

Pulsed Field Gradient NMR Directly Determined Polymer Self Diffusion Coefficients Compared with Those Derived from Sedimentation or Mutual Diffusion

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ABSTRACT: We show that self-diffusion coefficients derived indirectly from sedimentation or mutual diffusion do not agree with those obtained directly with PFGNMR. We believe that indirect determinations are not valid for random coils at finite concentrations. However the different physical factors governing self-diffusion and sedimentation can be exploited to obtain information on the static and dynamic critical exponents for polymers in semi-dilute solution. We show that such an analysis leads to an anomalously high static index for 110 000 M polystyrene in toluene.

INTRODUCTION

An indirect self-diffusion coefficient D_s^+ may be calculated from a knowledge of the mutual diffusion coefficient or the sedimentation coefficient according to

$$D_s^+ = D_m (1-\bar{v}c)^{-1} (1+2A_2 Mc + \dots)^{-1} \quad (1)$$

$$D_s^+ = s N_{Av} M^{-1} k_B T (1-\bar{v}\rho)^{-1} \quad (2)$$

ROOTS et al (1979) have demonstrated the internal consistency of these equations over a wide concentration range for random coil polystyrene (110 000 M) dissolved in toluene. However D_s^+ is a derived quantity and is not necessarily identical to the directly measured self-diffusion coefficient, D_s . Self-diffusion occurs under conditions of thermodynamic equilibrium by virtue of thermally driven random processes. The mechanisms governing mutual diffusion and sedimentation are not the same as those governing self-diffusion. This distinction is revealed in the different theoretical approaches to sedimentation and self-diffusion in the entangled regime. Sedimentation for entangled random coil polymer is viewed in terms of the motion of solvent through an essentially fixed network of interlocked coils akin to motion through a porous plug. We can use the scaling theory (BROCHARD and DE GENNES 1977) for sedimentation to obtain an entangled regime scaling law for D_s^+ , namely

$$s \sim c^{(\nu-1)/(3\nu-1)}$$

$$\therefore D_s^+ \sim c^{(\nu-1)/(3\nu-1)} \quad (3)$$

with very little error since $(1-\bar{v}\rho)$ is concentration insensitive. Using the Flory index, $\nu=0.6$, one obtains

$$D_s^+ \sim c^{-0.5}$$

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This contrasts markedly with the established scaling law (DE GENNES, 1976) for self diffusion

$$D_S \sim c^{(2-\nu)/(1-3\nu)} \quad (4)$$

with exponent approximately -1.75 . (HERVET et al, 1979; CALLAGHAN and PINDER, 1980). The discrepancy is not surprising since by contrast with the sedimentation model self-diffusion in the entangled regime concerns the relative motion of coils in a network regarded inherently as transient.

RESULTS AND DISCUSSION

D values have been obtained for 110 000 M polystyrene in deuterio-toluene at 25.0°C using PFGNMR. (Comparisons between diffusion rates in deuterio-benzene and benzene suggest that solvent deuteration has little effect on D_S for the polymer (CALLAGHAN and PINDER, 1981)). Figure 1 shows an echo attenuation plot for 110 000 M polystyrene in deuterio-toluene at 25.0°C . All data obeyed the Stejskal-Tanner relation for echo attenuation under the pulsed field gradient.

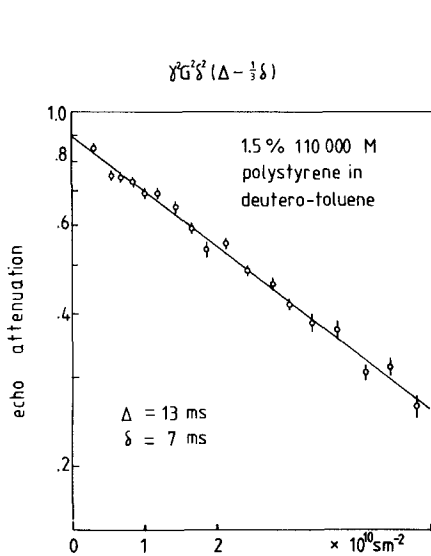


Figure 1: Spin echo attenuation plot for 110 000 M polystyrene in deuterio-toluene (1.5% w/v)

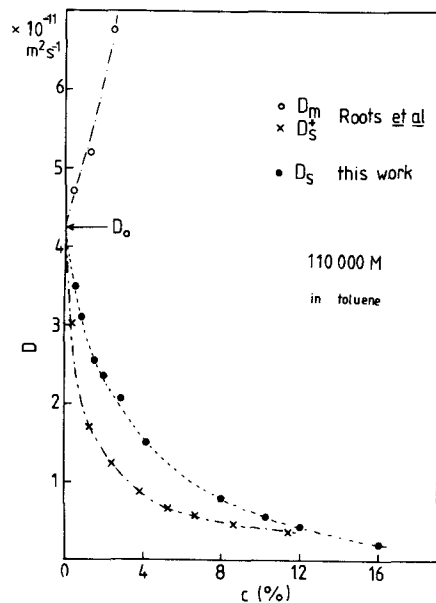


Figure 2: Directly measured (D_S) and indirect (D_S^+) self-diffusion coefficients for 110 000 M polystyrene in toluene at 25.0°C . Also shown are the mutual diffusion co-efficients (D_m) of ROOTS et al.

Figure 2 shows the measured self diffusion coefficients values at various concentrations along with the D_S^+ values of Roots et al for 110 000 M polystyrene in toluene at 25.0°C . These latter data were derived from both sedimentation and mutual diffusion measurements. The D_S and D_S^+

data converge as $c \rightarrow 0$ and yield the same D_0 value but elsewhere $D_S \neq D_S^+$. At low concentrations the discrepancy can be viewed in terms of a difference in the frictional coefficients, k_f , where

$$D_S^{-1} = D_0^{-1} (1 + k_f c) \quad (5)$$

The Roots et al data yield $k_f^+ = 96$ whereas our data gives $k_f = 43 \pm 3 \text{ (gm \%)}^{-1}$. Our lower value is in good agreement with a value of the frictional coefficient for 75 000 M polymer in toluene reported by CANTOW et al (1965) although the YAMAKAWA theory (1962) predicts a higher value similar to that obtained by ROOTS et al. However added weight is given to the directly measured D_S values by the behaviour of the data at higher concentrations. In figure 2 the data is plotted as $\log D_S$ vs $\log c$. The D_S data scale as predicted by the de Gennes model for reptation in a transient network whereas the D_S^+ data, while scaling with concentration, fail to exhibit the correct scaling index

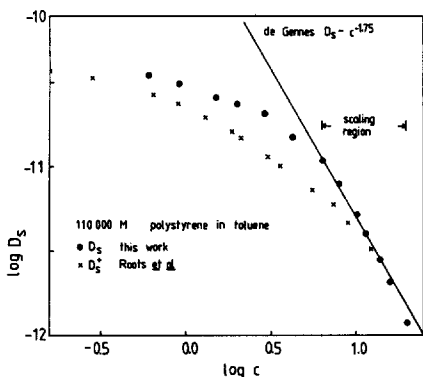


Figure 3: $\log D_S$ vs $\log c$ and $\log D_S^+$ vs $\log c$. The D_S data exhibit the correct scaling index for reptation. The D_S^+ data do not.

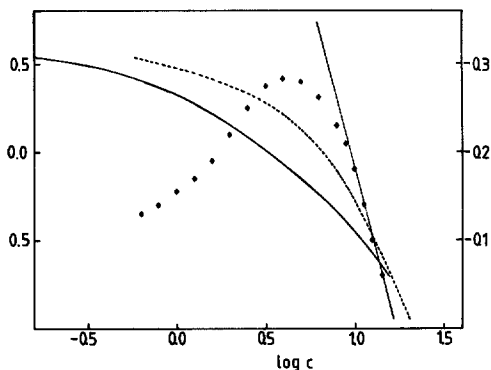


Figure 4: $\log D_S$ (dashed line), s (solid line) and D_S/s (data points) obtained from figure 3 by interpolation. D_S/s scales according to equation 9.

Comparisons between s and D_S can be used to investigate the suggestion by WEILL and DES CLOIZEAUX (1979) that the index ν should be replaced by the one of two other indices defined as

$$\begin{aligned} \nu_G &= \partial \ln R_G / \partial \ln N \\ \nu_D &= \partial \ln R_D / \partial \ln N \end{aligned} \quad (6)$$

where R_G is a static radius, R_D a dynamic radius and N the polymerization index. The indices ν_G and ν_D approach the asymptotic value (0.588) only as $N \rightarrow \infty$ but ν_G approaches the asymptotic value far more rapidly than does ν_D . Indeed for polystyrene of 233 000 molar mass in the semi-dilute regime ν_G is predicted to take a value close to 0.6 and ν_D a value close to 0.5 (CALLAGHAN and PINDER, 1981).

Callaghan and Pinder have applied the Weill-des Cloizeaux model to self-diffusion in the semi-dilute regime and have shown that

$$D_s \sim c^{(2-\nu_D)/(1-3\nu_G)} \quad (7)$$

Taking ν_D as 0.5 and ν_G as 0.6 they showed $D_s \sim c^{-1.87}$ in good agreement with experiment ($D_s \sim c^{-1.83(4)}$). POUYET et al (1980) have applied the Weill-des Cloizeaux model to sedimentation and have shown that

$$s \sim c^{(1-\nu_D)/(1-3\nu_G)} \quad (8)$$

Using equations 7 and 8 it is clear that

$$D_s/s \sim c^{1/(1-3\nu_G)} \quad (9)$$

and so the index ν_G may be obtained from the measurements of D_s and s .

The only polymer-solvent system investigated by both sedimentation and self-diffusion is polystyrene of 110 000 daltons molar mass in toluene. Figure 4 shows the logarithmic variation of D_s, s and D_s/s with the logarithm of polymer concentration. Smooth curves have been drawn through the s and D_s data to allow interpolation and hence D_s/s values. These data predict a value of ν_G a little greater than 0.7. This value is unexpectedly high for the Weill-des Cloizeaux model but it does lend some credence to the notion that ν_G should be afforded a value higher than ν_D and certainly higher than 0.5. Indeed FRANCOIS et al (1980) have recently published a modified theory which predicts that ν_G may assume values approaching 0.7 over a small molar mass range so the data of figure 3 can be considered as a verification of this effect.

However, caution must be exercised in the interpretation of this data for the 110 000 molar mass polystyrene used in this study is not particularly appropriate. It displays only very small concentration scaling regions for both sedimentation and self-diffusion and moreover, these scaling regions are not identical since s appears to scale at lower concentrations than does D_s . A better comparison could be effected if both sedimentation and self-diffusion measurements were available for a higher molar mass polymer.

CONCLUSIONS

The physical nature of self-diffusion and sedimentation (or mutual diffusion) for random coil polymers in solution is such as to render invalid the inherent assumptions in the D_s^+ equations. These equations are valid only in the limit as $c \rightarrow 0$ which suggests that entanglement effects may well play a significant part in determining D_s values even in the dilute regime. D_s values must be obtained by a technique which measures from first principles, the mean square displacements of molecules in random motion under conditions of thermodynamic equilibrium.

The comparison of s and D_s values for 110 000 M polystyrene in toluene has yielded a value for the static scaling index, ν_G . This value would seem to be in agreement with the recent model of FRANCOIS et al which predicts that ν_G can exceed the asymptotic limit of 0.6 for certain molar masses. However the restricted nature of the available data indicates that measurements on a higher molar mass polymer should be compared before firm conclusions may be drawn.

REFERENCES

- BROCHARD, F. and DE GENNES, P.G.: *Macromolecules* 10, 1157 (1977)
CALLAGHAN, P.T. and PINDER, D.N.: *Macromolecules* 13, 1085 (1980)
CALLAGHAN, P.T. and PINDER, D.N.: *Macromolecules*, to be published (1981)
CANTOW, M.J.R., PORTER, R.W. and JOHNSON, J.F.: *Polymer Preprints* 6, 338 (1965)
DE GENNES, P.G.: *Macromolecules* 9, 596 (1976)
FRANCOIS, J., SCHWARTZ, T. and WEILL G.: *Macromolecules* 13, 561 (1980)
HERVET, H., LEGER, C. and RONDELEZ, F.: *Phys. Rev. Lett.* 42, 1681 (1979)
POUYET, G., FRANCOIS, J., DAYANTIS, J. and WEILL, G.: *Macromolecules* 13 176 (1980)
ROOTS, J., NYSTROM, B., SUNDELOF, L.O. and PORSCHE, B.: *Polymer* 20, 377 (1979)
WEILL, G. and DES CLOIZEAUX, J.: *J des Phys.* 40, 99 (1979)
YAMAKAWA, H: *J. Chem. Phys.* 36, 2995 (1962)

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