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Preferential and Total Sorption in the Powerful Cosolvent System Poly(methyl methacrylate)/Acetonitrile + Chlorobutane

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ABSTRACT: Apparent molecular weights and second virial coefficients have been determined by light scattering in the title system at 25 °C. The total sorption potential, Y, and the preferential adsorption coefficient, λ, have been obtained as a function of mixed solvent composition. Y presents a marked maximum at acetonitrile volume fraction 0.43, while λ remains small and presents an inversion at acetonitrile volume fraction 0.45. The meaning of this inversion and its relationship with the thermodynamic conditions for cosolvency are discussed. The experimental results are compared with the predictions of the Flory–Huggins theory and the Flory–Patterson–Prigogine theory of polymer solutions. Only the latter theory permits the simultaneous description of λ and Y with only one adjustable parameter: the contact surface of the polymer molecule. The role played by nonrandom effects, such as order in the liquids, association of the polymer, and interactions between groups, is discussed.

Introduction

The liquid mixture composed of acetonitrile (MeCN) and 1-chlorobutane (ClBu) has been reported recently to be a cosolvent of poly(methyl methacrylate) (PMMA).[1-3] Several other cosolvent mixtures are also known for PMMA,[1,2,29] as well as a mixture showing the effect opposite to cosolvency, namely, a cononsolvent for PMMA.[4] The cosolvent or cononsolvent nature of these mixtures was determined by studying phase separation temperatures (cloud points) as a function of solvent mixture composition. In the case of the MeCN + ClBu pair, it was found that the solubility of PMMA is drastically changed when the two liquids are mixed. The UCST's of high molecular weight PMMA in pure MeCN or in pure ClBu are slightly above room temperature, but when small amounts of the other liquid are present, the UCST drops abruptly at a rate of several degrees (3–9 °C) per 1% variation in the mole fraction of the liquid mixture.[1-3]

In order to better understand the behavior of this cosolvent system, we study in the present paper the sorption of solvents by the polymer in dilute solution. The properties which we report here are the second virial coefficient, A_2, and the coefficient of preferential sorption, λ, determined by light scattering, both as a function of solvent mixture composition. The purpose is to gain information about the mechanism of the powerful cosolvent action observed in this system. To this end, we compare experimental values of the total sorption potential, Y, and the preferential sorption coefficient, λ, with values predicted by theory. In a companion paper[5] we study the influence of this same cosolvent mixture on polymer coil dimensions determined from limiting viscosity number measurements.

The only light scattering measurements in the literature for PMMA in a cosolvent mixture are those reported for λ in CCl_4 + MeOH,[6,33] which is a weaker cosolvent. In the case of polystyrene, a few more studies of λ and A_2 in cosolvent mixtures have been reported.[7-11] In general, the interpretation of these two properties in cosolvent systems is carried out by using the Flory–Huggins (FH) formalism. Cosolvency has been linked to the existence of 1–2–3 ternary contacts, and, accordingly, the calculation of the ternary interaction parameter, χ_T, has been one of the main efforts in explaining cosolvency.[7,8]

A more adequate thermodynamic theory of polymer solutions, based on the ideas of Prigogine and co-workers, has been made available by Flory[12] and Patterson.[13] This Flory–Patterson–Prigogine (FPP) formalism was first applied to polymers in mixed solvents by Pouchlý and Patterson,[14] who calculated total sorption (Y), and later by Horta,[15] who calculated preferential sorption (λ). In the latter work it was also shown that a molecular interpretation of χ_T in terms of free volume and contact surface dissimilarities is possible.[15] It seems, therefore, of interest to apply the FPP theory to the cosolvent system reported here. As we shall see, this theory gives an improved *simultaneous* description of the observed Y and λ.

Experimental Section

Polymer. The PMMA sample is a Monopol monodisperse standard supplied by Dr. T. G. Croucher (Polymer Laboratories Ltd., Shrewsbury, England). It was synthesized by anionic polymerization in THF at −78 °C, using cumylcesium as initiator, according to the method of Löhr and Schulz.[16] Polydispersity, as specified by the supplier from GPC analysis, is $M_w/M_n \lesssim 1.1$. The tacticity (determined by NMR) is 4% isotactic, 52% heterotactic, and 44% syndiotactic triads.

Solvents were Carlo Erba R.P.E., freshly distilled before use. MeCN + ClBu mixtures of known composition, used as the mixed solvent for the polymer, were prepared assuming additivity of volumes. Previously, we had determined V^E on this liquid mixture.[17] Corrections due to this small effect have been judged to be unnecessary for the present study.

Light Scattering. A FICA FGD Model 42000 instrument and 546-nm unpolarized incident light were used. Scattered intensities were calibrated by using $R_B = 16.3 \times 10^{-6}$ cm^{-1} [18] for the Rayleigh ratio of benzene at 25 °C. Solutions were clarified by filtration through 0.2-μm Millipore Teflon filters. Since MeCN does not wet Teflon, filtration of solutions having a high content of this liquid required previous conditioning of the membrane with a drop of MeOH. Subsequently, the initial volume of filtered solution was discarded. For comparison, some measurements were performed on single-liquid solutions clarified by 2 h of centrifugation at 17 000 rpm. The results were identical, within experimental error, with those of filtered solutions.

The intensity of the scattered light was measured at the 45, 90, and 135° to check dissymmetry ($Z \le 1.05$). With our polymer the form factor can be approximated to unity, and the excess Rayleigh ratio measured at 90°, ΔR, is sufficient for determining M_w.

The results obtained for solutions of different polymer concentrations, c, in the single solvents and in several of their mixtures are shown in Figure 1. The temperature was 25.0 ± 0.05 °C. Throughout this paper, ϕ_1 designates the volume fraction of component 1 in the liquid mixture (1 ≡ MeCN, 2 ≡ ClBu). K in Figure 1 is the optical constant.

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Table I
Light Scattering Results in the Cosolvent System PMMA/Acetonitrile + Chlorobutane at 25 °C

ϕ_1	dn/dc, cm^3 g^{-1}	$M_w^* \times 10^{-3}$	$A_2^* \times 10^4$, cm^3 mol g^{-2}	$A_2 \times 10^4$, cm^3 mol g^{-2}	Y	λ, cm^3 g^{-1}
0.00	0.0912	237		−1.56	−0.0128	
0.10	0.0958	232	1.22	1.19	0.0097	0.016
0.20	0.1026	203	2.82	2.42	0.0198	0.121
0.30	0.1042	220	3.59	3.33	0.0272	0.123
0.40	0.1095	232	3.55	3.48	0.0284	0.019
0.45		240	3.50	3.54	0.0289	0.000
0.50	0.1124					
0.60	0.1182	258	2.90	3.16	0.0258	−0.088
0.65		274	2.78	3.21	0.0262	−0.156
0.70	0.1222	249	2.23	2.34	0.0191	−0.053
0.80		270	1.63	1.86	0.0152	−0.150
0.90	0.1280	245	0.63	0.65	0.0053	−0.039
0.95		241	−0.41	−0.42	−0.0034	−0.020
1.00	0.1319	236		−1.0	−0.0082	

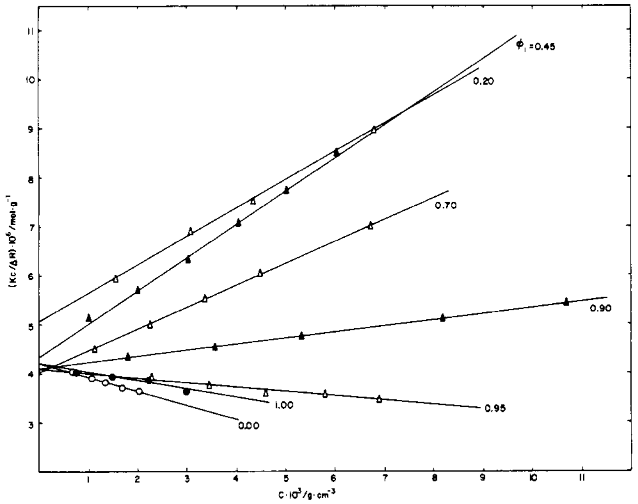

Figure 1. Rayleigh ratios at 90° as a function of polymer concentration, c, in the cosolvent system PMMA/acetonitrile + chlorobutane at 25 °C. The mixed solvent composition is expressed as ϕ_1, the volume fraction of acetonitrile in the liquid mixture.

Differential Refractometry. Refractive index increments were determined at 25.0 ± 0.05 °C by means of a Brice-Phoenix Model 2000V differential refractometer, using a 546-nm filter. Calibration was performed with aqueous KCl solutions.[19] dn/dc values of the polymer solutions (n being the refractive index of the solution) were determined in the same concentration range as the light scattering experiments (Figure 1). The results obtained for dn/dc as a function of ϕ_1 appear in Table I. Their smoothed variation with ϕ_1 is

$$(\mathrm{d}n/\mathrm{d}c)_{\phi_1} = 0.0926 + 0.0404\phi_1 \qquad (\mathrm{cm^3\ g^{-1}}) \tag{1}$$

dn/dϕ_1 of the liquid mixture has been determined previously.[17] It follows the dependence

$$(\mathrm{d}n/\mathrm{d}\phi_1)_{\phi_1} = -0.0635 + 0.0100\phi_1 \tag{2}$$

Results

The experimental results of scattered intensities are treated in the usual way (Figure 1) to obtain the apparent molecular weights, M_w^*, and apparent second virial coefficients, A_2^*:

$$Kc/\Delta R = 1/M_w^* + 2A_2^*c \tag{3}$$

A_2^* is converted into the true second virial coefficient according to the approximate relationship[20]

$$A_2 = A_2^* M_w^*/M_w \tag{4}$$

where M_w is the true molecular weight.

From M_w^* and the smoothed values of dn/dc and dn/dϕ_1 obtained by differential refractometry, we get the coefficient of selective sorption, λ, as

$$\lambda = [(M_w^*/M_w)^{1/2} - 1](\mathrm{d}n/\mathrm{d}c)/(\mathrm{d}n/\mathrm{d}\phi_1) \tag{5}$$

Since subscript 1 refers to MeCN, λ expresses the excess MeCN inside the coil (in cm^3/g of polymer).

From A_2 we calculate the total sorption potential, Y, according to

$$Y = (V_1/\bar{v}_3^2)A_2/F(X) \tag{6}$$

with $\bar{v}_3$ being the partial specific volume of the polymer ($\bar{v}_3$ = 0.81 cm^3 g^{-1}), V_1 the molar volume of MeCN, and $F(X)$ a function of excluded volume. As a usual approximation,[7,8] we take $F(X) = 1$.

The experimental values of M_w^* and A_2^*, as well as the values of A_2, Y, and λ calculated according to eq 4–6, are collected in Table I. We see that both single solvents are, in fact, poor solvents of the polymer and that their Θ temperatures are above 25 °C because the values of A_2 in MeCN and in ClBu are both negative. When the liquids are mixed, the solvent quality increases tremendously and the mixtures behave as good solvents for the polymer. For example, the A_2 determined by us for this same polymer in ethyl acetate is 2.23 × 10^{-4} cm^3 g^{-2}. Ethyl acetate is a good solvent whose Θ temperature for atactic PMMA is as low as −98 °C.[21] The values of A_2 obtained in MeCN + ClBu mixtures of intermediate composition are even higher than in ethyl acetate.

The dependences of Y and λ on ϕ_1 are shown in Figures 2 and 3.

Cosolvency and Inversion in λ

As we can see, the experimental values of λ suffer an inversion at ϕ_1 = 0.45, and the values of Y have a maximum at $\phi_1 \simeq 0.43$. The difference between both compositions is very small. According to thermodynamic theory,[22,23] the inversion in λ and the maximum in Y should coincide exactly only when l ($\equiv V_1/V_2$) = 1. In the system MeCN + ClBu, l is far from unity (l = 0.503).[17] However, for large values of the interaction parameter of the liquid mixture, χ_{12}, the points approach each other even if $l \neq 1$.[22] As we shall see in the next section, the value of χ_{12} in the present system is large. This may be the reason for the proximity of the (λ) inversion and the (Y) maximum in spite of the difference in molar volumes between the two liquids.

It has been proposed[24] that an inversion in λ should accompany the phenomenon of cosolvency in mixtures of two poor solvents. Our results are an example of this behavior. However, for PMMA it has been shown that

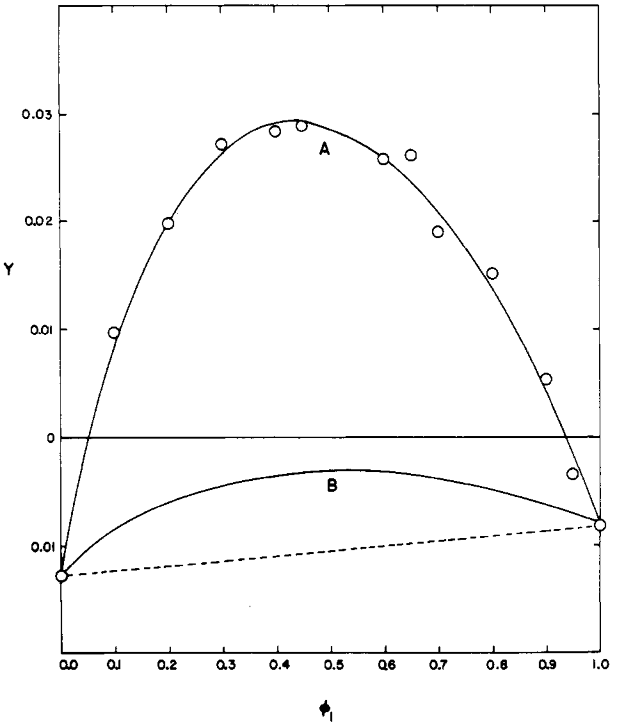

Figure 2. Total sorption potential, Y, as a function of solvent mixture composition, ϕ_1, in the cosolvent system PMMA/acetonitrile + chlorobutane at 25 °C: (O) experimental points obtained from second virial coefficient measurements; (—) theoretical curves calculated with eq 14 (FPP theory) (curve A, $s = 0.591$ and $\epsilon_{12} = \chi_{12}$ (or $s = 0.605$ and $\epsilon_{12} = \chi_{12}'$); curve B, $s = 0.51$ and $\epsilon_{12} = \chi_{12}$); (---) volume fraction average $\phi_1 Y_{13} + \phi_2 Y_{23}$.

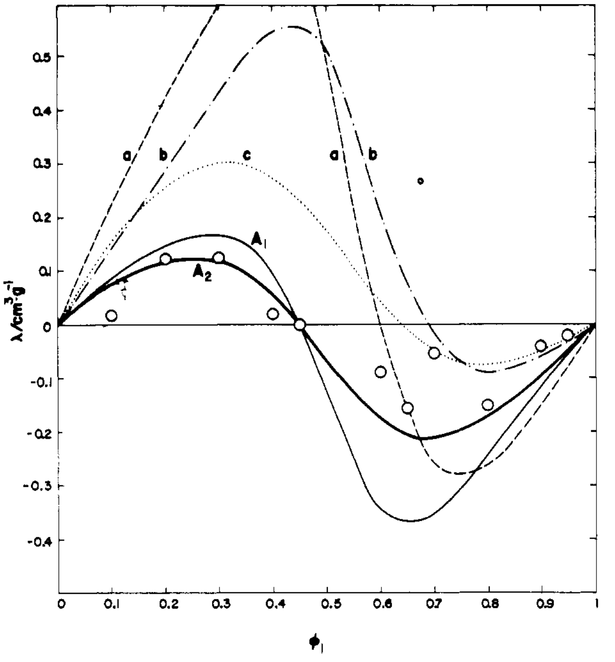

Figure 3. Preferential adsorption coefficient, λ, as a function of solvent mixture composition, ϕ_1, in the cosolvent system PMMA/acetonitrile + chlorobutane at 25 °C: (O) experimental points determined by light scattering; (continuous trace) FPP theory, calculated with eq 17 (curve A_1, $s = 0.597$ and χ_{12} given by eq 10; curve A_2, $s = 0.603$ and χ_{12} given by eq 20); (discontinuous trace) FH theory (curve a, eq 8 and $\chi_T = 0$; curve b, eq 8 and χ_T to match the experimental Y; curve c, eq 11 and χ_T to match the experimental Y).

inversion occurs also in mixtures of a good solvent and a precipitant.[25] The conditions for the existence of cosolvent behavior and those for the appearance of inversion in λ are not identical then, although they may be related.

The conditions of cosolvency can be obtained by looking for the existence of a minimum in the UCST of the system, T_c, as a function of liquid mixture composition. A minimum is guaranteed if the slope $dT_c/d\phi_i$ is positive at $\phi_i = 1$, where subscript i designates that component of the liquid pair for which the T_c of the polymer/single solvent i system is lowest. Using our previous derivation[3] of $(dT_c/dx)_{x=0}$ (x being the mole fraction) and applying the final expression to obtain the above condition for cosolvency, $(dT_c/d\phi_i)_{\phi_i=1} > 0$, we get

$$\chi_{j3} - \chi_{i3} + (V_j/V_i)\chi_{ij} > 0 \quad \text{at } T_{c_i} \qquad (7)$$

Here, T_{c_i} is T_c at $\phi_i = 1$, χ_{mn} is the interaction parameter of components m and n (per molecule of m), subscript 3 designates the polymer, and subscript j is the other liquid in the mixture with i. For the system PMMA/MeCN + ClBu, $T_{c_1} \simeq T_{c_2}$ and both are very close to 25 °C[3] so that the values of χ_{12}, χ_{13}, and χ_{23} obtained at 25 °C are a good guide in discussing cosolvency according to eq 7. Since $\chi_{12} > 1$ for any value of ϕ_1 (see below) and $|\chi_{13} - \chi_{23}| = 0.017$,[26] we conclude that the condition for cosolvency, expressed in eq 7, is fulfilled in this system.

The appearance of an inversion in λ and a maximum in Y is favored by low absolute values of $l - 1$ and $\chi_{13} - l\chi_{23}$, or partial compensation of them, and by high values of χ_{12}.[22,23] For the present system at 25 °C, $|l - 1| = 0.497$, $|\chi_{13} - l\chi_{23}| = 0.244$, and χ_{12} attains large positive values. A large positive χ_{12} means that contact between the molecules of the two liquids is unfavorable. The system tends toward diminishing such contact. This is achieved in the ternary system by shifting the composition of the solvent inside the polymer coils toward equimolar ($x_1 = 0.5$).

As we can see in Figure 3, qualitatively this is the behavior observed in the present system. However, MeCN adsorbs preferentially over a range of compositions wider than expected on the preceding argument, since the inversion appears at $\phi_1 = 0.45$, which corresponds to $x_1 = 0.71$ (instead of $x_1 = 0.5$). This is explained by the difference in molar volume between the two liquids, l, as well as by their mutual interaction, χ_{12} (which is a decreasing function of ϕ_1; see below). MeCN has a molecular volume smaller than that of ClBu, and combinatorial entropy favors the entrance of smaller molecules into the polymer domain.[22] The tendency of MeCN to be preferentially adsorbed is, in some part, compensated by the interactions of the two liquids with the polymer. The values $\chi_{13} \simeq \chi_{23}$ observed mean that the molecules of both liquids have similar affinity for the polymer. But, due to their difference in size, the interaction per unit volume ($\chi_{13} - l\chi_{23}$) favors the adsorption of ClBu. This opposes the combinatorial entropy effect, and the net result of this and χ_{12} is that MeCN tends to be preferentially adsorbed beyond $x_1 = 0.5$ (up to $\phi_1 = 0.45$).

In the previously studied cosolvent of PMMA, namely, PMMA/CCl$_4$ + MeOH, the adsorption of the precipitant MeOH, observed for the smaller values of ϕ_{MeOH}, was attributed to specific interactions between the alcohol and the C=O group of the polymer.[6] However, since in MeOH (1) + CCl$_4$ (2) pair l is also smaller than unity and χ_{12} attains large positive values, we see that the same simple thermodynamic reasoning discussed above serves to explain such an adsorption of MeOH. The question remains as to what role the specific interactions play in such polar systems. In the Nonrandom Effects section we discuss the question of specific interactions.

For the moment, we only conclude that the system PMMA/MeCN + ClBu fulfills, according to thermodynamic arguments, conditions for the appearance of inversion and of cosolvency. In general, both phenomena need not occur simultaneously.

In the case of polystyrene, cosolvency has been discussed in terms of the formation of 1–2–3 contacts because the maximum in Y was found to coincide with a minimum in the ternary interaction parameter, χ_T.[7] As discussed before,[22] the number of 1–2 contacts increases in the polymer domain (shift of composition toward $x_1 = 0.5$) because, in this way, the overall number of 1–2 contacts is kept at its lowest possible value. Whether this is adequately represented by a balance of binary interactions or requires the explicit introduction of ternary ones is something that is best discussed by quantitatively comparing experiment with theory under each of the assumptions. Such comparison is established in the next section for the present system.

Theory

In this section we try to give a quantitative description of λ and Y by means of the classical FH theory and of the more recent FPP theory. We start with the FH treatment in its modified version, which includes χ_T. The expression for λ is

$$\lambda = -\bar{v}_3 \frac{l - 1 + \chi_{13} - l\chi_{23} + (\chi_{12} - \chi_T)(\phi_1 - \phi_2)}{l\phi_1 + \phi_2 - 2\chi_{12}\phi_1\phi_2} \phi_1\phi_2 \qquad (8)$$

and the one for Y, in the single-liquid approximation, can be written as

$$Y = \phi_1 Y_{13} + \phi_2 Y_{23} + \phi_1\phi_2(\chi_{12} - 2\chi_T) \qquad (9)$$

where Y_{k3} is the value of Y at $\phi_k = 1$. For Y_{13}, Y_{23}, χ_{13}, and χ_{23} in eq 8 and 9 we take the values determined experimentally (Table I).[26] For χ_{12} we take also experimental values calculated from the G^E measured by us in the MeCN (1) + ClBu (2) system at 25 °C, using the light scattering technique.[17] The conversion of G^E into χ_{12} data is made according to

$$\chi_{12} = (x_1\phi_2)^{-1}[G^E/RT + x_1 \ln (x_1/\phi_1) + x_2 \ln (x_2/\phi_2)] \qquad (10)$$

The resulting $\chi_{12}(\phi_1)$ is plotted in Figure 4.

The results obtained with eq 8 and 9 are as follows. First we take $\chi_T = 0$. The function Y thus calculated reaches a maximum value of $Y = 0.320$ at $\phi_1 = 0.43$. As we see, the composition of the maximum is correct, but the value of Y is 1 order of magnitude larger than the experimental value (compare with $Y = 0.029$ of Figure 2). The inversion in λ is predicted for $\phi_1 = 0.60$, which is also in poor agreement with the observed one (Figure 3).

We can force agreement between calculated and experimental values of Y by treating χ_T as an adjustable parameter. The values of χ_T which give the best fit curve for Y are shown in Figure 4. Let us see how these values modify the agreement in the case of λ. Using these adjusted χ_T values of Figure 4, we calculate the inversion of λ, with the result $\phi_1 = 0.69$, that is, in worse agreement with experiment than previous prediction using $\chi_T = 0$. The complete curves calculated for λ using $\chi_T = 0$ and using for χ_T the values of Figure 4 are shown in Figure 3 compared with the experimental points. As we see, the whole trend of theoretical λ is unsatisfactory, not just the location of the inversion. To force agreement between theory and experiment at the inversion point of $\phi_1 = 0.45$, a negative value of χ_T is required, which, in turn, would worsen the predictions of Y.

We can conclude then that the use of χ_T in the FH theory is unable to properly account for our experimental results of λ and Y simultaneously. This conclusion is not affected by our use of the single-liquid approximation for Y because, near the maximum in Y, λ vanishes and the liquid mixture inside and outside the polymer coils is of constant composition. In the neighborhood of $\phi_1 \simeq 0.43$–0.45, the single-liquid approximation is thus valid in the system studied here.

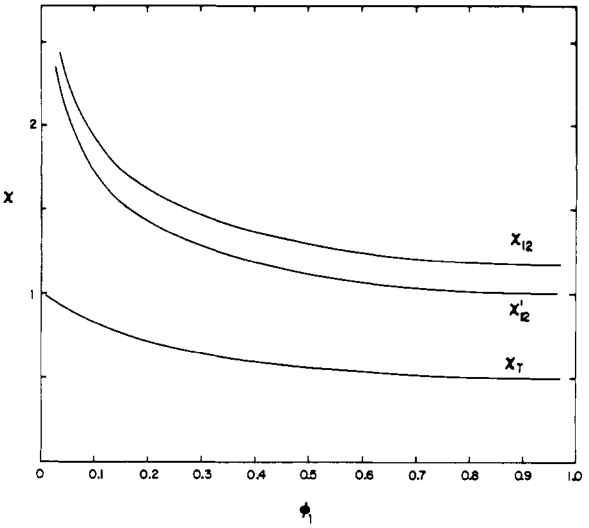

Figure 4. Interaction parameters at 25 °C as a function of solvent mixture composition, ϕ_1. χ_{12} and χ_{12}' = binary interaction parameter for the liquid pair acetonitrile (1) + chlorobutane (2), calculated according to eq 10 and 20, respectively. χ_T = ternary interaction parameter for the cosolvent system PMMA/acetonitrile + chlorobutane, calculated with eq 9 to fit the experimental Y's of Figure 2.

It has been proposed that it is necessary to take into account the derivatives of interaction parameters with respect to concentration. The FH expressions for λ and Y, accordingly modified, can be written as

$$\lambda = -\bar{v}_3 \left\{ l - 1 + \chi_{13} - l\chi_{23} + (\chi_{12} - \chi_T) \times (\phi_1 - \phi_2) - \left[\frac{d\chi_{12}}{d\phi_1} - \left(\frac{\partial \chi_T}{\partial \phi_1'} \right)_{\varphi_3} \right] \phi_1\phi_2 \right\} \phi_1\phi_2 \Big/ \left\{ l\phi_1 + \phi_2 - 2\chi_{12}\phi_1\phi_2 + 2(\phi_2 - \phi_1)\phi_1\phi_2 \frac{d\chi_{12}}{d\phi_1} + \phi_1^2\phi_2^2 \frac{d^2\chi_{12}}{d\phi_1^2} \right\} \qquad (11)$$

$$Y = \phi_1 Y_{13} + \phi_2 Y_{23} + \phi_1\phi_2[\chi_{12} - 2\chi_T + (\partial\chi_T/\partial\varphi_3)_{\phi_1'}] \qquad (12)$$

Here, ϕ_1' denotes composition of the liquid mixture inside the coil ($\phi_1' + \phi_2' = 1$) and φ_3 is the volume fraction of polymer in this same region ($\varphi_1 + \varphi_2 + \varphi_3 = 1$). If we neglect the contribution from $(\partial\chi_T/\partial\varphi_3)_{\phi_1'}$ in eq 12, we still have a single adjustable parameter because the derivatives of χ_{12} can be obtained from $\chi_{12}(\phi_1)$, and the derivative of χ_T with respect to ϕ_1 can be simplified ($\partial\chi_T/\partial\phi_1' = d\chi_T/d\phi_1$) and obtained from the values of χ_T adjusted to fit Y (Figure 4). If this approximation of neglecting the φ_3 dependence of χ_T is not introduced, then the number of adjustable parameters increases and the formulas lose their predictive character and become somewhat empirical correlations.

Therefore we attempt to improve the applicability of the FH theory to our system, only under the assumption of constancy of χ_T with respect to φ_3. Equation 12 then reduces to eq 9 and the values plotted in Figure 4 for $\chi_{12}(\phi_1)$ and $\chi_T(\phi_1)$ allow us to calculate the derivatives required in eq 11. The inversion in λ is then predicted by eq 11 to take place at $\phi_1 = 0.65$, a value in between those calculated before and which is worse than that predicted by the simpler eq 9 with $\chi_T = 0$. The more complex treatment, which introduces a nonzero χ_T and a solvent composition dependence of χ_{12} and χ_T, does not give improved agreement with the inversion point. However, it gives a better description of the magnitude of λ, as is seen in the corresponding curve of Figure 3.

We shall now treat the problem by using the more recent FPP formalism instead of the classical FH one. The advantages of the FPP theory are that it takes into account the differences in free volume and in molecular contact surfaces between polymers and low molecular weight liquids. The expression for λ, according to this theory, is[15]

$$\lambda = -\bar{v}_3 \frac{\tilde{V}_1}{\tilde{V}_3} \frac{l - 1 + s(\epsilon_{13} - l\epsilon_{23}) + (s - \alpha)\epsilon_{12}(\phi_1 - \phi_2)}{l\phi_1 + \phi_2 - 2\epsilon_{12}\phi_1\phi_2} \phi_1\phi_2 \tag{13}$$

and the one for Y (again in the single-liquid approximation) is[14]

$$Y = \phi_1 Y_{13} + \phi_2 Y_{23} + \phi_1\phi_2(s^2 - \alpha' - s\alpha)(\tilde{V}_1/\tilde{V}_3)^2\epsilon_{12} \tag{14}$$

Here $\tilde{V}_i$ is the reduced volume, $s \equiv s_3/s_1$, where s_i is the molecular surface to volume ratio; $\alpha \equiv \alpha_1 T(p_3^*/p_1^*)(1 - T_1^*/T_3^*)$, and $\alpha' \equiv \alpha p_3^*/p_1^*$, where p_i^* and T_i^* are characteristic reduced values for pressure and temperature,[12] respectively, and α_i is the thermal expansion coefficient. The ϵ_{ij}'s are interaction parameters defined according to $\epsilon_{ij} \equiv (-U_i/RT)X_{ij}/p_i^*$,[15] where U_i is the configurational energy, and X_{ij} is the binary exchange interaction parameter used by Flory.[12]

Equations 13 and 14 derive from more general and complex formulas under the simplifying assumption that the (small) differences in surface to volume ratio and in free volume between the two liquids composing the mixed solvent may be neglected in front of their difference with respect to the polymer. Because of this simplification, the magnitudes p_1^*, T_1^*, α_1, s_1, and $\tilde{V}_1$ (subscript 1) in fact correspond to the liquid mixture considered as a solvent of average properties. We use for these magnitudes the values $p_1^* = 435$ J cm^{-3}, $T_1^* = 4561$ K, $\alpha_1 = 1.31 \times 10^{-3}$ K^{-1}, $\tilde{V}_1 = 1.309$, and $s_1 = 1.03 \times 10^8$ cm^{-1}, which are averages of the values corresponding to the single liquids.[17] Due to the same simplification, ϵ_{12} may be equated to the interaction parameter χ_{12}.

The magnitudes which refer to the polymer are obtained as follows. From the values of α_3 reported for PMMA at temperatures above the glass transition,[21,27] we extrapolate to 25 °C and find $\tilde{V}_3$ and T_3^*. From the density of the amorphous polymer[21] at 25 °C we get V_3^*, and from the values of α_3 and of isothermal compressibility[21] we estimate p_3^*. The results are $\tilde{V}_3 = 1.153$, $T_3^* = 7380$ K, $V_3^* = 73.0$ cm^3 mol^{-1}, and $p_3^* = 455$ J cm^{-3}. These results yield $\alpha = 0.156$ and $\alpha' = 0.163$.

We estimate the parameter s_3 from the geometry of the polymer chain by assuming a (curved) cylindrical envelope whose axis is located at the line joining the C$^{\alpha}$'s of the polymer backbone. The length along this axis, per monomeric unit, is 2.68×10^{-8} cm, calculated according to the bond distances and valence angles of the PMMA backbone.[28] The radius of the cylinder, including pendant groups, is obtained from V_3^*, with the result 3.79×10^{-8} cm. This gives $s_3 = 0.53 \times 10^8$ cm^{-1}.

With all these data we calculate Y, according to the FPP theory (eq 14), using the χ_{12} values of Figure 4. We take for s the value obtained above from the geometrical model of PMMA, namely, $s = s_3/s_1 = 0.51$, and also use s as an adjustable parameter. The results obtained for Y with $s = 0.51$ and with the adjusted value which gives the best fit ($s = 0.591$) are shown in Figure 2. Clearly, the geometrical value of s underestimates the increase in total sorption exhibited by this powerful cosolvent system. It is necessary to take a contact surface about 15% larger than that dictated by geometry in order to get agreement with experiment. This is not surprising since the exact locations of the sorption sites of the polymer are not known a priori and the cylindrical envelope is only a crude model of the chain.

We can see in Figure 2 that the theoretical curve with $s = 0.591$ reproduces the experimental results of Y fairly well. The use of an adjustable s is a valid procedure if the same value of the parameter is adequate to predict other properties. We now proceed to test the FPP theory in the same way that we did with the FH theory; namely, we calculate λ and see if a unique value of the adjustable parameter s is compatible with Y and λ simultaneously.

To calculate λ according to eq 13 we need, besides the data already mentioned, the value of $\epsilon_{13} - l\epsilon_{23}$. The ϵ_{ij}'s involving the polymer cannot be equated to the corresponding χ_{ij}'s directly, as we did with ϵ_{12}. To obtain a relationship between $\epsilon_{13} - l\epsilon_{23}$ and the χ_{ij}'s, we go back to the original formulas expressing Y in the FPP theory[15] (under the same simplification regarding the solvent mixture which was used to derive eq 13 and 14). In such original formulas of Y for the ternary system we make $\phi_1 = 1$ and $\phi_1 = 0$ to obtain the theoretical Y_{13} and Y_{23}, respectively. Then we combine both values and write

$$\chi_{13} = 1/2 - Y_{13}$$
$$\chi_{23} = 1/2 - l^{-1}Y_{23} \tag{15}$$

to obtain finally

$$s(\epsilon_{13} - l\epsilon_{23}) = (s - \alpha)^{-1}\{[(1 - l)/2] \times [1 - (\tilde{V}_3/\tilde{V}_1)^2] + (\tilde{V}_3/\tilde{V}_1)^2(\chi_{13} - l\chi_{23})\} \tag{16}$$

which allows for the calculation of $\epsilon_{13} - l\epsilon_{23}$ in terms of the experimental results of χ_{13} and χ_{23}.

We substitute eq 16 into eq 13 and use $\epsilon_{12} = \chi_{12}$, as before, to obtain

$$\lambda = -\bar{v}_3 \frac{H'(l - 1) + H^{-1}(\chi_{13} - l\chi_{23}) + H\chi_{12}(\phi_1 - \phi_2)}{l\phi_1 + \phi_2 - 2\chi_{12}\phi_1\phi_2} \phi_1\phi_2 \tag{17}$$

with

$$H' \equiv (\tilde{V}_1/\tilde{V}_3)\{1 - [1 - (\tilde{V}_3/\tilde{V}_1)^2]/2(s - \alpha)\} \tag{18}$$

$$H \equiv (\tilde{V}_1/\tilde{V}_3)(s - \alpha) \tag{19}$$

All the interaction parameters needed for the calculation of λ can now, according to eq 17, be obtained from our experimental results. Equation 17 is, therefore, a version of the FPP theory for λ which is more useful than the original eq 13. Note that the parameter s appears always in the form of $s - \alpha$ (eq 18 and 19), so that differences in molecular surface to volume ratios and in free volume combine into a single quantity (besides $\tilde{V}_1/\tilde{V}_3$) to influence λ.

The value of the adjustable parameter s which reproduces the observed inversion in $\phi_1 = 0.45$ for the system PMMA/MeCN + ClBu is found by solving for the zero of the numerator in eq 17. The resulting s is 0.597, practically the same value adjusted to fit Y. The complete curve of λ calculated with this s value in eq 17 is shown in Figure 3 (curve A$_1$). We can see that the agreement with experiment is much better than in the case of the FH theory previously discussed (curves a, b, and c in Figure 3). It is possible, then, to describe correctly both λ and

Y with a single value of s. The more noticeable discrepancy is observed for λ in the region where ClBu is preferentially adsorbed, where theory exaggerates the negative value of λ. Even this disagreement can be corrected if we use a different calculation of ϵ_{12}.

Let us define a χ_{12}' representing the deviations of the liquid mixture from ideality (instead of from the residual value of the chemical potential, as does χ_{12} defined in eq 10). χ_{12}' is to be calculated from

$$\chi_{12}' = (x_1\phi_2)^{-1}G^E/RT \qquad (20)$$

The values of χ_{12}' thus calculated from the experimental G^E data[17] are shown in Figure 4. If we take $\epsilon_{12} = \chi_{12}'$, the disagreement between theoretical and experimental values of λ in the region of high ϕ_1's disappears. The value of s adjusted to reproduce the inversion at $\phi_1 = 0.45$ is then 0.603, which differs negligibly from the one previously determined. The inversion is thus not modified by the use of χ_{12}', but the curve of λ is notably improved, giving an excellent match of the experimental points for the whole composition range, as is seen in Figure 3 (curve A_2).

The use of χ_{12}' is also good for Y. The value of s that fits best Y when χ_{12}' is used is 0.605. There is practically no difference between this value and the one obtained from λ. The curve thus calculated with χ_{12}' for Y is indistinguishable from the previous one drawn in Figure 2 (curve A).

The fact that χ_{12}' improves agreement is probably related to the substitution of the individual liquids by their average in the theoretical equations. In many other applications of solution thermodynamics it is also customary to obtain interaction parameters from eq 20, even though the molecules may be of disimilar size.

In the Cosolvency and Inversion in λ section, we discussed the appearance of inversion at $\phi_1 = 0.45$ in terms of thermodynamic arguments and reasoned that combinatorial entropy tends to favor the adsorption of the smaller molecules of MeCN, while the balance of interaction parameters, $\chi_{13} - l\chi_{23}$, opposes this effect, with the net result that, due to this partial compensation and to the influence of χ_{12}, MeCN adsorbs preferentially for x_1 values beyond $x_1 = 0.5$, up to $x_1 \simeq 0.71$ (equivalent to $\phi_1 = 0.45$). We can now use the results of the FPP theory to corroborate, quantitatively, the arguments given before. To this end, we use eq 17 and consider the magnitude of each one of the three terms appearing in the numerator on the right-hand side. The first term, containing $l - 1$, represents the preference for the smaller molecules; its value is -0.42 (for $s = 0.60$). The second term contains the balance of interaction parameters, $\chi_{13} - l\chi_{23}$; its value is 0.48. Both terms almost compensate each other, their sum being 0.06. The leading term to decide the inversion is, then, the third one in eq 17 (that containing χ_{12}), which vanishes for $\phi_1 = 0.5$. The value 0.06 displaces the inversion slightly from $\phi_1 = 0.5$ to $\phi_1 = 0.45$.

The difference with respect to FH theory is that the combinatorial term $(l - 1)$, the balance of interactions term $(\chi_{13} - l\chi_{23})$, and the liquid–liquid interaction term $[\chi_{12}(\phi_1 - \phi_2)]$ are now *modulated* by means of the coefficients H and H', dependent upon free volumes and molecular surface to volume ratios ($s - \alpha$ and $\tilde{V}_i$; eq 18 and 19).

Nonrandom Effects

In our first report on powerful cosolvents of PMMA,[1,2] we stressed the possibly important role that order in the liquid state and association of the polymer would play in determining cosolvency. The two liquids composing the mixed solvent studied here may be good examples of these effects. MeCN is a liquid showing order due to orientational correlation of its molecules, and ClBu is a liquid where PMMA has been found to associate. Also specific interactions between groups may be present. PMMA carries a polar substituent with a C=O group, and the molecules of MeCN have the possibility of interacting in a variety of ways because they carry a strong dipole, a lone electron pair, and two bonding π orbitals. However, the solvation of PMMA by MeCN seems to be hampered by the preference of MeCN molecules to interact among themselves, producing a somewhat structurally ordered liquid. The single liquid MeCN is, then, to be a poor solvent for PMMA. Mixing MeCN with the cosolvent ClBu breaks such liquid order and frees the MeCN molecules to individually solvate the polymer. The reasoning in the case of ClBu as a single liquid would be that the ClBu molecules do not sufficiently solvate the polymer chain, which remains in a rather compact state with a predominance of polymer–polymer contacts. Addition of the polar MeCN molecules opens the compact structure and allows for penetration of ClBu molecules to solvate the chains.

Cosolvency in the closely related system PMMA/2-BuOH + ClBu has been attributed to the breaking of the associated structure of 2-BuOH by the presence of ClBu.[29] In the alcohol, a chemical equilibrium takes place due to hydrogen bonding. The degree of association varies strongly with composition of the mixed solvent and this affects cosolvency. In the range $\phi_{\mathrm{BuOH}} \rightarrow 0$, 2-BuOH exists as individual molecules and the cosolvent effect is much larger than in $\phi_{\mathrm{BuOH}} \rightarrow 1$, where multiassociated species are predominant.[29] No such large difference in cosolvent power is observed in our system for $\phi_{\mathrm{MeCN}} \rightarrow 0$ and $\phi_{\mathrm{MeCN}} \rightarrow 1$. The depression of T_c is of the same order of magnitude at both ends of the composition range ($\phi_{\mathrm{MeCN}} \rightarrow 0$ and $\phi_{\mathrm{MeCN}} \rightarrow 1$).[3] λ has not been measured in the PMMA/2-BuOH + ClBu system, but from the location of its critical points in the cloud point curves, it has been concluded that it presents an inversion in preferential sorption[29] (of the convergent neighborhood type),[22] similar to the system here studied.

Since the thermodynamic FPP theory, which successfully interprets both λ and Y in the present system, does not take into account, explicitly, the effects of liquid order, association, or specific interactions between groups, its good description of the phenomena could at first seem surprising. However, the influence of such nonrandom effects, and their participation in the synergic action of cosolvents, is, in fact, taken into account in our calculations by the use of empirical data for *all* the binary systems. The experimental values of χ_{12}, χ_{13}, and χ_{23} are used in the calculation and they contain the influence of such effects.

The success of the thermodynamic theory implies that the behavior of the ternary system is governed by the balance of all possible binary interactions in their actual (experimental) value. No extra ternary term is required.

We still have the problem of finding an explanation for the high value of s which is required to describe the data. Since the molecules of MeCN are smaller than the monomeric unit, it is possible that they can have access to parts of the polymer chain situated inside its cylindrical envelope. Or they might be able to solvate several sites of the chain, giving an apparent surface higher than the geometrical one. The idea that solvation of the polymer in a cosolvent mixture may be a cumulative, rather than competitive, process would also explain the need of a high s.

The microstructure of the polymer may be also thought to play a role in determining sorption of the cosolvent pair.

Probably, polymers of different tacticities would require slightly different values of s to represent their data. Our polymer sample is predominantly heterotactic, as indicated by its triad content. Polymers of this type have a rather stereoregular microstructure, as we have discussed recently.[30,31] However, the microstructure appears not to have a major influence on the magnitude of λ, according to literature data.[32] In particular, the data obtained in the cosolvent PMMA/CCl_4 + MeOH show that the differences in λ between samples of various tacticities are very small.[6] The dependence of λ on M_w may also affect our results, but we think that the molecular weight studied here should already be high enough to belong to the limiting range ($M_w \rightarrow \infty$). In the other cosolvent studied (PMMA/CCl_4 + MeOH), the dependence of λ on M_w is very small.[6]

Conclusions

In the PMMA/MeCN + ClBu cosolvent system the total sorption of mixed solvent by the polymer is large and the preferential sorption is small, presenting an inversion. Qualitatively, this is in accordance with what is expected for a cosolvent mixture whose interactions between the two liquids are unfavorable ($G^E \gg 0$) and whose interactions of the polymer with each of the single liquids are of comparable magnitude.

The quantitative behavior of total and preferential sorption as a function of solvent mixture composition can be described by thermodynamic theory, although the system is composed of polar species and may contain specific interactions and order effects. The contribution from such nonrandom effects seems to be properly taken into account by using empirical values for the binary systems.

Agreement between theory and experiment is reached simultaneously for both properties when the thermodynamic theory is based on the FPP formalism and the molecular surface offered by the polymer to the solvent is used as an adjustable parameter. However, no simultaneous agreement is possible if the thermodynamic theory is based on the FH formalism, even if a ternary interaction parameter is introduced. More than one empirical parameter would be required in this formalism to represent the data.

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