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Coil Dimensions in the Powerful Cosolvent System Poly(methyl methacrylate)/Acetonitrile + Chlorobutane

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ABSTRACT: Limiting viscosity numbers ([η]) and Schulz-Blaschke constants (k_S) have been determined in the title system at 25 °C as a function of solvent mixture composition for PMMA samples differing in molecular weight. [η] shows a very pronounced maximum at intermediate compositions. k_S attains very large values ($k_S > 1$) in the component solvents, indicating a tendency to association. In the mixtures, k_S reduces to ~0.3, typical of unassociated swollen coils in good solvents. The unperturbed dimensions in the component solvents are higher than those corresponding to atactic PMMA. The samples studied are predominantly heterotactic, and for this microstructure, higher values of the unperturbed dimensions are theoretically predicted by rotational isomeric state calculations. In the cosolvent mixtures the unperturbed dimensions are higher than in the component solvents, as they correspond to a mixed solvent having $G^E \gg 0$, but the increase in unperturbed dimensions is only moderate ($\Delta K_\Theta \lesssim 15\%$). In each of the component solvents the macromolecular coils are in a contracted state ($\alpha_\eta < 1$). In the cosolvent mixtures they become highly expanded and attain values of α_η similar to those in good solvents. When the cosolvents are mixed, the coil configuration undergoes a contracted-highly expanded-contracted transition, without a change in temperature. The variation of the interaction parameter B with solvent composition is compared with previous results of second virial coefficients.

Introduction

Many studies can be found in the literature about coil dimensions of synthetic polymers in mixed solvents. Most of these studies involve liquid mixtures composed of a good and a poor solvent of the polymer. In such systems, the size of the macromolecular coils grows as the proportion of the good solvent increases in the mixture, as a consequence of excluded volume effects. The action of mixed solvents has been reported to change dimensions, not only because of excluded volume expansion but also because the interactions between liquids modify the unperturbed dimensions of the coil.[1,2]

Fewer studies exist on the dimensions of coils in mixtures of two liquids which are poor solvents or nonsolvents of the polymer. If the mixture is a cosolvent, expansion of the coil takes place in spite of the negative excluded volume of the individual components. The interactions between the two liquids are, then, a decisive factor in promoting such coil expansion. The cosolvent system in which the dependence of coil dimensions on solvent mixture composition has been studied in most detail is that formed by polystyrene in acetone + cyclohexane[3-5] (+methylcyclohexane[6]). The combination cyclohexane + alcohols also gives cosolvent mixtures for polystyrene in which dimensions have been studied.[7]

For the polymer poly(methyl methacrylate) (PMMA), a whole series of cosolvents has been reported recently.[8-11] Several of these cosolvents are formed by mixing acetonitrile with other liquids. The purpose of the present paper is to report on the variation of coil dimensions as a function of solvent composition in one of those cosolvents, namely, acetonitrile (MeCN) + 1-chlorobutane (ClBu). The system PMMA/MeCN + ClBu has the practical advantage that the Θ temperatures of the component solvents are only slightly above room temperature so that the entire range of solvent compositions can be easily covered at 25 °C without risking phase separation. This system has been characterized previously by studying the depression of its critical temperature of phase separation (UCST) caused by cosolvency[8,11] and the solvation (total and preferential) of the macromolecule in the cosolvent mixture.[12]

As has been shown, the MeCN + ClBu mixture is very powerful in promoting polymer solubility[8,11] and coil solvation[12] (it is a powerful cosolvent). We shall show here that it is also very effective in expanding the macromolecular coils and in breaking the association of PMMA. That PMMA tends to form associated structures in solutions has been detected by a variety of experimental techniques, for example, viscometry, light scattering, NMR, and cloud point measurements.[13-15] In a previous study of PMMA in cosolvent mixtures it was suggested that the associating tendency of this polymer may be diminished by the use of mixed solvents which act synergically to solvate the polymer chains.[8,9]

The property which we study here is solution viscosity, η, at 25 °C for several samples of PMMA differing in molecular weight, M. From the [η]-M dependence ([η] = limiting viscosity number) we obtain unperturbed dimensions and the expansion factor, α_η, as a function of cosolvent composition. We also determine Schulz-Blaschke constants, k_S, to study the influence of cosolvency on the tendency of the polymer to aggregate in dilute solution. Preliminary results of this work were the subject of a recent communication.[16] Coil dimensions of PMMA in a cosolvent mixture have been published previously only for the system PMMA/CCl_4 + MeOH,[17,18] which is a weaker cosolvent than the one reported here.

Experimental Section

Polymer. The samples studied are monodisperse Monopol standards supplied by Dr. T. G. Croucher of Polymer Laboratories Ltd. (Shrewsbury, England). They were obtained by the method of Löhr and Schulz[19] in THF at -78 °C, using cumylcesium as initiator. Their polydispersity, determined by the supplier from GPC data, is $M_w/M_n \lesssim 1.1$ for all samples. The tacticity of these polymers has been determined by NMR[20-22] and is given in Table I, expressed as percent triads.

Absolute values of the molecular weights of the samples have been determined by light scattering, using a Model 42000 Fica instrument. The measurements were carried out in ethyl acetate at 25 °C in the concentration range $c = (1-11) \times 10^{-3}$ g·cm^{-3}. Solutions were clarified by filtration through 0.2-μm Millipore Teflon membranes. The optical constant, determined by measuring dn/dc with a Model 2000V Brice-Phoenix differential refractometer (dn/dc = 0.1163 cm^3·g^{-1}), is $K_{EtAc/PMMA} = 7.665 \times$

Table I
Molecular Weight and Tacticity of PMMA Samples

		tacticity, % triads		
sample	$M_w \times 10^{-3}$	iso-tactic	hetero-tactic	syndio-tactic
I	73.4	5	51	44
II	124.4	8	52	40
III	189	5	51	44
IV	232	4	52	44

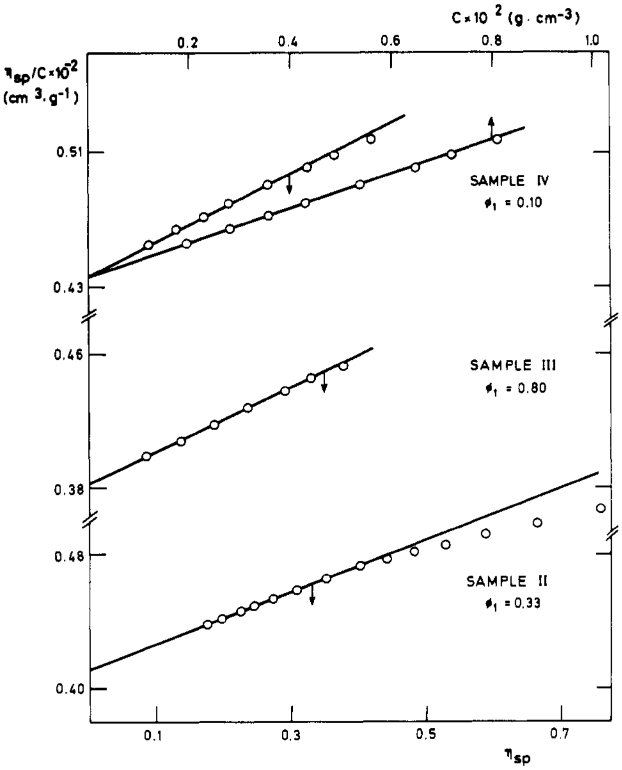

Figure 1. Schulz–Blaschke and Huggins extrapolations of viscosity data for samples of PMMA in acetonitrile + chlorobutane (ϕ_1 = acetonitrile volume fraction in the liquid mixture).

10^{-3} cm^6·g^{-2}. The molecular weights thus obtained are shown in Table I.

Solvents. MeCN and ClBu were Carlo Erba RPE, freshly distilled before use.

Viscometry. Viscosity at 25 °C was measured in a modified, previously calibrated Ubbelohde viscometer. Precision in efflux times was 0.1 s and temperature was maintained to ±0.05 °C.

MeCN + ClBu mixtures were prepared by weight. Polymer solutions were prepared by successive dilution of an initial solution whose PMMA concentration, c, never exceeded 2×10^{-2} g·cm^{-3}. In all cases solution viscosities were obtained by applying corrections for kinetic energy (always less than 3%) and density (always less than 1%).

Limiting viscosity numbers were determined by means of Schulz–Blaschke type extrapolations:

$$\eta_{sp}/c = [\eta] + k_S[\eta]\eta_{sp} \qquad (1)$$

The extrapolations of Huggins (η_{sp}/c vs. c) and Kraemer ($\ln \eta_r/c$ vs. c) were also tested, leading to slightly lower (0–2%) $[\eta]$ values. Several examples of extrapolating data are shown in Figure 1 as η_{sp}/c vs. η_{sp} and η_{sp}/c vs. c.

Results

The limiting viscosity numbers for the different molecular weights are shown in Figure 2 as function of solvent mixture composition, expressed by the volume fraction of MeCN in the mixed liquid, ϕ_1. As we can see, $[\eta]$ is much greater for the MeCN + ClBu mixture than for the component solvents. For example, for the highest molecular weight sample, the value of $[\eta]$ at ϕ_1 = 0.4 is 3 times the average value of $[\eta]$ in the component solvents. Such large effects in the viscosity of nonionic polymers in mixed solvents are unusual. The best documented example in which an increase of similar magnitude takes place is polystyrene/acetone + cyclohexane,[3-5] which is also a cosolvent system.

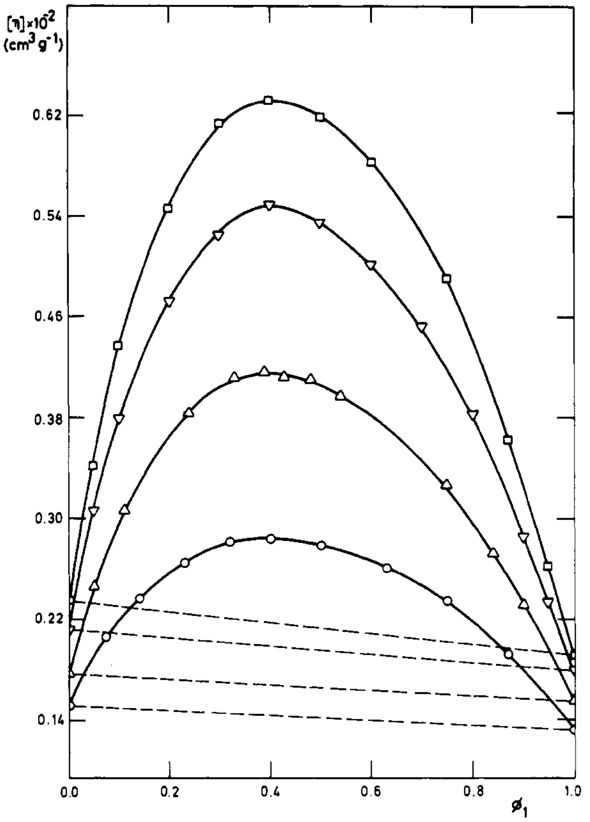

Figure 2. Limiting viscosity numbers of PMMA in acetonitrile + chlorobutane. Samples: (○) I; (△) II; (▽) III; (□) IV.

It should be pointed out that a maximum in $[\eta]$ as a function of liquid mixture composition is not an indication of the existence of cosolvency. The increase in $[\eta]$, and eventual appearance of a maximum, reveals that the mixture is a better solvent for the polymer than the pure solvents. But the mixture would not be termed a cosolvent unless both component liquids are nonsolvents of the polymer at the temperature of reference. The system PMMA/benzene + MeOH, for example, presents a maximum in $[\eta]$ at 25 °C,[23] but is it not a cosolvent because, at that temperature, benzene is a good solvent of the polymer and dissolves it completely, no matter how high its molecular weight. On the other hand, the system PMMA/MeCN + ClBu at 25 °C presents a maximum in $[\eta]$ and is a cosolvent because the Θ temperatures of our PMMA samples in MeCN and in ClBu are both above 25 °C, as previous results on second virial coefficients indicate.[12]

The Schulz–Blaschke constant, k_S, also shows a dramatic variation with ϕ_1. The results are shown in Figure 3A. In the component solvents, k_S reaches very high values. The Huggins constant, k_H, is even higher than k_S.[24] For isolated coils in Θ solvents k_H is expected to take values between 0.5 and 0.7.[25] It has also been proposed that the Θ state corresponds to k_S = 0.447.[3] According to measurements of second virial coefficients,[12] Θ conditions in this system are attained at compositions close to the pure solvents, namely, $\phi_1 \simeq 0.04$ and ϕ_1 = 0.93. However, for ϕ_1 = 0 and ϕ_1 = 1, k_S (and k_H) takes values much higher than 0.7.

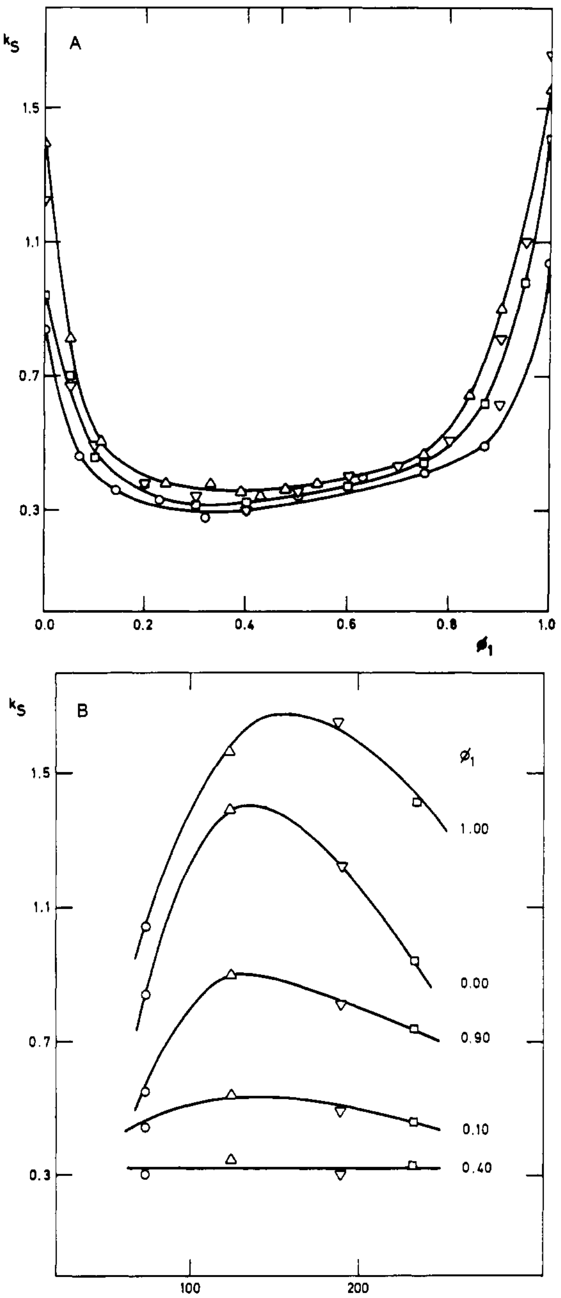

Figure 3. Schulz–Blaschke constants for PMMA in acetonitrile + chlorobutane. Samples and symbols as in Figure 2. (A) k_S as a function of solvent composition. (B) k_S as a function of molecular weight.

Such high values have been shown to indicate polymer aggregation or association.[26] For $\phi_1 \simeq 0$ and $\phi_1 \simeq 1$ the system at 25 °C is below its Θ temperature and incipient aggregation of the polymer may take place. However, no phase separation or precipitation is observed at the low concentrations used here. The solutions with $\phi_1 \simeq 0$ or $\phi_1 \simeq 1$ belong to region IV in the temperature–concentration diagram, as defined by Daoud and Jannink.[27] In this region the interactions between polymer segments are attractive but high dilution prevents phase separation.

As we see in Figure 3A, a small proportion of the cosolvent is sufficient to produce a very rapid decrease of k_S (and k_H). k_S finally reaches a plateau where it adopts the value $k_S \simeq 0.3$ ($k_H \simeq 0.4$), typically found for unassociated, swollen, flexible coils in good solvents. Therefore, k_S is another indication that the mixture MeCN + ClBu behaves as a good solvent of PMMA.

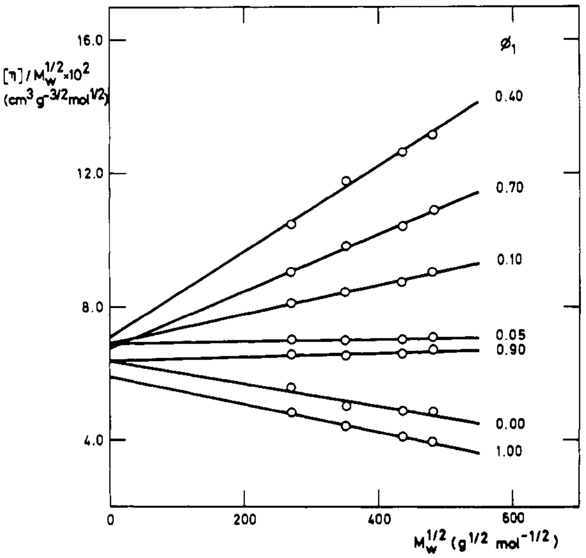

Figure 4. Data from Figure 2 represented according to a Stockmayer–Fixman type plot (eq 2).

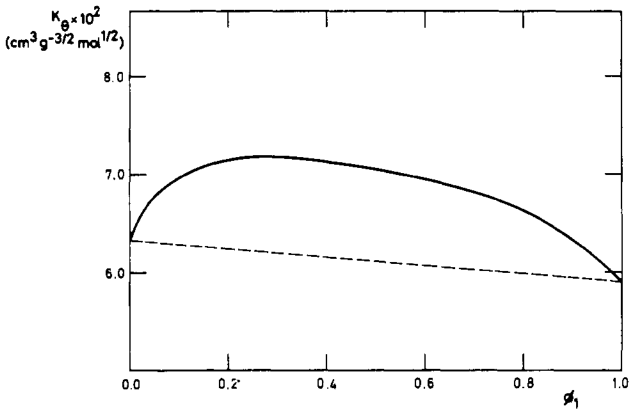

Figure 5. Unperturbed dimensions of PMMA in acetonitrile + chlorobutane, calculated as the intercept of the Stockmayer–Fixman type plots of Figure 4.

The molecular weight variation of k_S is shown on Figure 3B for several solvent compositions. In the component solvents, k_S passes through a maximum and drops for the higher M_w's. As the two liquids are mixed, the maximum in the k_S–M_w plot gradually fades away until a flat variation is reached for the best solvent composition.

Unperturbed Dimensions

We treat the $[\eta]$ results of Figure 2 according to the extrapolation procedure of Stockmayer and Fixman (SF) in order to obtain the unperturbed dimensions of the polymer, K_Θ:

$$[\eta]M_w^{-1/2} = K_\Theta + C'\Phi B M_w^{1/2} \qquad (2)$$

Here B is the interaction parameter, Φ is Flory's viscosity constant ($\Phi = 2.6 \times 10^{23}$ mol^{-1}),[28] and C' is a purely numerical factor (usually 0.51). A SF plot of $[\eta]M_w^{-1/2}$ vs. $M_w^{1/2}$ is shown in Figure 4 for several compositions of the liquid mixture (using the interpolating curves of Figure 2 when needed). We see that linearity is reasonably good in this plot. The values of K_Θ, calculated as intercepts in these SF plots, are given in Figure 5 as a function of ϕ_1.

A linearity even better than the one of the SF plot is obtained by plotting log $[\eta]$ vs. log M_w, according to the Mark–Houwink (MH) equation: $[\eta] = KM_w^a$. This MH plot is shown in Figure 6.

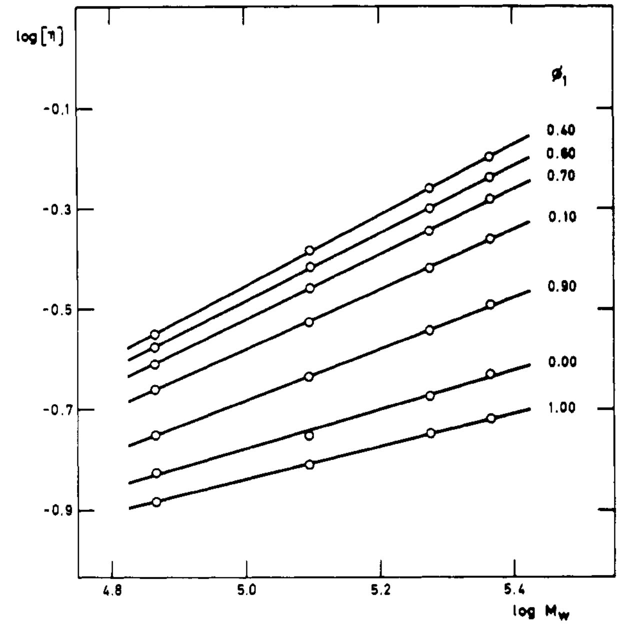

Figure 6. Data from Figure 2 represented according to a Mark–Houwink type plot.

The Θ points of the system, determined either from $a = 0.5$ in the MH plot or from $B = 0$ in the SF plot, are situated at $\phi_1 = 0.044$ and $\phi_1 = 0.912$. The values of K_Θ corresponding to these ϕ_1's are (in cm^3·g^{-1}) 6.83 × 10^{-2} and 6.35 × 10^{-2}, respectively.

The Θ compositions determined here from the $[\eta]$–M_w plot are practically the same as those defined by the vanishing of the second virial coefficient,[12] $\phi_1 \simeq 0.04$ and $\phi_1 = 0.93$, which were mentioned before. In principle, the intramolecular Θ points determined from coil dimensions and the intermolecular Θ points determined from second virial coefficients may not coincide because of the influence of preferential adsorption, λ. However, in the present system, the differences are very small and probably within the uncertainty of the data. The similitude of intra- and intermolecular Θ points is presumably due to the relatively small λ found in this system[12] and to the steep variation of total sorption near Θ dictated by strong cosolvency.

Let us now discuss the K_Θ results of Figure 5. We first consider the values of K_Θ corresponding to the component solvents and, later, the variation of K_Θ with ϕ_1 in the mixtures.

In MeCN alone, $K_\Theta = 5.91 \times 10^{-2}$ cm^3·g^{-1}, and in ClBu alone, $K_\Theta = 6.35 \times 10^{-2}$ cm^3·g^{-1}. These values are higher than the ones attributed to atactic PMMA. In a variety of solvents, including MeCN, K_Θ for atactic PMMA has been determined to be[29] 4.8 × 10^{-2} cm^3·g^{-1}, while in ClBu it has been found to be a little higher:[30,31] $K_\Theta = 5.3 \times 10^{-2}$ cm^3·g^{-1}. The differences between our K_Θ's and those in the literature for the atactic polymer are larger than experimental uncertainties and show that our PMMA adopts a stiffer or more open conformation than the random atactic one. The average tacticity of our samples, expressed as the fraction of meso diads, w_m, is 0.32, according to the data in Table I. This is to be compared with the value usually found in atactic polymers which is around 0.2.

According to rotational isomeric state theoretical calculations,[32,33] in the region of $w_m < 0.7$ the unperturbed dimensions increase with w_m. Therefore, a higher value of K_Θ is predicted for $w_m = 0.32$ than for $w_m = 0.2$ and our experimental results confirm this prediction. The detailed theoretical calculation of the characteristic ratio as a function of w_m shows[33] an increase of 15% on going from $w_m = 0.2$ to $w_m = 0.32$. The empirical results [(5.91–4.8) × 10^{-2} in MeCN and (6.35–5.3) × 10^{-2} in ClBu] correspond to an increase of 20–23%, slightly higher than the calculated one. We can say that the unperturbed dimensions determined here follow the trend expected theoretically according to the overall tacticity of the samples.

The unperturbed dimensions for isotactic PMMA chains are still higher than the ones determined here. For example, K_Θ(iso) = 7.5 × 10^{-2} cm^3·g^{-1} in MeCN[34,35] and K_Θ(iso) = 7.7 × 10^{-2} cm^3·g^{-1} in ClBu.[13] Our values are intermediate between those of the atactic and isotactic polymers.

As we have seen along the discussion, the value of K_Θ in ClBu is found to be slightly higher than in MeCN, for all tacticities. This is in accordance with expectations if we take into account the ordered liquid nature that MeCN has,[36] because K_Θ should be lower in liquids whose molecules present some kind of association than in molecularly disoriented liquids.[1] However, differences between solvents for a given tacticity are smaller than corresponding differences between tacticities.

Let us now discuss the variation of K_Θ with ϕ_1. We can see in Figure 5 that addition of small amounts of the cosolvent gives an increase in the unperturbed dimensions of the polymer. Over the entire range of compositions the unperturbed dimensions are higher than the volume fraction average $\phi_1 K_{\Theta_1} + \phi_2 K_{\Theta_2}$. The largest increment in K_Θ is reached in the range $\phi_1 \simeq 0.25$–0.60, where $\Delta K_\Theta \simeq 15\%$ (ΔK_Θ being defined by $[K_\Theta/(\phi_1 K_{\Theta_1} + \phi_2 K_{\Theta_2}) - 1] \times 100$).

To interpret variations of K_Θ with ϕ_1 in mixed solvents, it has been assumed that the unperturbed dimensions depend on the thermodynamic interactions between the two liquids.[2] In the case of a pair of liquids having positive G^E, the molecules of the two solvents repel each other and it is supposed[1] that their interactions tend to stiffen the chain, raising K_Θ.[1] Under this same assumption, it has been proposed[2] that ΔK_Θ should be proportional to G^E. This is a reasonable explanation for the increase in K_Θ obtained here by means of the SF plots because G^E of the MeCN + ClBu pair at 25 °C attains large positive values.[37] However, it has been argued[38] that the increase in unperturbed dimensions in mixed solvents may be only apparent because the concentration dependence of interaction parameters modifies the meaning of the intercept in the SF plots, adding an extra term B_2, such that the intercept should be equated to $(1 + B_2)K_\Theta$, instead of to K_Θ.[38]

In order to see how much the K_Θ values determined here depend on the extrapolation procedure followed to plot the $[\eta]$–M_w data, we have used also the recent method of Dondos and Benoit[39] (DB). This method has been proposed to improve linearity in the representation of $[\eta]$–M_w data over the conventional SF plot. The DB method is based on the expression

$$([\eta]M_w^{-1/2})^{-1} = A_1 - A_2(1 - DM_w^{1/2})M_w^{1/2} \tag{3}$$

where A_1 and A_2 are constants. A_1 is related to K_Θ through

$$A_1 = K_\Theta^{-1} - A' \tag{4}$$

A' being a measure of the molecular weight dependence of the coil segment density, ρ. It is obtained from[40]

$$[\eta]^{-1} - [\eta]_\Theta^{-1} = \Delta\rho_\infty - A'M_w^{-1/2} \tag{5}$$

D in eq 3 has been found empirically to be related, in a number of systems, to the MH exponent a by[39]

$$D = 0.0012(a - 0.5) \tag{6}$$

We have plotted $[\eta]^{-1} - (K_\Theta M_w^{1/2})^{-1}$ vs. $M_w^{-1/2}$ (using the K_Θ's of Figure 5) in order to calculate A', according to eq

5. Then we have plotted $M_w^{1/2}[\eta]^{-1}$ vs. $M_w^{1/2}(1 - DM_w^{1/2})$, with D calculated according to eq 6, using the a's of the MH plot. This $M_w^{1/2}[\eta]^{-1}$ vs. $M_w^{1/2}(1 - DM_w^{1/2})$ plot deviates too much from linearity and is not useful in the case of the poor solvents MeCN and ClBu. However, in their cosolvent mixtures which behave as good solvents, the plot is nicely linear and allows determination of A_1 by extrapolation, according to eq 3. The values thus obtained yield K_Θ's (using eq 4) which are slightly lower than the ones from the SF plot. For example, for $\phi_1 = 0.40$, $A_1 = 12.3$ g·cm^{-3}, $A' = 2.2$ g·cm^{-3}, and $K_\Theta = 6.90 \times 10^{-2}$ cm^3·g^{-1}. This K_Θ is 3% lower than the value calculated from the SF plot (Figure 5). This difference is very small and lends confidence to the correctness of the K_Θ's appearing in Figure 5.

We shall end our discussion of unperturbed dimensions by noting that in the other cosolvent of PMMA in which K_Θ has been determined (CCl_4 + MeOH), variations of the order of 100% in K_Θ have been reported.[18] This same system has been analyzed according to the DB method for one composition of the solvent mixture,[41] and the K_Θ obtained has been found to be noticeably higher than in single Θ solvents. Contrary to these cases, the largest ΔK_Θ found here is only of moderate magnitude ($\Delta K_\Theta \simeq 15\%$). Our results show that the interactions between the two liquids act overwhelmingly as an excluded volume potential and that they do not affect unperturbed dimensions in a dramatic way.

Excluded Volume

The values of the MH exponent a (calculated from the plot of Figure 5) show that the effect of excluded volume is very large in mixtures of intermediate ϕ_1's. This exponent reaches values around $a = 0.70$ (for $\phi_1 = 0.40$–0.45), which correspond to good-solvent behavior, although in the single liquids it is as low as 0.33 (MeCN) and 0.38 (ClBu). For comparison, the value of a determined in benzene (at 25 °C) for the same PMMA samples is 0.74.

The same conclusion regarding the large magnitude of the excluded volume present in the cosolvent mixtures is reached by looking at the coil expansion coefficient, α_η, calculated through

$$\alpha_\eta^3 = [\eta]/K_\Theta M_w^{1/2} \qquad (7)$$

The values of α_η thus calculated for sample IV are, for example, 0.87 (MeCN), 0.91 (ClBu), and 1.23 (MeCN + ClBu, $\phi_1 = 0.42$). We see that this powerful cosolvent system allows us to cover an extended range of α_η values (all at the same fixed temperature of 25 °C) by simply changing the composition of the liquid mixture. On going from $\phi_1 = 0$ to $\phi_1 = 1$ (or vice versa), the polymer coils experience a reversible isothermal transition: from a contracted conformation ($\alpha_\eta < 1$), to a highly expanded one ($\alpha_\eta > 1$), and back again to a contracted state. This transition is obtained by progressively *adding always the same liquid*: the cosolvent. In systems where the mixed solvent is composed of a good solvent and a precipitant no such transition is possible, even if $[\eta]$ presents a maximum. Only cosolvent systems, such as the present one, have two ϕ_1's at which $\alpha_\eta = 1$ (two isothermal Θ points).

The action of the cosolvent mixture in expanding the coil, initially in a contracted state in either component liquid, is similar to the action of temperature, T. On increasing T, in a poor pure solvent, the macromolecule also expands. The remarkable aspect of powerful cosolvents, such as the present one, is that the addition of cosolvent is a much more efficient way of improving solvent quality and expanding the coil than is increasing T.[42,43] A similar conclusion is reached regarding the tendency to association, as reflected in k_S. Mixing cosolvents is more effective in disrupting association tendency than is increasing T.[42,43]

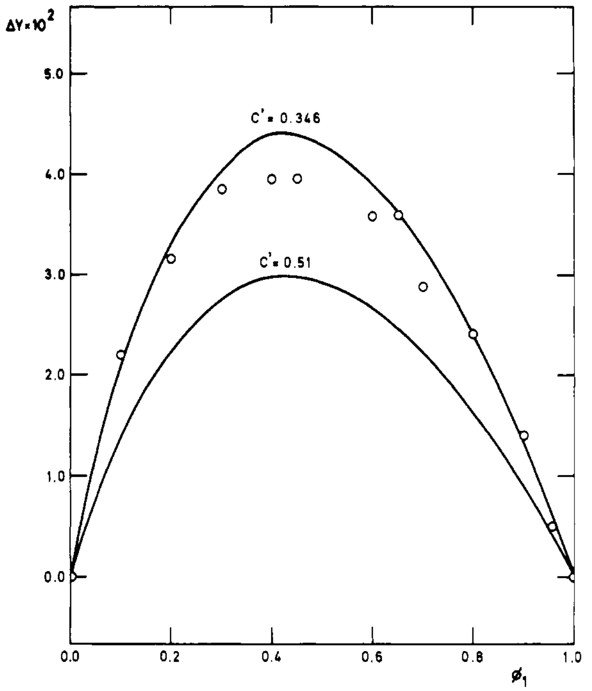

Figure 7. Total sorption function of PMMA in acetonitrile + chlorobutane: (—) calculated from viscosity data (eq 2, 8, and 9); (○) from second virial coefficients of ref 12.

The interaction parameter, B, can be used to calculate the total swelling function or total sorption potential, Y, and to compare it with the results of second virial coefficients previously determined.[12] For this comparison we first calculate ΔY from B as

$$\Delta Y = (V_1 N_A / 2\bar{v}_3^2)\Delta B \qquad (8)$$

where ΔB means "excess" value of B over the volume fraction average in the single liquids:

$$\Delta B = B - (\phi_1 B_1 + \phi_2 B_2) \qquad (9)$$

N_A is Avogadro's constant, V_1 solvent molar volume, and $\bar{v}_3$ polymer partial specific volume (we take $\bar{v}_3 = 0.81$ cm^3·g^{-1}).

The $[\eta]$–M extrapolations usually give correct values of unperturbed dimensions, but their estimates of B are not so satisfactory.[25] In eq 2, if the numerical coefficient C' is taken as 0.51, then the values of B are usually underestimated.[25] A coefficient $C' = 0.346$ was found empirically to be more satisfactory for many systems.[25] The results of ΔY obtained from ΔB using $C' = 0.51$ and $C' = 0.346$ are shown in Figure 7 as smooth curves. The points in this figure represent the experimental values from second virial coefficients.[12]

We see that, in fact, a coefficient of 0.51 underestimates the value of the sorption potential in this system also and that 0.346 gives a better estimate of ΔY. A value of C' intermediate between 0.51 and 0.346 only slightly higher than 0.346 would give close agreement between viscosity and second virial coefficient results. Both techniques are practically coincidental in the location of the maximum ΔY: $\phi_1 \simeq 0.42$ from viscosity and $\phi_1 \simeq 0.43$ from virial coefficients.

References and Notes

(1) Dondos, A.; Rempp, P.; Benoit, H. *J. Polym. Sci., Part C* **1970**, *30*, 9.
(2) Dondos, A.; Benoit, H. *Macromolecules* **1971**, *4*, 279.

(3) Deb, P. C.; Palit, S. R. *Makromol. Chem.* **1969**, *128*, 123.
(4) Deb, P. C.; Prasad, J.; Chatterjee, S. R. *Makromol. Chem.* **1977**, *178*, 1455.
(5) Maillols, H.; Bardet, L.; Gromb, S. *Eur. Polym. J.* **1978**, *14*, 1015.
(6) Palit, S. R.; Colombo, P.; Mark, H. F. *J. Polym. Sci.* **1951**, *6*, 295.
(7) Scornaux, J.; Leemput, R. V. *Makromol. Chem.* **1976**, *177*, 2721.
(8) Fernández-Piérola, I.; Horta, A. *IUPAC Symp. Macromolecules, Florence, Prepr.* **1980**, *3*, 47.
(9) Fernández-Piérola, I.; Horta, A. *Makromol. Chem.* **1981**, *182*, 1705.
(10) Fernández-Piérola, I.; Horta, A. *Polym. Bull.* **1980**, *3*, 273.
(11) Horta, A.; Fernández-Piérola, I. *Polymer* **1981**, *22*, 783.
(12) Horta, A.; Fernández-Piérola, I. *Macromolecules*, preceding paper in this issue.
(13) Schulz, G. V.; Wunderlich, W.; Kirste, R. *Makromol. Chem.* **1964**, *75*, 22.
(14) Spěváček, J.; Schneider, B. *Makromol. Chem.* **1975**, *176*, 3409.
(15) Suzuki, H.; Hiyoshi, T.; Inagaki, H. *J. Polym. Sci., Polym. Symp.* **1977**, *No. 61*, 291.
(16) Prolongo, M. G; Masegosa, R. M.; Hernández-Fuentes, I.; Horta, A. *IUPAC Symp. Macromolecules, Florence, Prepr.* **1980**, *3*, 51.
(17) Deb, P. C.; Palit, S. R. *Makromol. Chem.* **1973**, *166*, 227.
(18) Katime, I.; Tamarit, J.; Teijón, J. M. *An. Quim.* **1979**, *75*, 7.
(19) Löhr, G.; Schulz, G. V. *Eur. Polym. J.* **1974**, *10*, 121.
(20) Fernández-Piérola, I. Doctor Thesis, Universidad Complutense, Madrid, Spain, Feb 1981.
(21) Fernández-Martín, F.; Fernández-Piérola, I.; Horta, A. Sixth International Conference on Thermodynamics, Merseburg, Aug 26–29, 1980, Preprints, Paper No. 144.
(22) Fernández-Martín, F.; Fernández-Piérola, I.; Horta, A. *J. Polym. Sci., Polym. Phys. Ed.*, in press.
(23) Živný, A.; Pouchlý, J.; Šolc, K. *Collect. Czech. Chem. Commun.* **1967**, *32*, 2753.
(24) In the linear range of concentrations, k_S and k_H should be related through $k_H = k_S(1 + k_Hc[\eta])$. With our measurements $0 < k_Hc[\eta] < 0.3$, so that k_H is, at most, 30% larger than k_S.
(25) Yamakawa, H. "Modern Theory of Polymer Solutions", Harper and Row: New York, 1971.
(26) Elias, H. G. *Makromol. Chem.* **1966**, *99*, 291.
(27) Daoud, M.; Jannink, G. *J. Phys. (Paris)* **1976**, *37*, 973.
(28) Flory, P. J. "Statistical Mechanics of Chain Molecules"; Interscience: New York, 1969.
(29) Fox, T. G. *Polymer* **1962**, *3*, 111.
(30) Schulz, G. V.; Kirste, R. *Z. Phys. Chem. (Frankfurt am Main)* **1961**, *30*, 171.
(31) Inagaki, H.; Kawai, S. *Makromol. Chem.* **1964**, *79*, 42.
(32) Sundararajan, P. R; Flory, P. J. *J. Am. Chem. Soc.* **1974**, *96*, 5025.
(33) Saiz, E.; unpublished results.
(34) Krause, S.; Cohn-Ginsberg, E. *J. Phys. Chem.* **1963**, *67*, 1479.
(35) Katime, I.; Roig, A.; León, L. M.; Montero, S. *Eur. Polym. J.* **1977**, *13*, 59.
(36) Michel, H.; Lippert, E. In "Organic Liquids: Structure, Dynamics, and Chemical Properties"; Buckingham, A. D., Lippert, E., Bratos, S., Eds; Wiley: New York, 1978.
(37) Fernández-Piérola, I.; Horta, A. *J. Chim. Phys. Phys.-Chim. Biol.* **1980**, *77*, 271.
(38) Pouchlý, J.; Patterson, D. *Macromolecules* **1973**, *6*, 465.
(39) Dondos, A.; Benoit, H. *Polymer* **1978**, *19*, 523.
(40) Dondos, A.; Benoit, H. *Polymer* **1977**, *18*, 1161.
(41) Dondos, A. *Polymer* **1978**, *19*, 1305.
(42) Horta, A.; Prolongo, M. G.; Masegosa, R. M.; Hernández-Fuentes, I. *Polymer*, in press.
(43) Prolongo, M. G.; Masegosa, R. M.; Hernández-Fuentes, I.; Horta, A. Fourth Annual Meeting of the Portuguese Chemical Society, Lisbon, April 6–11, 1981.

Efforts toward an Exact Kirkwood–Riseman Theory of the Intrinsic Viscosity

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ABSTRACT: A new, formally exact formula is derived for the steady-flow Newtonian intrinsic viscosity of a polymer chain. The result is expressed as a sum of two terms: One is an upper bound for the exact intrinsic viscosity and requires the evaluation of only two kinds of equilibrium moments of the friction tensor. The other involves the velocities of the chain segments and vanishes only if the molecule rotates as a whole around its center of mass with the rotational component of the solvent flow. The upper bound formula is found to give the known exact results for the rigid rod, polygon, and dumbbell models and to be a very good approximation for nearly rigid dumbbells. By explicit calculation for the stiff dumbbell model it is also shown that the coupling between chain flexibility and hydrodynamic interactions causes segment motions to deviate from the rotational component of the solvent flow.

1. Introduction

In their pioneering theory of the steady-flow intrinsic viscosity, Kirkwood and Riseman[1] made two important simplifications. First, ignoring the Brownian motion of the polymer chain, they set the velocities of the chain segments (or beads) equal to the rotational component of the solvent flow field. Second, they preaveraged the Oseen hydrodynamic interaction tensor over all conformations of the molecule. It is now known from the work of Gotlib and Svetlov[2] that these two approximations are not independent. Rigid-body rotation in steady laminar flow at low shear rates follows from the solution to the polymer diffusion equation, regardless of the chain model considered, when the diffusion tensor is preaveraged. However, when preaveraging is avoided, segment velocities generally can deviate from the rotational part of the solvent flow. This will be explicitly demonstrated in section 3 for the stiff elastic dumbbell model. It is also implicit in the earlier work of Pyun and Fixman[3] on flexible coils.

The work reported here was motivated by the desire to develop an exact Kirkwood–Riseman theory for the steady-flow Newtonian intrinsic viscosity. Our goal was to avoid the two above approximations and obtain a formula involving only equilibrium averages of quantities

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