Notes

Reassessment of Khazanovich's Theory of Thermal Diffusion of Polymers in Solution

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Introduction

Despite the existence of several effective theories that describe the common transport properties of polymers in solution, the thermal diffusion coefficient (D_T) of solvated polymers is poorly understood. Some of the difficulty in understanding thermal diffusion coefficients has been related to the difficulty in accurately measuring D_T. With the advent of thermal field flow fractionation (ThFFF)[1] in the 1960s, a convenient method was established by which D_T could be measured. In several papers, Giddings and co-workers combined ThFFF with estimates or measurements of the ordinary diffusion coefficient (Fickian) of polymers in solution to obtain thermal diffusion coefficients.[2-5] Giddings and co-workers have made an attempt to understand the observed D_T using existent theories, but the general outcome of their work was that none of the theories tested was adequate to explain the date.

In this note we consider Giddings' data and apply Khazanovich's theory[6] for the thermal diffusion of polymers in solution, and we show that this theory is consistent with existing D_T data.

Theory

Several basic properties of the thermal diffusion coefficients of polymers in solutions have slowly become apparent. Experiments indicate that thermal diffusion coefficients of polymers in solution (1) are not dependent on molecular weight of the polymer and (2) vary with solvent and with polymer; (3) branched and linear polymers seem to have the same D_T. Points 1 and 3 strongly distinguish the behavior of thermal diffusion coefficients from that of simple Fickian diffusion coefficients.

In 1967, Khazanovich[6] proposed a model for the thermal diffusion coefficient of highly dilute polymer solutions that satisfies the conditions in the above paragraph. Using a free-draining flexible polymer model, Khazanovich calculated that the thermal diffusion coefficient is proportional to the Fickian diffusion constant of the "bead" or monomer segment that makes up the model "pearl necklace" chain. Khazanovich found

$$D_T = D_b F / R_g T^2 \tag{1}$$

where F is the bead friction coefficient activation energy (which according to Stokes law is equal to that for the solvent viscosity), R_g is the gas law constant, T is the temperature in kelvin, and D_b is the average Fickian diffusion coefficient for a bead on the chain. Khazanovich pointed out that, using existent thermal diffusion coefficient data for polystyrene in toluene, his equation combined with the Stokes–Einstein equation gave a reasonable polystyrene bead, or segment, hydrodynamic radius of 0.45 nm. At that time, limited data were available for the D_T of polymers in solutions so Khazanovich was unable to further test his theory.

To restate Khazanovich's results for D_T we (1) assign F in eq 1 to be equal to the activation energy for the solvent viscosity and (2) assume that the Stokes–Einstein equation describes the Fickian diffusion of the bead in the pearl necklace model. Under those assumptions we find that the thermal diffusion coefficient is given by

$$D_T = \frac{kT}{6\pi\eta R_b} \frac{F}{R_g T^2} \tag{2a}$$

$$D_T = F / 6\pi\eta N_a R_b T \tag{2b}$$

where k is the Boltzmann constant, η is the solvent viscosity at the temperature T, N_a is Avogadro's number, and R_b is the hydrodynamic radius of the average bead in the polymer chain.

Equation 2b explicitly shows that Khazanovich's original theory of the thermal diffusion of polymers in solution depends on the nature of the solvent (through F and η) and the nature of the monomer making up the polymer (R_b). Schimpf and Giddings[5] recognized these features of Khazanovich's theory but felt that the theory could not be fully tested without data on the self-diffusion coefficients and the viscosity of the monomers that make up the subject polymers. In our following analysis of literature data we will see that reasonable progress can be made in testing Khazanovich's theory without such data.

Results

Equation 2b requires values for both the solvent viscosity and the activation energy for the solvent viscosity. In this work, we describe the temperature dependence of the viscosity of these solvents using fit parameters from the DIPPR database at the Pennsylvania State University. The DIPPR database represents the viscosity data with the equation

$$\eta = \exp(A + B/T + C \times \ln(T) + DT^E) \tag{3}$$

where the parameters A, B, C, D, and E are constants. The activation energy for the solvent viscosity is given by

$$F = -R_g T^2 \frac{\mathrm{d} \log \eta}{\mathrm{d}T} \tag{4}$$

which when substituted into eq 3 gives

$$F = (R_g/2.303)(B - CT - DET^{E+1}) \tag{5}$$

The DIPPR parameters used to calculate F are given in Table 1.

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Table 1. DIPPR Viscosity Parameters for Various Solvents

solvent	*A*	*B*	*C*	*D*	*E*
tetrahydrofuran	−10.321	900.92	−0.069128		
2-butanone	−0.8134	509.78	−1.5324		
ethyl acetate	14.354	−154.60	−3.7887		
toluene	−60.666	3148.6	7.4817	-5.7091×10^{-27}	10.0
ethylbenzene	−10.452	1048.4	−0.0715		
benzene	6.7636	336.41	−2.687		

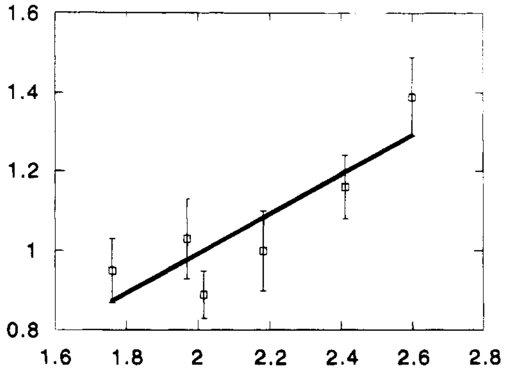

Figure 1. Test of eq 2b using thermal diffusion coefficient data for polystyrene in six different solvents at 298 K.

One of the largest collections of D_T data available is found in Schimpf and Giddings work.[5] In that reference, the thermal diffusion of polystyrene (PS) in seven different solvents is given. We will not consider the data from that reference for the cyclohexane/PS system, because that system was run with a ThFFF cold wall temperature that was approximately 10 K below the known Θ point for that polymer/solvent system, and it is possible that some adsorption of the polymer to the ThFFF channel wall may have occurred (thereby causing a systematic error in the D_T observed).

Figure 1 shows a test of eq 2b using that polystyrene data. In Figure 1, the intercept of the line is set to zero and the slope gives the reciprocal of R_b. The R_b found for this system is 0.201 nm. The scatter about the line may seem large, but when we compare the predicted D_T to the observed D_T, we find that all predicted D_T fall within 10% of the observed D_T. This scatter is only slightly larger than twice the standard deviation the experimenters estimated for their D_T values.

Table 2 shows a comparison of predicted D_T versus observed D_T for all the polymer/solvent systems in ref 5. The results in Table 2 indicate that eq 2b roughly fits the remainder of the available thermal diffusion coefficient data. There are some points where the differences between predicted and observed thermal diffusion coefficients are larger than the experimental error and these will be discussed later in this note.

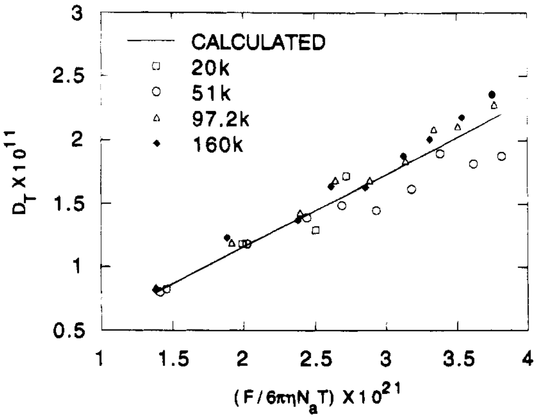

Figure 2. Test of eq 2b using the thermal diffusion coefficient data for polystyrene in ethylbenzene at temperatures from 273 to 437 K.

One further test of eq 2b is to consider the temperature dependence of thermal diffusion coefficients. From the assumptions that were made in modifying Khazanovich's theory, it is apparent that the bead radius is a "hard radius". If that assumption is correct, this bead radius should not vary as the temperature of the system is changed. Reference 2 contains a detailed listing of the D_T of polystyrene in ethylbenzene over a wide range of temperatures and this provides a set of data to check the temperature dependence of the bead radius in eq 2b. Figure 2 shows a plot of the observed thermal diffusion coefficients from ref 2 versus $F/6\pi\eta N_a T$. We see that the data scatter around a straight line with a zero intercept. The inverse of the slope of this line is the bead radius for polystyrene in ethylbenzene. We see that over a wide range of temperatures (273−437 K) and a limited molecular weight range (20 000−160 000) the bead radius is effectively constant. The calculated bead radius from this plot is 0.173 nm, which is different from that estimated for PS in Figure 1, but this difference could easily be a result of the differences in how the two sets of experimenters estimate the Fickian diffusion coefficients for the polymer/solvent systems.

The reasonable agreement of eq 2b with the data for polystyrene in Figures 1 and 2 must be contrasted with the poorer agreement of eq 2b with the data shown in Table 2. It is obvious that errors in the assignment of the mutual diffusion coefficient for polymers considerably influence the values one determines for thermal diffusion coefficients. Literature data are scarce for the mutual diffusion of polymers other than polystyrene in various solvents, and this might explain the disagreement between the results from eq 2b and the observed constants for the non-polystyrene polymer systems.

Another possible source of the poorer agreement of this theory for D_T with the data in Table 2 is that the bead diffusion coefficient model used to derive eq 2b may

Table 2. Test of Khazanovich's Theory versus Literature D_T Data[a]

	PS[b]		pMMA[c]		pAMS[d]		PI[e]	
solvent	$D_{T\,obs}$	$D_{T\,calc}$	$D_{T\,obs}$	$D_{T\,calc}$	$D_{T\,obs}$	$D_{T\,calc}$	$D_{T\,obs}$	$D_{T\,calc}$
toluene	1.03	0.98	1.63	1.29	1.19	1.12	0.69	0.54
tetrahydrofuran	1.00	1.07	1.31	1.41	1.29	1.22	0.57	0.59
benzene	0.95	1.00	1.34	1.32	1.02	1.14	0.44	0.56
ethylbenzene	0.89	0.88						
ethyl acetate	1.16	1.20						
2-butanone	1.39	1.29	1.50	1.70				

[a] All D_T values are given as 1×10^{11} (M^2/K·s). [b] PS, polystyrene; R_b used, 0.201 nm. [c] pMMA, poly(methyl methacrylate); R_b used, 0.153 nm. [d] pAMS, poly(α-methyl)styrene; R_b used, 0.176 nm. [e] PI, polyisoprene; R_b used, 0.362 nm.

need to be modified to allow for the thermodynamic nonideality of the solvent/solute pair. In the Onsager analysis[7] of the simple diffusion of one component of a binary system within that system, one finds that the mutual diffusion coefficient of the diffuser is directly proportional to a simple Stokes–Einstein-type argument multiplied by a thermodynamic nonideality factor for the system. That observation along with the fact that previous workers[3] have successfully used cohesive energy densities of the studied polymer/solvent pairs to improve empirical correlations of thermal diffusion coefficients may indicate that the simple model used here to derive the bead diffusion coefficient needs to beexpanded to allow for the effect of solvent quality on the diffusion coefficient of the polymer bead.

References and Notes

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