer matrix appears to yield a consistent result in terms of its dependence on polymer concentration.

We also note from Figure 2 that eq 1 can describe the dependence of D on the polymer concentration for the system with hydrogen-bonding interaction. The simple binding model used previously for the system with specific interaction did not yield a good fit especially for the *p*-MR system, likely due to the stronger hydrogen bonding.[15] The plot yields slope 0.62 ± 0.06 for both *o*-MR and *p*-MR, which are significantly smaller than the ν value observed from the system without specific interaction. We also found a similar value for *o*-MR diffusion in a PMMA/toluene solution, $\nu = 0.65 \pm 0.07$.[16] A somewhat similar trend in ν was reported for the latex diffusion in aqueous polymer solutions when the ionic strength was varied to alter the interaction between latex particles and the polymer.[11] On the other hand, a values for *o*-MR and *p*-MR differ significantly from each other although their hydrodynamic radii in toluene are identical within experimental uncertainty as shown in Table I. It thus appears that the effect of hydrogen-bonding interaction on D is reflected not only in ν but also in a, and the strength of the interaction seems to be manifested in a.

All the a and ν values are listed in Table I, and the solid lines in Figure 1 are drawn according to eq 1 by use of these a and ν values. The quality of the fit appears indeed satisfactory. Although this concentration dependence still lacks theoretical support, it is consistent with the experimental results. Since this kind of specific interaction can play an important role in numerous applications, further theoretical and experimental effort is called for.

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