Diffusion of Polystyrene in a Theta Mixed Solvent (Benzene–2-Propanol) by Photon-Correlation Spectroscopy

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ABSTRACT: The diffusion coefficient D of polystyrene in a mixture of benzene and 2-propanol with benzene volume fraction $\phi = 0.64$ has been measured using photon-correlation spectroscopy. Measurements were made as a function of polymer concentration c (up to 10 mg/ml) and molecular weight M (between 3.3×10^4 and 2×10^6) at 25.0 and 25.5 °C. Conventional light-scattering studies with dialyzed solution have shown that $A_2 = 0$ at 25.5 °C, the true theta temperature, whereas use of undialyzed solution gives an apparent $A_2 = 0$ at 25.0 °C for $\phi = 0.64$. Although D was measured to 1 or 2%, no systematic difference was detected between the results at 25.0 and 25.5 °C. D varied linearly with c, $D = D_0 (1 + k_{\mathrm{D}}c)$, and D_0 varied as M^{-b} with $b = 0.497 \pm 0.006$; no deviation was found in the D_0–M relation corresponding to the nonlinearity which has been observed in the Stockmayer–Fixman plot for $[\eta]$. Further, according to theory relating k_{D} to A_2M, a difference in k_{D} at 25.0 and 25.5 °C should have been detectable, but none was found.

Solutions of polystyrene in the mixed solvent benzene–2-propanol have been studied at 25 °C by a number of workers. Elias and Etter[1] determined the theta composition of the solvent to have a benzene volume fraction $\phi = 0.64$ at 25 °C, where they found the second virial coefficient A_2 to be zero using conventional light-scattering techniques.

More recently Takashima et al.[2] have carried out a comprehensive light-scattering investigation of this system between 23 and 40 °C and determined that A_2 is zero at 25.5 °C for the solvent composition $\phi = 0.64$. They obtained the true values of A_2 and the polymer molecular weight M by using a solution which had been brought into dialysis equilibrium with the solvent rather than the original undialyzed solution which gives apparent values A_2^* and M^*. For this system, where the preferential adsorption coefficient λ' is large, they showed that the relation $A_2M = A_2^*M^*$ ceases to hold. Using thermodynamic arguments they derived a relationship between the true and apparent values and confirmed experimentally that a small finite difference exists.

The intrinsic viscosity $[\eta]$ of this system has also been investigated by Takashima et al.[2] for M between 2.5×10^5 and 2.9×10^6, and by Dondos and Benoit[3] for M between 6×10^4 and 5.3×10^5. The composite picture which emerges is that $[\eta]$ varies as M^a with $a = 0.59$ for M up to about 7×10^5 and $a = 0.5$ above. This nonlinearity in the Stockmayer–Fixman plot is attributed to the value of λ' increasing as M decreases; such behavior has been observed by Dondos and Benoit[4] in other binary theta solvents.

As a complementary study we have used photon-correlation spectroscopy[5] to measure the diffusion coefficient D of polystyrene in this mixed solvent at 25.0 and 25.5 °C. Measurements were made as a function of polymer concentration c up to 10 mg/ml for values of M between 3.3×10^4 and 2×10^6.

In general D_0 (D at infinite dilution) varies as M^{-b}, akin to the $[\eta]$ behavior, and the exponents a and b are connected by the relation $b = (a + 1)/3$.[6] We wished to enquire whether b is constant over this wide range of M, or mirrors the discontinuity in slope of the Stockmayer–Fixman plot, and also whether there is any detectable change in b between the true and apparent theta temperatures. In addition, current theories relating the slope of the D–c plots to A_2M can be tested.

Experimental Section

The polystyrene samples were obtained from the Pressure Chemical Co. and had values of $\overline{M}_{\mathrm{w}}$ from 3.3×10^4 to 2.05×10^6. The polydispersity index $\overline{M}_{\mathrm{w}}/\overline{M}_{\mathrm{n}}$ ranged from <1.06 for low $\overline{M}_{\mathrm{w}}$ to <1.20 for $\overline{M}_{\mathrm{w}} = 1.8 \times 10^6$; for $\overline{M}_{\mathrm{w}} = 2.05 \times 10^6$ the sample was even more polydisperse than the quoted value of 1.30. The sample with $\overline{M}_{\mathrm{w}} = 1.0 \times 10^6$ was kindly given by Professor J. M. G. Cowie of the University of Stirling. B. D. H. Chemicals Analar grade solvents were used in preparing the solutions, and dust was removed by either filtering through 0.2 μm Millipore filters or centrifuging at 35 000 g.

The optical cell containing the solution was housed in an enclosure which maintained the temperature constant to ±0.05 °C. A Coherent Radiation Model CR2 argon-ion laser operating at 488 nm was used as the light source, and the light scattered at 90° was detected by an ITT FW130 photomultiplier tube. The output pulses were fed into a 48-channel digital correlator (Malvern Instruments type K7023). A function of the form $A \exp(-B\tau) + C$ was fitted by computer to the correlation function $G(\tau)$ with A, B, and C as adjustable parameters. In general the fit was good, and the time dependent part of $G(\tau)$ was a single exponential. Thus a value of D, reproducible to a percent or so from run to run, was obtained from the parameter B ($=2DK^2$, where K is the scattering vector).

Results and Discussion

In a ternary system there are three independent diffusion coefficients each of which is associated with the diffusion of one of the components in the other two. However, the intensity of the light scattered by the polymer is usually much greater than that from the solvent diffusion and increases with $\overline{M}_{\mathrm{w}}$ as well as c. Thus as $\overline{M}_{\mathrm{w}}$ increases, the contribution of the solvent to the correlation function becomes vanishingly small. Moreover the diffusion coefficients of the solvent components are comparable with the mutual diffusion coefficient of the pure binary solvent, and this is typically much greater than D_0 for the polymer (which varies as $\overline{M}_{\mathrm{w}}^{-1/2}$). Therefore correlation functions with widely differing time scales would be required to measure the solvent and polymer diffusion coefficients, and this difference would be accentuated as $\overline{M}_{\mathrm{w}}$ increased. The effects of the solvent become apparent only in low $\overline{M}_{\mathrm{w}}$ solutions at low concentrations.

By way of illustration from our measurements, the intensity of the light scattered at 90° by a solution with $\overline{M}_{\mathrm{w}} = 6.7 \times 10^5$ and $c = 2$ mg/ml is over 20 times that from the pure binary solvent. The mutual diffusion coefficient was found to be approximately 10^{-5} cm^2 s^{-1} in comparison with a value of 1.59×10^{-7} cm^2 s^{-1} for D_0.

The variation of D with polymer concentration c at 25.5 °C is shown in Figure 1 for samples with $\overline{M}_{\mathrm{w}}$ from 1.11×10^5 to 2.05×10^6. For these dilute solutions D is seen to vary linearly with c:

$$D = D_0 (1 + k_{\mathrm{D}}c) \tag{1}$$

and the values of D_0 and k_{D} at 25.5 °C are listed in Table I. The values of D measured at 25.0 and 25.5 °C agree to a percent or two, and no systematic difference was detected.

The low $\overline{M}_{\mathrm{w}}$ solutions are weak scatterers, and the scattering from the diffusion of each of the solvent components in this ternary system can make a noticeable contribution to

Table I
Values of D_0, k_D, $\bar{v}_h$, and $-(k_D + \bar{v})/\bar{v}_h$ at 25.5 °C

$\overline{M}_w$	$D_0 \times 10^7$, cm^2 s^{-1}	$-k_D$, cm^3 g^{-1}	$\bar{v}_h$, cm^3 g^{-1}	$-(k_D + \bar{v})/\bar{v}_h$
3.3×10^4	8.2[a]			
1.11×10^5	4.14[a]	21.0[a]	12.6[a]	1.60[a]
1.8×10^5	3.367 ± 0.012	31.6 ± 1.2	15.0 ± 0.2	2.05 ± 0.10
3.92×10^5	2.266 ± 0.006	34.4 ± 0.6	22.6 ± 0.2	1.48 ± 0.04
6.7×10^5	1.751 ± 0.007	45.0 ± 1.0	28.6 ± 0.3	1.54 ± 0.05
8.6×10^5	1.512 ± 0.014	48.7 ± 2.6	34.6 ± 1.0	1.38 ± 0.11
1×10^6	1.411 ± .001	50.3 ± 0.8	36.6 ± 0.1	1.35 ± 0.02
1.8×10^6	1.065 ± 0.004	58.5 ± 1.0	47.3 ± 0.5	1.17 ± 0.03
2.05×10^6	0.942 ± 0.006	64.6 ± 1.7	51.1 ± 1.0[b]	1.24 ± 0.06[b]

[a] Extrapolated values. [b] Values corrected for polydispersity.

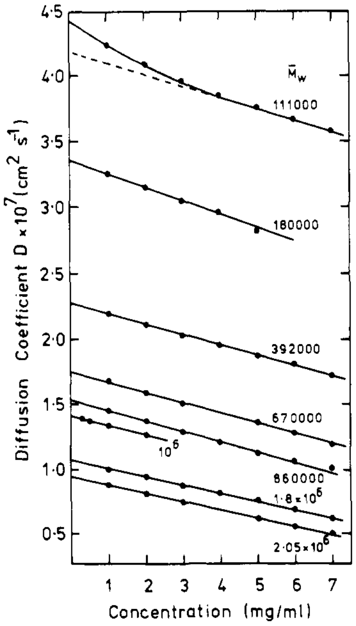

Figure 1. Variation of the diffusion coefficient at 25.5 °C with polymer concentration for samples with $\overline{M}_w$ between 1.11×10^5 and 2.05×10^6.

$G(\tau)$, particularly at low concentrations. The time-dependent part of $G(\tau)$ is no longer a single exponential, and the slight curvature at low c in the $\overline{M}_w = 1.11 \times 10^5$ plot is a result of force-fitting the three-parameter function to $G(\tau)$. However, an accurate value for D_0 can be obtained by extrapolating from the linear part of the curve at high c. The curvature of the $\overline{M}_w = 3.3 \times 10^4$ plot, which is not shown, is much more marked, and the value of D_0 obtained is an upper estimate. At the other extreme, the polydispersity of the nominal $\overline{M}_w = 2.05 \times 10^6$ sample results in uncertainty in D_0 since the time-dependent part of $G(\tau)$ is not a single exponential.

In Figure 2 log D_0 is plotted against log $\overline{M}_w$ for the results at 25.5 °C. The value of the slope and its uncertainty have been found by a least-squares-fit procedure and regression analysis to be -0.497 ± 0.006 when the less certain points at $\overline{M}_w = 3.3 \times 10^4$ and 2.05×10^6 are omitted, and this agrees well with the value of -0.5 expected at the theta point. However, the value of the slope at 25.0 °C is not different from that at 25.5 °C within the uncertainty, thus even accurate diffusion measurements cannot locate the theta temperature to better than 0.5 °C.

More significantly, the plot is linear over a wide range of $\overline{M}_w$ unlike the Stockmayer–Fixman plot of intrinsic viscosity, and the diffusion in a theta mixed solvent shows no departure from the behavior in a single theta solvent. It is interesting to note that in another study of a mixed-solvent theta system[7] where λ' is even greater (polystyrene in carbon tetrachloride and methanol) log D_0 was also found to vary linearly with log $\overline{M}_w$ although the Stockmayer–Fixman plot showed a discontinuity in slope[4] but in the opposite sense to that found in the benzene–2-propanol mixture.

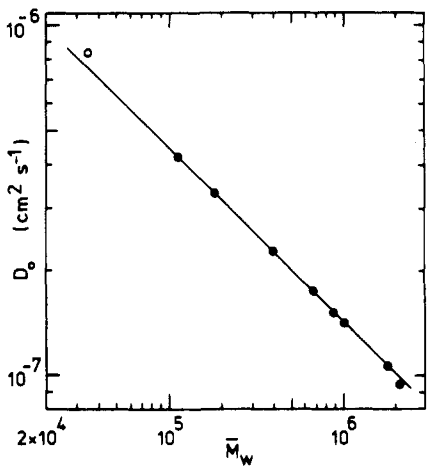

Figure 2. Variation of D_0 with $\overline{M}_w$ at 25.5 °C.

The dependence of D on c (eq 1) can also be expressed in terms of the friction coefficient f: $D = kT/f$ with $f = f_0(1 + k_f c + \ldots)$. The two concentration coefficients k_D and k_f are related[8] by the expression

$$k_D = 2A_2M - k_f - \bar{v}$$

where $\bar{v}$ is the partial specific volume of the polymer.

Using the random-flight model, Yamakawa[9] has obtained an expression for k_f in the nondraining limit:

$$k_f = \lambda A_2 M + \bar{v}_h \qquad (2)$$

where $\bar{v}_h$ is the specific hydrodynamic volume of the polymer, and λ is a parameter which has a limiting maximum value of 1.345 at the theta point and decreases gradually away from it.

Pyun and Fixman[10] have also derived expressions for k_f in the case of two models, for hard spheres and also for interpenetrable spheres of uniform density ("soft spheres"): $k_f = k_f^{\Phi}\bar{v}_h$, where k_f^{Φ} equals 7.16 for hard spheres and 2.23 for soft spheres at the theta point but increases to the hard-sphere value away from the unperturbed state.

Thus at the theta state, where $A_2 = 0$, the expressions for k_f reduce to

$k_f^{\theta} = \bar{v}_h$ (Yamakawa)
$k_f^{\theta} = 7.16\ \bar{v}_h$ (Pyun and Fixman hard sphere)
$k_f^{\theta} = 2.23\ \bar{v}_h$ (Pyun and Fixman soft sphere)

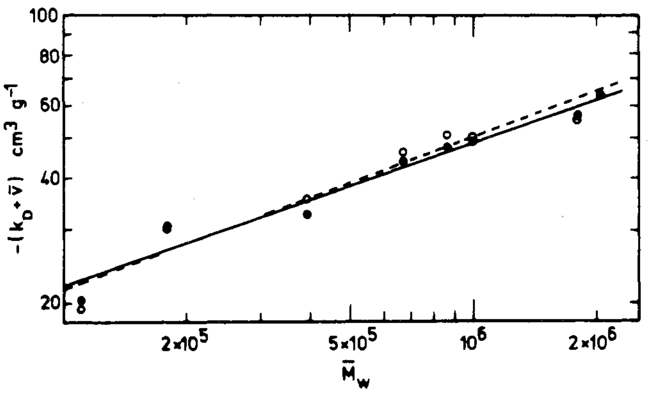

Figure 3. Variation of $-(k_D + \bar{v})$ with $\bar{M}_w$ at 25.0 °C (○) and 25.5 °C (●).

Another theory by Imai[11] gives the same expression for k_f^θ as Yamakawa's theory. All the theories predict that k_f^θ should be proportional to $\bar{v}_h$. In Table I we also list the values of $\bar{v}_h$ and $-(k_D + \bar{v})/\bar{v}_h$ ($=k_f^\theta/\bar{v}_h$) for different $\bar{M}_w$. The quotient of the latter term is seen to lie between 1.2 and 2, intermediate between the predictions of Yamakawa (and Imai) and the soft-sphere model of Pyun and Fixman.

Another way of displaying the results is to plot log ($-k_D - \bar{v}$) against log $\bar{M}_w$ as shown in Figure 3 for the data at 25.0 and 25.5 °C. The slope at 25.5 °C is 0.35 ± 0.04 and at 25.0 °C is 0.37 ± 0.05. These values are not in agreement with the theoretical prediction of 0.5. In the only reported work in a single solvent (cyclohexane) at the theta temperature, King et al.[12] obtained an index slightly less than 0.5 (0.48 ± 0.04). This is in closer agreement than our result with the theory, and it may be that the theory for k_D in a binary solvent requires more careful consideration.

No systematic change in k_D was detected on increasing the temperature from 25.0 to 25.5 °C, and indeed the values reproduce to a few percent. However, Takashima et al.[2] have shown that A_2M and $A_2^*M^*$ change by about 10 cm^3 g^{-1} over this temperature interval for high $\bar{M}_w$, and according to the theories for k_f this should produce a detectable change in k_D. For example in Yamakawa's theory (eq 2) the fractional change in $(k_D + \bar{v})$ for a change in temperature of 0.5 °C should be $8/\bar{v}_h$. For $\bar{M}_w = 10^6$, the fractional change is $8/35 \simeq 0.2$; such a change should be easily detectable but none was found.

This work, which forms part of a wider investigation on binary solvents, shows that it is now possible to obtain accurate values for D which can prove a sensitive test of current theories of polymer solutions.

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Frictional Coefficient and Its Concentration Dependence for Monodisperse Poly(α-methylstyrene) in Solution

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ABSTRACT: The sedimentation coefficient and its polymer concentration dependence for monodisperse poly(α-methylstyrenes) were measured in theta and nontheta solvents over a wide range of molecular weights. The expansion factor of the dimension of polymer coil estimated from the frictional coefficients agrees with the α^5-type theory of Flory. The polymer concentration dependence of the frictional coefficient in good solvents agrees with the theory of Pyun and Fixman at small excluded volumes but deviates from the theory at large excluded volumes. It is suggested that the variation of the concentration dependence of frictional coefficient with excluded volume may be similar to that of the second virial coefficient.

It is no doubt important to study the hydrodynamic interaction between two polymer coils in solution as well as the hydrodynamic properties of a polymer coil at infinite dilution. Many theoretical[1] and experimental works[2] have so far been carried out not only on intrinsic viscosity but also on concentration dependence of specific viscosity of linear polymers. However, less attention has been paid to the concentration dependence of the translational frictional coefficient of linear polymers. To study the hydrodynamic properties of linear polymers, it may be more desirable to measure the translational frictional coefficient rather than the intrinsic viscosity, since more rigorous theories have been presented for the translational frictional coefficient and its concentration dependence.[1,3]

In order to examine the existing theories without ambiguity, it is also important to obtain experimental data on translational frictional coefficient of linear polymers together with the data on their thermodynamic properties. Although several experimental studies of the frictional coefficient and its concentration dependence for linear polymers have been carried