Polymer Cosolvent Systems V. Poly(methyl methacrylate) (3)/ CCl₄ (1)/1-Alkanol (2) (1-Propanol and 1-Butanol)

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ABSTRACT: In this paper the Poly(methyl methacrylate) (3)/CCl₄ (1) 1-propanol (2) and poly(methyl methacrylate) (PMMA) (3)/CCl₄ (1)/1-butanol (2) cosolvent mixtures are studied at 303 K by light scattering, viscometry and interferometry. An inversion in solvation has been found in both systems, in the alcohol content ranging between 25 and 30 vol% depending of the 1-alkanol which is used in the cosolvent mixture.

KEY WORDS   Cosolvent Mixtures / Excess Gibbs Free Energy / Self-Association / Liquid Order / Preferential Adsorption Coefficient /

In a previous paper,[1] a study was made of the behaviour of syndiotactic PMMA in CCl₄ (1)/ methanol (2) cosolvent mixture at 303 K. In this system, an inversion in solvation occurs at $u_2 = 20\%$, where u_2 represents the volume fraction of alcohol. It is suggested[2,3] that the sign of the excess Gibbs free energy, G^E, for the binary mixture is a suitable guide for potential cosolvent mixtures. Thus, when $G^E > 0$, the two liquids are relatively incompatible and the 1-2-3 contacts are more favourable than the 1-2. Thus, G^E which is large and positive for the CCl₄ (1)/1-alkanol (2) binary mixtures[4] explains why the CCl₄ (1)/methanol (2) cosolvent mixture and the binary liquid mixtures in this study behave as cosolvents for PMMA. However, as will be seen later, for a satisfactory explanation of this phenomenon, the self-association of 1-alkanols must also be considered.

EXPERIMENTAL PROCEDURES

The syndiotactic samples used are described in a previous paper.[5] Molecular weight determinations by both light scattering and osmometry (made with a Knauer membrane osmometer in toluene at 310 K) on several fractions showed that $M_w/M_n = 1.15$. Binary solvent mixtures were made up by volume. Refractive indices of the solvents and binary solvent mixtures were measured with an Abbé refractometer.

Refractive Index Increments

Differential refractive indices of polymer solutions were measured, at 303 K, with a Carl Zeiss interferometer and a Brice-Phoenix differential refractometer, model BP-2000 V. The refractometer was thermostated to ± 0.05°C. Polymer solutions were equilibrated in the refractometer cell for 10—15 min prior to the measurements. All measurements were made at 546 nm, using the mercury green light as a monochromatic source of light.

Dialysis experiments were carried out in the cell described in ref 6, using commercial cellophane membranes.

Preferential adsorption coefficient, λ, was calculated by differential refractometry of dialysis equilibrium and interferometry using the equation[7]

$$\lambda = \frac{(dn/dc)_\mu - (dn/dc)_k}{dn/dk} \tag{1}$$

were $(dn/dc)_\mu$ and (dn/dc) are the variations in the refractive index with concentration at constant chemical potential and constant composition, respectively, and dn/dk is the variation in the re-

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fractive index of the binary solvent mixture with composition.

Viscometry

Viscosity measurements were made using a modified Ubbelohde viscometer. The kinetic energy correction was less than 0.2%. The temperature of the water bath was maintained within ±0.01°C. Intrinsic viscosity values, $|\eta|$, were obtained by graphical extrapolation of the reduced viscosities to zero concentration of the polymer.

RESULTS AND DISCUSSION

Solubility tests carried out for CCl_4 (1)/1-propanol (2) and CCl_4 (1)/1-butanol (2) mixtures showed PMMA to be soluble in the mixtures with u_2 between 10 and 50%. Thus, these mixtures are typical cosolvents for PMMA. Evidence in support of this conclusion can be found in the data for intrinsic viscosity as a function of molecular weight and solvent composition. Figure 1 illustrates typical intrinsic viscosity data for PMMA fractions with $M_w = 8.98 \times 10^5$ and 9.77×10^5 in the two mixtures concerned. It can be seen that intrinsic viscosity increases with increasing u_2 and passes through a maximum at $u_2 = 23\%$ and 28% for the 1-propanol and 1-butanol binary solvent mixtures, respectively. It is shown below that these compositions coincide with the inversion points ($\lambda = 0$) of solvation.

Figures 2 and 3 illustrate the K_θ parameter characterizing the unperturbed dimensions of PMMA and the B polymer-cosolvent mixture interaction parameter, respectively. Both quantities were obtained using the Stockmayer–Fixman equation[8]
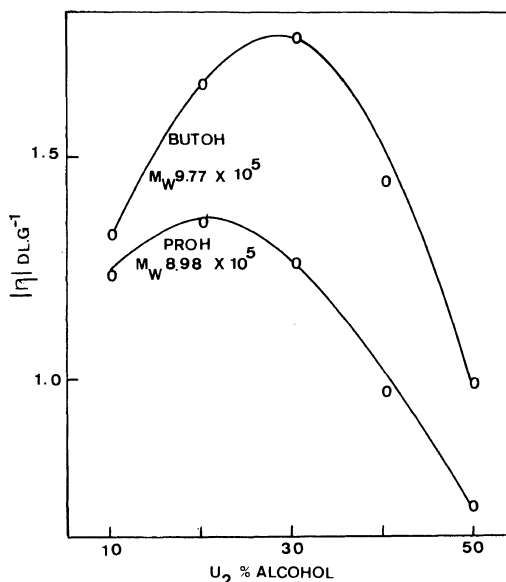

Figure 1. Intrinsic viscosity variation with composition in two fractions of syndiotactic PMMA in the cosolvent mixtures.
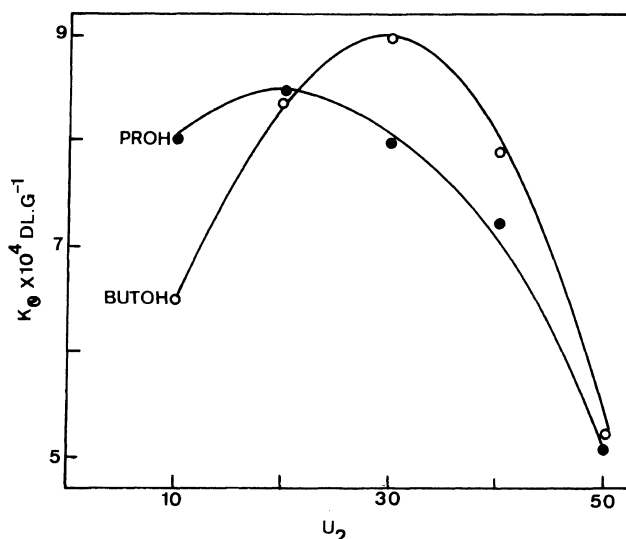

Figure 2. Plot of K_θ parameter against 1-alcohol composition for the two systems.
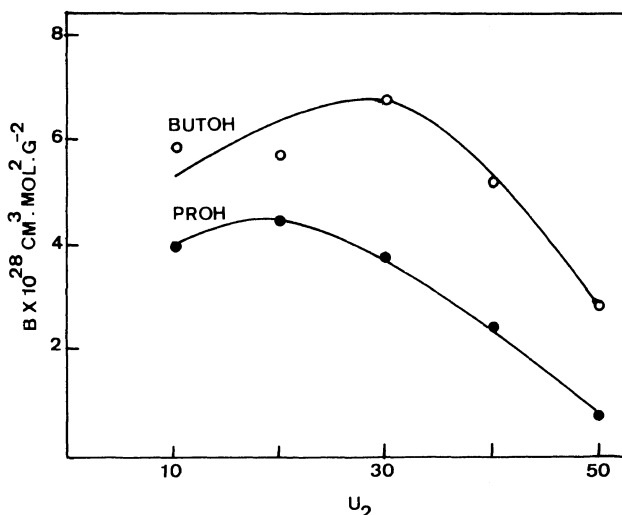
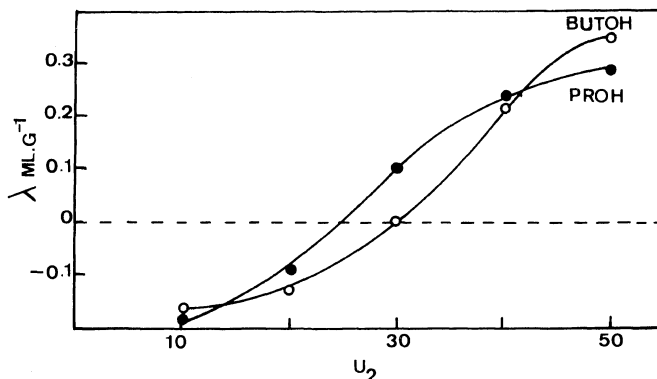**Figure 3.** Plot of B parameter as a function of 1-alcohol composition for both cosolvent mixtures.

Figure 4. Plot of λ parameter against 1-alcohol composition for the two cosolvent mixtures.

$$|\eta| M^{-1/2} = K_\theta + 0.51 B \phi_0 M^{1/2} \qquad (2)$$

where M is the molecular weight and ϕ_0 the Flory's universal constant.

Both parameters become maximum at 20 and 30% of 1-propanol and 1-butanol, respectively. Therefore, these compositions are the most compatible with the polymer. Moreover, variation in the B parameter indicates that the CCl_4 (1)/1-butanol (2) binary solvent mixture is a better cosolvent mixture than the CCl_4 (1)/1-propanol (2). In Figure 4 a plot of the λ parameter against u_2 is shown for both systems studied. The variation in the λ parameter in these binary mixtures is typical of cosolvent mixtures: as G^E is large and positive[4] for the CCl_4 (1)/1-alcohol (2) mixture, the solvent com-

ponent contained in an amount smaller than the inversion composition is always preferentially adsorbed and decreases unfavourable interaction between the two liquid components. The results obtained (Figure 4) show that 1-propanol and 1-butanol are selectively adsorbed as u_2 decreases below the inversion point, while CCl_4 is preferentially adsorbed as u_2 increases beyond this point, in agreement with the interpretation above. We know only one cosolvent mixture for PMMA which does not follow this behaviour: CCl_4 (1)/n-butyl chloride (2),[9] where the polar component (n-butyl chloride) is always preferentially adsorbed. This behaviour was explained taking into account the small and positive G^E of this binary solvent mixture.[9]

As can be seen in Figures 1, 3 and 4, for both cosolvent systems, the solvent compositions at which $|\eta|$ and B reach the maximum value almost coincide with the inversion points of solvation: $u_2 = 25$ and 29% for 1-propanol and 1-butanol, respectively. The slight desplacement for both mixtures can be explained by the difference in molar volume of the liquid components.[10] This result indicates that the inversion points are located at the mixture composition which is most compatible with the polymer.

On the other hand, for a better picture of the behaviour of these cosolvent mixtures, it is necessary to bear in mind the alcohol's self-association through hydrogen bonds. Wolf and Blaum[11] have shown that when butyl chloride is mixed with 1-butanol, the hydrogen bonds of the alcohol are broken. In the same way, the addition of CCl_4 to 1-propanol or 1-butanol breaks this self-association and, therefore, both alcohols interact with the PMMA carbonyl groups. Consequently, the alcohols are preferentially adsorbed onto the macromolecular coil. When the alcohol composition increases beyond the inversion point, the alcohol's self-association becomes more important and then CCl_4 is selectively adsorbed.

As we have already seen, the CCl_4 (1)/1-butanol system is a better cosolvent mixture than the CCl_4 (1)/1-propanol (2), as was found by using the bulk composition of the mixture, without taking into account the preferential adsorption. However, owing to this preferential adsorption, the solvent composition in the vicinity of the macromolecular coil (local composition) is quite different from that in the region far removed from it (bulk composition). In the next paper, we will study this effect and its influence on the cosolvent power of a series of CCl_4/1-alcohol mixtures.

REFERENCES

1. I. Katime, J. Tamarit, and J. M. Teijón, *Anal Quimica (Madrid)*, **75**, 7 (1979).
2. J. M. G. Cowie and J. T. McCrindle, *Eur. Polym. J.*, **8**, 1185 (1972).
3. A. Dondos and D. Patterson, *J. Polym. Sci., A*, **2**, 7, 209 (1969).
4. G. Scatchard and L. B. Ticknor, *J. Am. Chem. Soc.*, **74**, 3724 (1952).
5. I. Katime and J. M. Teijón, *Eur. Polym. J.*, **15**, 291 (1979).
6. I. Katime, P. Garro, and J. M. Teijón, *Eur. Polym. J.*, **11**, 881 (1975).
7. B. E. Read, *Trans. Faraday Soc.*, **56**, 382 (1960).
8. W. H. Stockmayer and M. Fixman, *J. Polym. Sci., C*, **1**, 137 (1963).
9. I. Katime, J. R. Ochoa, L. C. Cesteros, and J. Peñafiel, *Polym. Bull.*, **6**, 429 (1982).
10. A. Zivny, J. Pouchly, and K. Solc, *Collect. Czech. Chem. Commun.*, **32**, 2753 (1967).
11. B. A. Wolf and G. Blaum, *J. Polym. Sci.*, **13**, 1115 (1975).
12. A. Dondos and H. Benoit, *Macromolecules*, **6**, 242 (1973).