Temperature dependence of probe diffusion in polymer matrix

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The temperature dependence of diffusion of methyl red derivatives through semidilute toluene solutions of poly(vinyl acetate) was studied by forced Rayleigh scattering. The magnitude of the hydrogen bonding effect on probe diffusion was estimated from the activation energy of the diffusion process.

(Keywords: probe diffusion; polymer solution; temperature dependence; hydrogen bonding interaction)

Introduction

Material transport 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. In the absence of a specific interaction, the retarded transport of a small probe in polymer solutions or gels is attributed mainly to the hydrodynamic interaction between polymer chains and the probe. Under such circumstances it is generally accepted that diffusion coefficients of probes follow a stretched exponential relation[1–4]:

$$D/D_0 = \exp(-\alpha C^{\nu}) \qquad (1)$$

where D_0 is the diffusion coefficient in pure solvent, C is the concentration of the polymer, α is a parameter related to the size of the diffusant and ν is a characteristic exponent depending on the system.

Recently, the diffusion of small probes in polymer solutions was found to be greatly affected by the presence of a specific interaction, such as hydrogen bonding between the diffusant and the polymer backbone[5]. It has also been found that equation (1) apparently describes the matrix concentration dependence of probe diffusion in the presence of hydrogen bonding interaction, although this equation has been established for systems where no specific interaction between the diffusant and the matrix exists[6].

In this communication we report a study on the temperature dependence of tracer diffusion coefficients of methyl red (MR) derivatives in the toluene solution of poly(vinyl acetate) (PVAc), to show quantitatively the effect of the hydrogen bonding interaction in such a transport process.

Experimental

Two isomers of MR, {2-[4-(dimethylamino)phenylazo]-benzoic acid} (o-MR) and {4-[4-(dimethylamino)phenylazo]benzoic acid} (p-MR), were used for this study. The free acid form of o-MR was used as received from Aldrich. The sodium salt form of p-MR was acquired from Kodak and its free acid form was obtained by lowering the pH of the aqueous salt solution and extracting with dichloromethane. PVAc was from Aldrich and its M_w and M_w/M_n, determined by gel permeation chromatography, were 85 600 and 1.13 relative to polystyrene standards, respectively. Polystyrene (PS) was prepared in this laboratory by anionic polymerization; its M_w and M_w/M_n were 660 000 and 1.09, respectively. The molecular weights of these polymers were large enough to ensure that the experimental condition, 10% polymer volume fraction, was in the semidilute solution regime. The polymer/dye/toluene solutions were filtered through 0.45 μm pore poly(tetrafluoroethylene) membrane filters (Gelman) directly to 5 mm path length spectroscopic cuvettes for forced Rayleigh scattering (FRS) measurements.

The FRS apparatus used in this study has been described in detail elsewhere[7]. The temperature of the cell was controlled to better than ±0.1°C by circulating water through a sample holder made of a copper block. The concentration of the probe dye was kept low, about 0.2 mg ml^{-1}, so that the measured diffusion coefficients were independent of concentration.

Results and discussion

Tracer diffusion coefficients of two dyes in 10% (v/v) polymer/toluene solutions were obtained at five temperatures: 15, 25, 35, 45 and 55°C. The results are presented in *Table 1* and plotted in *Figure 1*. As can be seen in the figure, the diffusion coefficients of both dyes apparently follow Arrhenius behaviour, $D = A\exp(-E_A/RT)$, quite well. The activation energy of diffusion, E_A, is obtained from the slope of the semilog plot. This type of Arrhenius behaviour has been observed for small-probe diffusion in polymer solutions of low concentration, i.e. the experimental temperature is well above the glass transition temperature of the system[8]. At high polymer concentration, Williams–Landel–Ferry behaviour was observed[9].

In *Table 1*, D_0, the diffusion coefficient in pure toluene, of p-MR is slightly lower than that of o-MR, probably due to the more elongated shape of p-MR. The hydrodynamic radii of both dyes, deduced from the Stokes–Einstein relation, $R_h = kT/6\pi\eta D_0$ (where η is viscosity), are practically independent of temperature. This indicates that the diffusion of the small probe in toluene follows the Stokes–Einstein relation very well. Although the hydrodynamic radius should depend on the frictional boundary condition, $R_h = 3$ Å appears to be

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Table 1 Diffusion coefficients ($\times 10^{-6}$ cm^2 s^{-1}) of o-MR and p-MR at different temperatures, and the activation energy of diffusion in toluene, 10% (v/v) PS/toluene and 10% (v/v) PVAc/toluene solution media[a]

Temperature (°C)	Toluene		PS/toluene		PVAc/toluene	
	o-MR	p-MR	o-MR	p-MR	o-MR	p-MR
15	11.2±0.4	10.3±0.4	7.4±0.6	6.5±0.3	3.5±0.1	2.1±0.3
	(3.0±0.1)[b]	(3.3±0.1)[b]				
25	13.2±0.9	12.3±0.6	8.9±0.2	8.0±0.3	4.2±0.4	2.6±0.3
	(3.0±0.2)[b]	(3.2±0.2)[b]				
35	15.3±0.7	14.5±0.7	10.7±0.7	9.6±0.3	5.4±0.9	3.6±0.2
	(3.0±0.1)[b]	(3.2±0.2)[b]				
45	18.2±0.8	17.1±1.2	12.9±0.3	12.0±1.0	6.9±0.6	4.8±0.3
	(2.9±0.1)[b]	(3.1±0.2)[b]				
55	20.2±0.5	19.4±1.2	14.5±0.7	13.7±0.5	8.7±0.6	6.1±0.3
	(3.0±0.1)[b]	(3.1±0.2)[b]				
E_A (kJ mol^{-1})	11.9±0.7	12.6±0.4	13.6±1.2	15.1±1.2	17.2±2.4	21.7±3.3

[a] Uncertainties represent the 95% confidence limit

[b] Stokes radius, R_h (in Å) calculated by $R_h = kT/6\pi\eta D_0$

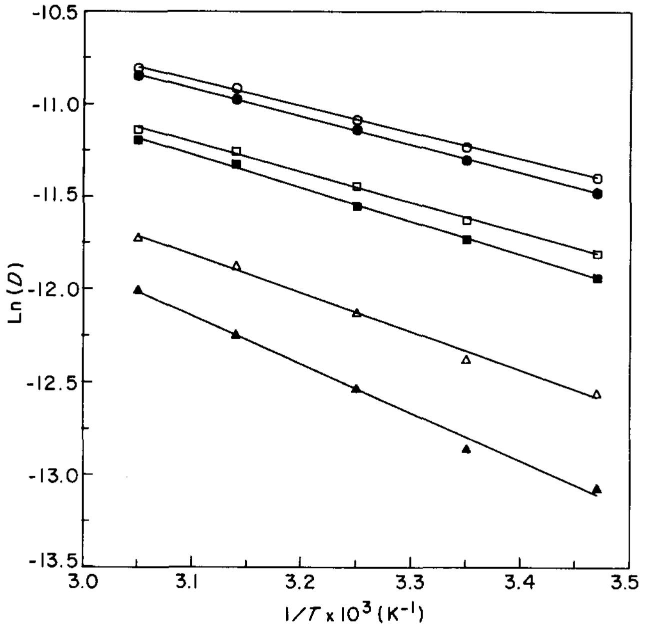

Figure 1 Temperature dependence of diffusion coefficients of o-MR and p-MR represented by Arrhenius plot of ln D *versus* $1/T$: ○, o-MR/toluene; ●, p-MR/toluene; □, o-MR/PS/toluene; ■, p-MR/PS/toluene; △, o-MR/PVAc/toluene; ▲, p-MR/PVAc/toluene. Polymer concentrations are 10% volume fraction

reasonable for the given molecular dimension of the dyes. Also, the activation energy of p-MR diffusion in toluene is slightly larger than that of o-MR. If diffusion follows the Stokes–Einstein relation, the activation energy should be related to the viscosity of the medium. The activation energy of T/η of toluene was found to be 11.5 kJ mol^{-1}, which is slightly lower but in reasonable agreement with the E_A of probe diffusion.

In PS/toluene solution, the diffusion of the dye molecules is clearly retarded due to the presence of polymer matrix and the activation energy of diffusion increases. In addition, it is seen from *Figure 1* that the difference between the diffusion coefficients of o-MR and p-MR increases slightly relative to that in pure toluene. This behaviour is essentially the principle of separation by molecular sieving, although it is barely beyond the experimental precision in this case. Differentiation should become more effective with larger probes or at higher polymer concentrations. Also, the effect can be greatly amplified when a specific interaction exists, such as in the PVAc/toluene system.

The diffusion of two probes is far more retarded in the PVAc/toluene solution, due to the hydrogen bonding interaction between the probe and the polymer backbone[5,6]. Also, the difference between the diffusion coefficient of p-MR and o-MR becomes much larger. This difference is attributed to the internal hydrogen bonding of carboxyl hydrogen with nitrogen in the azo moiety in o-MR, which in turn leads to weak intermolecular interaction between o-MR and the PVAc backbone relative to p-MR[6]. From *Table 1* and *Figure 1*, we find not only the diffusion coefficient itself, but E_A of p-MR diffusion is also distinctly larger than that of o-MR compared to the case of pure toluene or PS/toluene systems. In comparison with the PS/toluene solution at the same polymer volume fraction, o-MR and p-MR in PVAc/toluene solution exhibit additional activation energies of 3.6 and 5.6 kJ mol^{-1}, respectively, due to the hydrogen bonding interaction. This is considerably larger than the effect of adding 10% PS to the pure solvent, which increases E_A by 1.7 and 2.5 kJ mol^{-1} for o-MR and p-MR, respectively. Considering that the strength of a typical hydrogen bond is of the order of 10 kJ mol^{-1}, this value for the additional activation energy barrier appears reasonable. The smaller E_A for o-MR relative to p-MR is also consistent with the view that the hydrogen bonding interaction of o-MR with PVAc is weaker than that of p-MR due to internal hydrogen bonding.

We have shown previously that equation (1) apparently describes the concentration dependence of the probe diffusion in a system with hydrogen bonding interaction between diffusant and polymer[6]. However, the result is no more than an experimental observation, which lacks theoretical justification at present. It is well known that equation (1) can fit many different types of relaxation behaviour. More theoretical effort is called for to explain this observation.

Nonetheless, probe diffusion in semidilute polymer solution clearly follows Arrhenius behaviour and the effect of hydrogen bonding interaction is reflected in the activation energy of diffusion. Therefore we are now studying the polymer concentration dependence of the activation energy in a system with hydrogen bonding interaction, which should provide important information for understanding the concentration dependence of probe diffusion in a polymer matrix with specific interaction.

Acknowledgements

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