# Preferential and Total Sorption of Poly(methyl methacrylate) in the Cosolvents Formed by Acetonitrile with Pentyl Acetate and with Alcohols (1-Butanol, 1-Propanol, and Methanol)

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ABSTRACT: Second virial coefficients, $A_2$, and preferential adsorption coefficients, $\lambda$, have been determined by light scattering in the title systems at 25 °C as a function of mixed-solvent composition. The pure liquids acetonitrile and pentyl acetate are poor solvents of poly(methyl methacrylate) (PMMA) ($A_2$ is negative in them) and the alcohols are nonsolvents of the polymer. When the liquids are mixed, $A_2$ changes from negative to positive and passes through a maximum, with values comparable to those in good solvents. In acetonitrile + methanol the liquid preferentially adsorbed by the polymer is methanol. In the other acetonitrile + alcohol mixtures it is acetonitrile. No inversion in $\lambda$ is observed in these systems. They are, thus, examples of cosolvent behavior without inversion. In the acetonitrile + pentyl acetate mixture, acetonitrile is preferentially adsorbed over most of the composition range but a small inversion tentatively occurs. The relative values of the maxima in $A_2$ and the different trends of $\lambda$ are interpreted by taking into account the molecular characteristics of the systems: molar volumes, group interactions, etc. Thermodynamic theories are used to calculate $A_2$ and $\lambda$ and to compare with the experimental results.

## Introduction

In polymer/cosolvent systems the overall sorption of solvent by the polymer is enhanced due to the synergic action of the two liquids. In dilute solution, the second virial coefficient, $A_2$, is a measure of such total solvent sorption. The dependence of $A_2$ on liquid mixture composition has been determined for a number of polymer/cosolvent systems.[1-6] It is also of great interest to study the selective or preferential adsorption of each of the liquids in the cosolvent mixture by the polymer. The preferential adsorption coefficient, $\lambda$, of polymers in cosolvent mixtures has been determined in numerous systems.[1-11] With respect to poly(methyl methacrylate) (PMMA), measurements of both $A_2$ and $\lambda$ have been reported for the powerful cosolvent acetonitrile (MeCN) + 1-chlorobutane (ClBu),[6] as well as measurements of $\lambda$ in the weaker cosolvents $CCl_4$ + MeOH (methanol)[7] and $CCl_4$ + ClBu;[10] selective sorption data, but not $\lambda$, in MeCN + MeOH have also been reported.[11] In the present paper we report on thermodynamic study of PMMA in the cosolvent mixtures of MeCN with an ester, pentyl acetate (PAc), and with three alcohols, 1-butanol (BuOH), 1-propanol (PrOH), and MeOH. The cosolvent character of the MeCN + PAc and MeCN + alcohol mixtures for PMMA was previously established by phase separation temperature determinations.[12] We now study the phenomenon of cosolvency in these systems by means of the light scattering technique. With this technique we determine $A_2$ and $\lambda$ and we try to supply experimental evidence that can help in explaining the possible relationship between cosolvency and preferential adsorption.

## Experimental Section

**Polymer.** The sample was a monodisperse Monopol standard, supplied by Dr. T. G. Croucher (Polymer Laboratories Ltd., Shrewsbury, England) of the type described before.[13] Its tacticity as determined by $^1$H NMR was (in triads) 6% isotactic, 51% heterotactic, and 43% syndiotactic. Its molecular weight, determined by us using light scattering, in ethyl acetate at 25 °C was $M_w = 169 \times 10^3$, and its polydispersity, determined by the supplier from GPC, was $M_w/M_n \leq 1.1$.

**Solvents** were Carlo Erba RPE, freshly distilled before use. Composition of the cosolvent mixtures was calculated by assuming additivity of volumes ($V^E$ is very small in all mixtures[14]).

**Table I**
**Refractive Index Derivative, $dn/d\phi$, as a Function of Composition (Coefficients *A* and *B* of Eq 1) and Excess Gibbs Function at Equimolar Composition for the Liquid Mixtures at 25 °C[a]**

| mixture | $A \times 10^2$ | $B \times 10^3$ | $G^E$, J·mol$^{-1}$ |
|---|---|---|---|
| MeCN + PAc | −5.89 | −0.80 | 646 |
| MeCN + BuOH | −5.91 | 5.6 | 1044 |
| MeCN + PrOH | −4.28 | 1.6 | 785 |
| MeCN + MeOH | 2.16 | −13 | 614[b] |

[a] From ref 21. [b] At 30 °C from ref 22.

**Light Scattering.** The instrument was a FICA 42000 photogoniodiffusometer. Unpolarized incident light of 546 nm was used. Rayleigh ratios were calculated by taking $R_B = 16.3 \times 10^{-6}$ cm$^{-1}$ for benzene at 25 °C as standard.[15] Measurements at angles 45°, 90°, and 135° showed that dissymmetry for the sample was in all cases $Z \leq 1.07$, and the form factor was close to unity. Hence, Rayleigh ratio increments, $\Delta R$, as a function of polymer concentration, $c$ (in g·cm$^{-3}$), were obtained from measurements at 90° only. The concentration range spanned was $c < 7 \times 10^{-3}$ g·cm$^{-3}$. Measuring temperature was 25.0 ± 0.05 °C.

Solutions were filtered through 0.2-$\mu$m Teflon filters (Millipore). In the case of solutions having a high MeCN content, previous conditioning of the filter with a drop of MeOH was necessary, since MeCN does not wet Teflon. The first portion of the solution being filtered was discarded.

**Differential Refractometry.** The instrument was a Brice-Phoenix 2000V, calibrated with aqueous KCl solutions.[16] The wavelength of light was 546 nm, and temperature control was 25.0 ± 0.05 °C.

The same polymer solutions measured in light scattering were used to determine $dn/dc$ ($n$ is the refractive index). In the liquid mixtures the variation of $n$ with composition (expressed as MeCN volume fraction, $\phi_{MeCN}$) follows a linear law for $dn/d\phi$:

$$(dn/d\phi)_\phi = A + B\phi \quad (1)$$

The constants $A$ and $B$ determined for the different mixtures were reported elsewhere.[21] They are given on Table I.

## Second Virial Coefficient

The experimental parameters are molecular weight, $M_w$*, and second virial coefficient, $A_2$* both apparent values, obtained from Rayleigh ratios, $\Delta R_{90°}$, as

$$Kc/\Delta R_{90°} = M_w^{*-1} + 2A_2^*c \quad (2)$$

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**Table II**
**Light Scattering Results in PMMA/Cosolvent Systems at 25 °C**

| $\phi_{MeCN}$ | $dn/dc$, $cm^3 \cdot g^{-1}$ | $M_w^* \times 10^{-3}$ | $A_2^* \times 10^4$, $cm^3 \cdot g^{-2} \cdot mol$ | $A_2 \times 10^4$, $cm^3 \cdot g^{-2} \cdot mol$ | $\lambda$, $cm^3 \cdot g^{-1}$ |
|---|---|---|---|---|---|
| | | | MeCN + PAc | | |
| 0 | 0.0948 | 164 | −0.76 | −0.76 | 0.0 |
| 0.1 | 0.1023 | 140 | 0.57 | 0.48 | 0.150 |
| 0.2 | 0.1078 | 124 | 1.81 | 1.33 | 0.260 |
| 0.3 | 0.1145 | 124 | 2.52 | 1.85 | 0.276 |
| 0.4 | 0.1180 | 129 | 2.91 | 2.24 | 0.245 |
| 0.5 | 0.1223 | 138 | 3.13 | 2.58 | 0.191 |
| 0.6 | 0.1263 | 146 | 2.79 | 2.43 | 0.143 |
| 0.7 | 0.1277 | 155 | 2.13 | 1.97 | 0.083 |
| 0.8 | 0.1301 | 167 | 1.52 | 1.51 | 0.005 |
| 0.9 | 0.1318 | 171 | 0.52 | 0.53 | −0.020 |
| 0.95 | 0.1330 | 172 | −0.06 | −0.06 | −0.026 |
| | | | MeCN + BuOH | | |
| 0.3 | 0.1072 | 117 | −1.28 | −0.89 | 0.317 |
| 0.4 | 0.1125 | 124 | 1.70 | 1.25 | 0.292 |
| 0.5 | 0.1181 | 138 | 2.30 | 1.87 | 0.212 |
| 0.6 | 0.1237 | 145 | 2.59 | 2.22 | 0.172 |
| 0.7 | 0.1260 | 161 | 2.35 | 2.24 | 0.063 |
| 0.8 | 0.1291 | 167 | 1.51 | 1.48 | 0.027 |
| 0.9 | 0.1323 | 168 | 0.53 | 0.53 | 0.020 |
| | | | MeCN + PrOH | | |
| 0.3 | 0.1136 | 151 | 0.18 | 0.16 | 0.161 |
| 0.4 | 0.1191 | 145 | 1.93 | 1.66 | 0.222 |
| 0.5 | 0.1252 | 145 | 2.52 | 2.16 | 0.231 |
| 0.6 | 0.1272 | 156 | 2.42 | 2.30 | 0.129 |
| 0.7 | 0.1293 | 164 | 2.07 | 2.01 | 0.057 |
| 0.8 | 0.1339 | 166 | 1.34 | 1.32 | 0.045 |
| 0.9 | 0.1334 | 170 | 0.60 | 0.60 | 0.005 |
| | | | MeCN + MeOH | | |
| 0.5 | 0.1460 | 159 | −0.58 | −0.55 | −0.324 |
| 0.55 | 0.1460 | 158 | −0.01 | −0.01 | −0.372 |
| 0.6 | 0.1447 | 159 | 0.10 | 0.10 | −0.361 |
| 0.7 | 0.1427 | 159 | 0.40 | 0.38 | −0.372 |
| 0.8 | 0.1403 | 161 | 0.37 | 0.36 | −0.355 |
| 0.9 | 0.1373 | 167 | 0.06 | 0.06 | −0.146 |
| 1 | 0.1340 | 172 | −0.97 | −0.97 | 0.0 |

**Table III**
**Maximum Sorption and Intermolecular Θ Points in PMMA/Cosolvent Systems at 25 °C**

| | $A_2$ max | | $A_2 = 0$ | |
|---|---|---|---|---|
| cosolvent | $\phi_{MeCN}$ | $A_2 \times 10^4$, $cm^3 \cdot g^{-2} \cdot mol$ | $\phi_{MeCN}$ | $\phi'_{MeCN}$ |
| MeCN + PAc | 0.5 | 2.58 | 0.93 | 0.06 |
| MeCN + BuOH | 0.65 | 2.23 | 0.93 | 0.34 |
| MeCN + PrOH | 0.6 | 2.30 | 0.93 | 0.29 |
| MeCN + MeOH | 0.75 | 0.37 | 0.90 | 0.58 |

($K$ is an optical constant). The correct second virial coefficient, $A_2$, is obtained from the apparent one by means of[18]

$$A_2 = A_2^* M_w^* / M_w \quad (3)$$

where $M_w$ is the true molecular weight of the sample. The results obtained for $M_w^*$, $A_2^*$, and $A_2$ are given in Table II. In Figure 1 we plot $A_2$ vs. the cosolvent composition, $\phi_{MeCN}$, for the four systems studied. Also included in Figure 1 are the results previously reported for the cosolvent system MeCN + ClBu.[6]

As we can see in Figure 1, our PMMA is below Θ conditions in the pure liquids MeCN, PAc, and ClBu and cannot be dissolved in the pure alcohols. The behavior of $A_2$ as a function of $\phi_{MeCN}$ is typical of cosolvent systems: the values of $A_2$ corresponding to the pure liquids are negative; when the liquids are mixed, $A_2$ changes from negative to positive, passing through two isothermal Θ points, where $A_2 = 0$, and at intermediate cosolvent compositions, $A_2$ is positive and presents a maximum. In these powerful cosolvents, the value of $A_2$ at the maximum is comparable to the $A_2$ in good solvents. For example, $A_2 = 2.2 \times 10^{-4}$ $cm^3 \cdot g^{-2} \cdot mol$ in EtAc at 25 °C for the same polymer sample. The coordinates of the maximum sorption and of the two isothermal Θ points ($A_2 = 0$) are given in Table III. These are intermolecular Θ points. Their locations are very close to the intramolecular Θ points determined from intrinsic viscosity.[19] The differences between them are probably within experimental uncertainties.

The maxima in $A_2$ occur in the same relative order as the maxima in intrinsic viscosity reported elsewhere for the mixtures of MeCN with PAc,[19] MeCN with BuOH,[19] and MeCN with ClBu.[20] The order is ClBu > PAc > BuOH. The same arguments used to explain $[\eta]$[20] are also valid for $A_2$. The liquids MeCN, PAc, and ClBu are of similar solvent quality toward the polymer and the main factor determining the order of $A_2$ is the $G^E$ of their

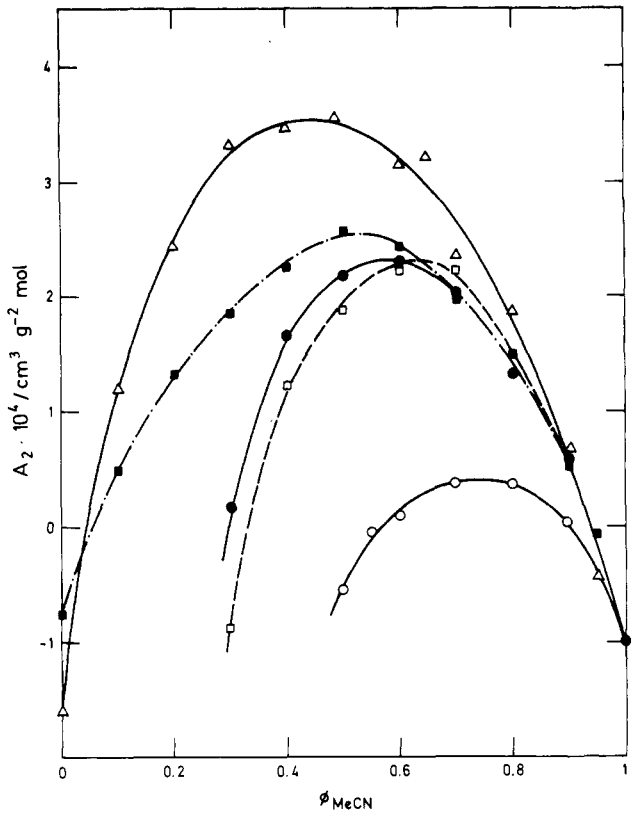


**Figure 1.** Second virial coefficients, $A_2$, as a function of solvent mixture composition, $\phi_{MeCN}$, in the cosolvent mixtures MeCN + ClBu (△),[6] MeCN + PAc (■), MeCN + BuOH (□), MeCN + PrOH (●), and MeCN + MeOH (○) at 25 °C.

mixtures. In Table I we give the values of $G^E$ at equimolar composition for the cosolvent mixtures studied at 25 °C.[21] The order MeCN + ClBu > MeCN + PAc in $A_2$ is clear, since $G^E$ is larger in the first of these mixtures. Comparison with the system MeCN + BuOH is not so simple because $A_2$ does not follow the order fixed by $G^E$. In MeCN + BuOH, $G^E$ is larger than in MeCN + PAc but $A_2$ is lower. The explanation comes from the different affinity for the polymer of each of the liquids. BuOH is a much worse solvent of PMMA than PAc is and this lowers the maximum $A_2$ attainable in MeCN + BuOH mixtures. Thus, $A_2$ depends not only on the magnitude of the unfavorable interactions in the mixture ($G^E$) but also on the difference in interaction between the polymer and each of the liquids.

Let us compare now the maxima $A_2$ in the three mixtures containing alcohol. PrOH and BuOH lead to similar $A_2$ values. This in spite of two factors favoring a larger solvent sorption in the BuOH mixtures: i.e., MeCN + BuOH has a larger value of $G^E$ (Table I) and PrOH is a worse solvent for PMMA. Another factor that acts in the opposite sense and favors sorption by the PrOH mixtures is molar volume (smaller for PrOH). This could compensate the other two factors and justify a similar sorption in PrOH and BuOH mixtures.

Molar volume influences the thermodynamic equilibrium of the system through combinatorial contributions. But in the case of PMMA/MeCN + alcohol systems, it can also influence the specific interactions. Let us consider this point of specific interactions in some detail. MeCN is of small molar volume, and its molecule is highly dipolar. We have suggested elsewhere that the interaction of MeCN with PMMA may occur in two opposing ways: attractively, with the pendant ester group of the polymer, and repulsively, with its methylene backbone.[21] MeCN can thus become a good solvent of PMMA once the orientational correlations of pure MeCN are broken by the second liquid[6,12] and once the unfavorable interactions with the polymer backbone are compensated by stronger repulsive interactions between the two liquids.

The molecules of alcohol can interact with PMMA through hydrogen bonding of the OH group of the liquid to the CO group of the polymer. The alcohol can become a good solvent of PMMA once its autoassociated structure is disrupted by the second liquid.[21] This type of interaction between the OH of the alcohol and the CO of the polymer should be favored by a shorter alkyl chain attached to the OH.[21] Hence alcohols of lower molar volume should be favored. PrOH, once its autoassociation is broken, should be a better solvent of PMMA according to this. Hence, a larger $A_2$ should be expected in MeCN + PrOH than in MeCN + BuOH due to this influence of molar volume on specific interactions. But there are also unfavorable interactions between the CN group of MeCN and the methylene groups of the alkyl chain of the alcohol. This type of unfavorable interaction has been made responsible for an important part of the positive $G^E$ in the MeCN + alcohol mixtures.[21] Since the relative order of $G^E$ in the MeCN + PrOH and MeCN + BuOH pairs acts in oposition to the effect of molar volume discussed above (Table I), the net result can be similar $A_2$'s in these two systems. We see that in mixtures, the concept of good or poor solvent may be changed with respect to its meaning for pure liquids.

In the case of the MeCN + MeOH mixture, its maximum $A_2$ is much lower than in the other systems (almost an order of magnitude smaller). This can be explained by considering that MeOH is more hydrogen bonded than its higher homologues and its autoassociated structure is not completely destroyed except at very high dilutions and also by the lower value of $G^E$ in MeCN + MeOH mixture (Table I). Nevertheless, it is remarkable that mixing a typical precipitant of PMMA, as it is MeOH, with a poor solvent, MeCN ($\Theta$ = 48 °C[23]), gives a good solvent mixture having positive $A_2$ values at 25 °C.

### Preferential Adsorption Coefficient

The coefficient of preferential adsorption, $\lambda$, is calculated according to

$$\lambda = [(M_w^*/M_w)^{1/2} - 1](dn/dc)/(dn/d\phi) \qquad (4)$$

from the experimental values of $M_w^*$, $dn/dc$, and $dn/d\phi$ (Tables I and II). Thus defined, $\lambda$ expresses the excess MeCN inside the coil (in $cm^3$ per gram of polymer). The results of $\lambda$ are given in the last column of Table II, and they are presented in Figure 2. Also plotted in Figure 2 are the results previously reported for the cosolvent MeCN + ClBu.[6] This system presents a clear inversion, with MeCN being preferentially adsorbed below $\phi_{MeCN}$ = 0.45 and ClBu above this composition. The system MeCN + PAc also seems to present an inversion point but this time at $\phi_{MeCN}$ = 0.80. The preferential adsorption of MeCN in this system is clearly seen for $\phi_{MeCN} < 0.80$. However, at $\phi_{MeCN} > 0.80$ the preferential adsorption of PAc is not so clearly established because the small values of $\lambda$ fall within the precision range of the measurements. The MeCN + alcohol systems do not present an inversion at all. MeCN is preferentially adsorbed at all compositions in the mixtures with BuOH or PrOH, while MeOH is preferentially adsorbed in MeCN + MeOH.

According to thermodynamic theory,[24] preferential adsorption is determined by the following factors: (a) the difference in molar volume between liquids, expressed as $l - 1$, where $l = V_1/V_2$ ($V_i$ is the molar volume of liquid $i$), (b) the difference in affinity of both liquids for the

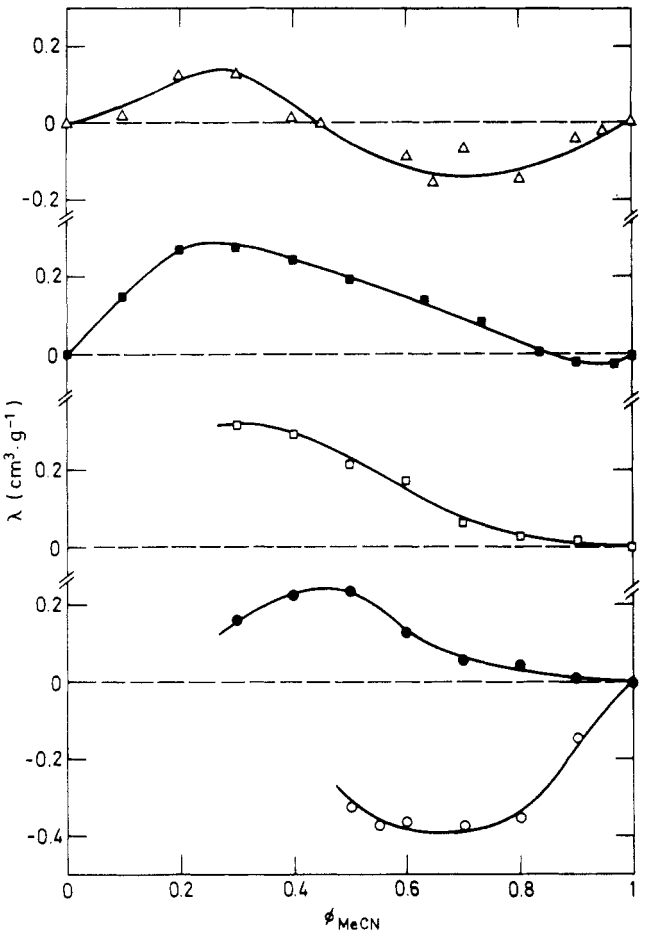


**Figure 2.** Preferential adsorption coefficient, λ, as a function of solvent mixture composition, $\phi_{MeCN}$, in the cosolvent mixtures MeCN + ClBu (△),[6] MeCN + PAc (■), MeCN + BuOH (□), MeCN + PrOH (●), and MeCN + MeOH (○) at 25 °C.

polymer, expressed by $\chi_{13} - l\chi_{23}$, where $\chi_{13}$ and $\chi_{23}$ are the interaction parameters of liquids 1 and 2 with the polymer (MeCN is taken always as liquid 1 in this work), and (c) the interaction between both liquids, represented by their interaction parameter, $\chi_{12}$. The reasons for the inversion of λ in the MeCN + ClBu mixture were discussed before.[6] In this system, $l - 1 = -0.497$, the smaller molar volume of MeCN favors the adsorption of this liquid, but $\chi_{13} - l\chi_{23} = 0.244$ partly compensates this tendency and the overall effect is that λ inverts at $\phi_1 = 0.45$. The existence of large repulsive effects between the liquids ($\chi_{12} = 1.3$ at $x_1 = 0.5$) induces the polymer to adsorb inside the coils a composition closer to $x_1 = 0.5$ than the analytical one in order to minimize the overall number of 1–2 contacts and hence induces λ to invert approaching $x_1 = 0.5$.

The larger effect of $l - 1$ over $\chi_{13} - l\chi_{23}$ displaces the inversion point from $x_1 = 0.5$ to $\phi_1 = 0.45$, which corresponds to $x_1 = 0.71$. Thus the smaller solvent MeCN adsorbs preferentially over a wider range of $x_1$ than ClBu.

In the case of the MeCN + PAc system, the value of $l - 1$ is −0.646. We can estimate $\chi_{13}$ and $\chi_{23}$ from the $A_2$ values of Table II as

$$\chi_{i3} \simeq \frac{1}{2} - \frac{V_i}{\bar{v}_3^2}(A_2)_i \qquad (5)$$

($\bar{v}_3$ is the partial specific volume of the polymer (0.81 $cm^3 \cdot g^{-1}$)). The results are $\chi_{13} \simeq 0.508$ and $\chi_{23} \simeq 0.517$. Hence, $\chi_{13} - l\chi_{23} \simeq 0.325$. The sum of $l - 1$ and $\chi_{13} - l\chi_{23}$ is larger in MeCN + PAc than in MeCN + ClBu and consequently the range of $\phi_1$ over which MeCN adsorbs preferentially is wider. In the MeCN + PAc system an inversion at $\phi_1 = 0.80$ is equivalent to $x_1 = 0.90$. PAc is more voluminous than ClBu, and therefore its preferential adsorption is hampered; the inversion in λ moves to higher $\phi_1$, almost disappearing.

In the system MeCN + MeOH the contribution from the difference in molar volumes, $l - 1$, is of opposite sign, since the molecules of MeOH are smaller than those of MeCN. Here, $l - 1 = 0.306$; this factor favors the adsorption of MeOH. For the alcohols we cannot estimate $\chi_{23}$ using eq 5 because the polymer is not soluble and $A_2$ cannot be determined in the pure liquids. However, it is clear that $\chi_{23} > \chi_{13}$, since the alcohols are worse solvents than MeCN. Therefore, $\chi_{13} - l\chi_{23} < 0$, and this factor should partly compensate the effect of the smaller size of the MeOH molecules. This means that it is theoretically possible for the system MeCN + MeOH to have an inversion point in the range $\phi_1 < 0.5$ if this range were accessible experimentally. The large adsorption of MeOH observed experimentally ($\phi_1 > 0.5$) is probably a consequence of the specific interactions between this small alcohol and PMMA. Methanol is preferentially adsorbed (in a certain composition range) by PMMA not only in admixture with MeCN but also with $CCl_4$ and even with a very good solvent such as benzene or chloroform.[7,11,25,26]

In the case of the MeCN + BuOH mixtures, the alcohols are of the larger molecular size than MeCN and $l - 1$ favors selective entrance of MeCN inside the coil. Compared to ClBu, BuOH has a very similar molar volume and hence $l - 1$ is close in MeCN + ClBu and MeCN + BuOH. However, BuOH should have a larger $\chi_{23}$ than ClBu and hence a smaller $\chi_{13} - l\chi_{23}$, thus leaving a larger portion of $l - 1$ uncompensated. The inversion point, which is clearly seen in MeCN + ClBu is so much displaced toward $\phi_1 \rightarrow 1$ in MeCN + BuOH that it degenerates into a tangential approach to $\lambda = 0$ at $\phi_1 \rightarrow 1$. The MeCN + PrOH system also presents this behavior with no inversion, and the explanation is similar. The differences between PrOH and BuOH are that PrOH is of smaller molar volume and presumably larger $\chi_{23}$. Therefore, $|l - 1|$ and $\chi_{13} - l\chi_{23}$ are both lower with PrOH than with BuOH. Since these two factors act in opposite senses, they partly compensate, leaving a similar λ. (Only at the lowest $\phi_1$'s is the preferential adsorption of MeCN a little lower with PrOH, probably due to the smaller $|l - 1|$.) Besides, $\chi_{12}$ is smaller with PrOH (Table I), so that the tendency toward inversion is even weaker in the MeCN + PrOH system.

Contrary to the case of MeCN + MeOH, the systems MeCN + BuOH and MeCN + PrOH do not have the theoretical possibility of a hypothetical inversion for compositions in the range $\phi_1 < 0.3$, which are now experimentally restricted because of lack of polymer solubility. The values of $\chi_{12}$ in the MeCN + alcohol mixtures are positive and therefore the inversion in λ, if it occurs, is of the convergent type.[27] This means that the selective adsorption in the neighborhood of $\phi_1 \rightarrow 0$ should be of liquid 1. It is then not possible for the preferential adsorption to invert from MeCN to BuOH or PrOH as $\phi_1 \rightarrow 0$.

Inversion of λ has been generally found in cosolvent systems.[2-9] This has led to the notion that the phenomenon of cosolvency is associated with the sigmoidal form of λ.[2,3,28] The argument goes that the inversion in λ produces the largest number of 1–2–3 contacts possible and thus is associated with the maximum solvation of the polymer by the liquid mixture. Inversion and cosolvency should then be associated phenomena. The thermodynamic conditions for the occurrence of cosolvency have been recently discussed.[29] These conditions have been compared with those for the appearance of inversion,[6] with

Table IV
Molecular Surface, Thermal Expansion Coefficient, Reduced Volume, and Characteristic Reduction Parameters for Pressure and Temperature of the Pure Liquids

| liquid | $s_1 \times 10^{-8}$, $cm^2 \cdot mol^{-1}$ | $\alpha_1 \times 10^3$, $K^{-1}$ | $\tilde{V}_1$ | $p_1^*$, $J \cdot cm^{-3}$ | $T_1^*$, K |
|---|---|---|---|---|---|
| MeCN | 0.431 | 1.378 | 1.3204 | 651 | 4449 |
| PAc | 1.155 | 1.224 | 1.2940 | 660 | 4707 |
| BuOH | 0.763 | 0.993 | 1.2463 | 500 | 5251 |
| PrOH | 0.628 | 1.000 | 1.2480 | 486 | 5231 |
| MeOH | 0.347 | 1.271 | 1.3008 | 548 | 4621 |

the conclusion that cosolvency and inversion need not occur simultaneously.[6] Our present results provide experimental evidence confirming such a conclusion. All the mixtures studied here are cosolvents of PMMA at 25 °C, but some do not show inversion in λ. The MeCN + BuOH and MeCN + PrOH systems are good examples of powerful cosolvents with no inversion. In both systems, when the alcohol is added to MeCN, the total sorption ($A_2$) increases tremendously, but no preferential sorption of the alcohol takes place.

## Thermodynamic Calculations

Up to this point we have discussed our experimental results in terms of qualitative considerations about molar volumes and interaction parameters. Let us now see if the data can be quantitatively described by thermodynamic theory.

The functions to be calculated theoretically are $Y$ and λ. $Y$ is related to the experimental $A_2$ through

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

with $F(X)$ a function of excluded volume, which we approximate by $F(X) = 1$ in converting $A_2$ into experimental values of $Y$ to be compared with theory, as is usually done. For the theoretical $Y$ we use the single-liquid approximation.

In the classical Flory–Huggins theory, extended to take into account a ternary interaction parameter, $\chi_T$, the functions $Y$ and λ are given by[27,30]

$$Y = \phi_1 Y_{13} + \phi_2 Y_{23} + \phi_1\phi_2(\chi_{12} - 2\chi_T) \tag{7a}$$

$$\lambda = -\bar{v}_3[(l - 1 + \chi_{13} - l\chi_{23} + (\chi_{12} - \chi_T) \times (\phi_1 - \phi_2))/(l\phi_1 + \phi_2 - 2\chi_{12}\phi_1\phi_2)]\phi_1\phi_2 \tag{7b}$$

where $Y_{k3}$ is the value of $Y$ at $\phi_k = 1$.

The thermodynamic theory which considers that interaction takes place between molecular surfaces and incorporates free volume gives for $Y$ and λ[31,32]

$$Y = \phi_1 Y_{13} + \phi_2 Y_{23} + \phi_1\phi_2(s^2 - s\alpha - \alpha')\left(\frac{\tilde{V}_1}{\tilde{V}_3}\right)^2 \chi_{12} \tag{8a}$$

$$\lambda = -\bar{v}_3[(H'(l - 1) + H^{-1}(\chi_{13} - l\chi_{23}) + H\chi_{12}(\phi_1 - \phi_2))/(l\phi_1 + \phi_2 - 2\chi_{12}\phi_1\phi_2)]\phi_1\phi_2 \tag{8b}$$

where

$$H = \frac{\tilde{V}_1}{\tilde{V}_3}(s - \alpha) \tag{8c}$$

$$H' = \frac{\tilde{V}_1}{\tilde{V}_3}\left\{1 - \left[1 - \left(\frac{\tilde{V}_3}{\tilde{V}_1}\right)^2\right]/2(s - \alpha)\right\} \tag{8d}$$

In eq 8, $\tilde{V}_i$ are reduced volumes, $s = s_3/s_1$, where $s_i$ is the molecular surface-to-volume ratio, $\alpha = \alpha_1 T(p_3^*/p_1^*)(1 - T_1^*/T_3^*)$, and $\alpha' = \alpha p_3^*/p_1^*$, where $p_i^*$ and $T_i^*$ are reduction parameters for pressure and temperature, respectively,[33] and $\alpha_i$ is the thermal expansion coefficient. Subscript 1 refers to the liquid acting as solvent (pure 1, pure 2, or the mixture).

The characteristic parameters for the pure liquids have been obtained in the usual way[17,21] from density, thermal expansion coefficient, and isothermal compressibility data. Literature values of density as a function of temperature have been used for $\alpha_i$.[16] The isothermal compressibilities have been determined by light scattering measurements.[21] The molecular surface has been obtained by group contributions following Bondi,[34] and $s_i$ from such surface and the reduction volume. The values of $s_i$, $p_i^*$, $\alpha_i$, $T_i^*$ and $\tilde{V}_i$ thus obtained for the pure liquids are given in Table IV. For the mixtures, mean values of the pure components are taken for these same quantities. The characteristic parameters for the polymer have been taken from ref 6.

The $Y_{k3}$'s used in both theoretical expressions (eq 7a and 8a) are obtained from the experimental $A_2$, and in the case of $k$ = MeCN and $k$ = PAc, from the value of $A_2$ determined in pure liquid $k$. In the case of the alcohols this is not possible, and $Y_{k3}$'s have been calculated by putting $Y = 0$ for the Θ mixed-liquid composition at which $A_2 = 0$ ($\phi'_{MeCN}$ in Table III).

The results for $Y$ and λ calculated with eq 7 and 8 are shown in Figures 3 and 4. Equation 7a for $Y$ with $\chi_T = 0$ fails utterly, giving estimates of $Y$ about an order of magnitude larger than experimental values—thus the need of a nonzero $\chi_T$. Equation 8a predicts correctly the order of magnitude of $Y$ and gives, in general, good agreement. In the MeCN + PAc case, theory somewhat overestimates $Y$. Both PAc and PMMA contain ester groups, and some competing action of these groups in their interaction with MeCN is expected. This may lead to a smaller sorption, lower than predicted by thermodynamic theory.

Both eq 7b with $\chi_T = 0$ and eq 8b give very poor descriptions of λ in all the systems now reported, with the possible exception of MeCN + PAc, for which eq 7b with $\chi_T = 0$ gives a reasonable approximation of experimental results. The agreement using eq 7b can be improved by introducing $\chi_T$ as an empirically adjustable parameter. We obtain the empirical value of $\chi_T$ by fitting eq 7a to the experimental $Y$'s and use such adjusted $\chi_T$'s in eq 7b to calculate λ. The results thus obtained are shown in Figure 4. The agreement improves but still it is only satisfactory in the MeCN + PAc system. The adjusted theoretical curves of λ for the MeCN + alcohol systems are not so good. In the cases of PrOH and BuOH they predict inversions that are not supported by the experimental results. The cosolvent MeCN + ClBu previously analyzed[6] shows a clear inversion at the midpoint of the composition range, and in this case agreement between eq 8b and experiment has been found to be satisfactory.

In general, it seems that the experimental λ is more sensitive to differences in molar volume or in interaction parameters than what theory predicts. As examples of this lack of sensitivity of the theory to such differences, we can cite the comparison between the results of MeCN + ClBu,

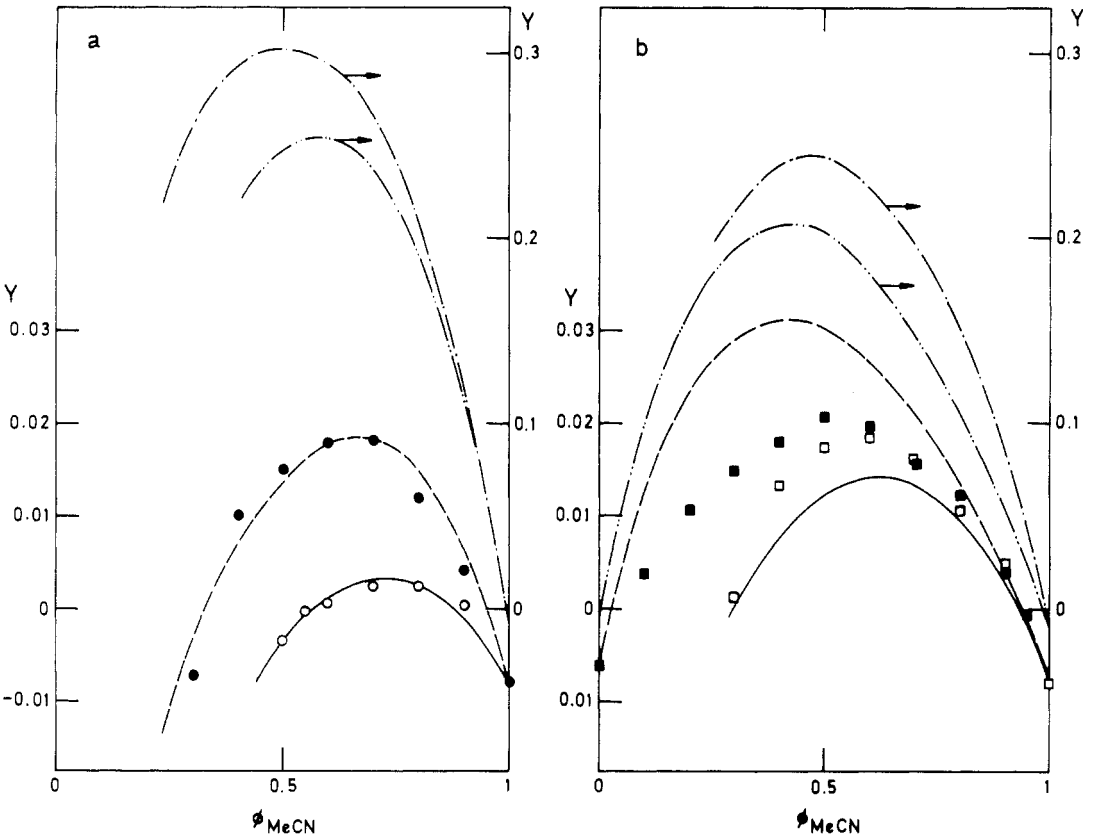


**Figure 3.** Total sorption potential, $Y$, as a function of solvent mixture composition, $\phi_{MeCN}$, in the mixtures (a) MeCN + MeOH (○) and MeCN + BuOH (●) and (b) MeCN + PrOH (□) and MeCN + PAc (■). Curves are theoretical results calculated by means of eq 7a with $\chi_T = 0$ [(-·-) MeCN + BuOH or MeCN + PrOH; (-··) MeCN + MeOH or MeCN + PAc] and eq 8a [(---) MeCN + BuOH or MeCN + PAc; (—) MeCN + MeOH or MeCN + PrOH].

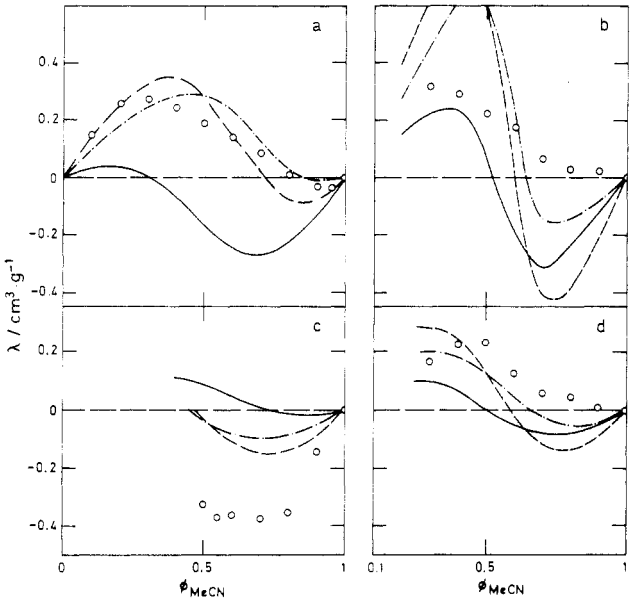


**Figure 4.** Preferential adsorption coefficient, λ, as a function of solvent mixture composition, $\phi_{MeCN}$, in the cosolvent mixtures MeCN + PAc (a), MeCN + BuOH (b), MeCN + MeOH (c), and MeCN + PrOH (d). Points: experimental results. Curves: theoretical results. Calculated by means eq 7b with $\chi_T = 0$ (---), eq 7b with $\chi_T$ to match experimental $Y$ (-·-), and eq 8b (—).

MeCN + PAc, and MeCN + BuOH. As discussed in an earlier section, ClBu and PAc are solvents of similar quality for the polymer but PAc has a larger molar volume. On the other hand, ClBu and BuOH are of similar molar volume but very different solvent quality. Therefore, when comparing the MeCN + ClBu system with MeCN + PAc, we see that the effect of the larger molar volume of PAc is to displace the inversion point to almost disappearance, and when comparing the MeCN + ClBu system with MeCN + BuOH, we see that the effect of the lower solvent quality of BuOH is to practically eliminate such inversion. However, the theoretical curves for MeCN + PAc and MeCN + BuOH (without adjusted parameter) still predict an inversion in both systems larger than observed and not so different from the one predicted for MeCN + ClBu. The inclusion of free volume and the consideration of interactions at the molecular surface in the theory make eq 8b even less sensitive to molar volume differences than eq 7b.

Another example can be cited in which the effect of molar volume seems to be much more important in experiment than in theoretical predictions: the different MeCN + alcohol systems. The alcohol is preferentially adsorbed only when its molar volume is lower than that of MeCN (the case of MeOH). However, the theoretical curves predict preferential adsorption of the alcohol in all cases in a certain range of compositions ($\phi_{MeCN} \rightarrow 1$).

In summary, theory tends to predict differences in λ between systems less drastic than experimentally observed and to predict always some adsorption of both liquid components. In the systems studied here, certain specific interactions are present that could contribute to enhance differences in behavior. Thermodynamic theory does not explicitly include such specific interactions (unless adjusted parameters are introduced).

**Registry No.** PMMA, 9011-14-7; MeCN, 75-05-8; PAc, 628-63-7; MeOH, 67-56-1; BuOH, 71-36-3; PrOH, 71-23-8.

## References and Notes

(1) Tuzar, Z.; Kratochvil, P. *Collect. Czech. Chem. Commun.* **1967**, *32*, 3358.
(2) Cowie, J. M. G.; McCrindle, J. T. *Eur. Polym. J.* **1972**, *8*, 1185.

(3) Cowie, J. M. G.; McCrindle, J. T. *Eur. Polym. J.* **1972**, *8*, 1325.
(4) Cowie, J. M. G.; McEwen, J. J. *Macromolecules* **1974**, *7*, 291.
(5) Scornaux, J.; Van Leemput, R. *Makromol. Chem.* **1976**, *177*, 2721.
(6) Horta, A.; Fernández-Piérola, I. *Macromolecules* **1981**, *14*, 1519.
(7) Katime, I.; Strazielle, C. *Makromol. Chem.* **1977**, *178*, 2295.
(8) Maillols, H.; Bardet, L; Gromb, S. *Eur. Polym. J.* **1979**, *15*, 307.
(9) Gargallo, L; Radic, D.; Katime, I. *Eur. Polym. J.* **1981**, *17*, 439.
(10) Katime, I.; Ochoa, J. R.; Cesteros, L. C.; Peñafiel, J. *Polym. Bull.* **1982**, *6*, 429.
(11) Wenqing, Z.; Chengwei, X. *Fenzi. Kexue Xuebao* **1982**, *2*, 73.
(12) Fernández-Piérola, I.; Horta, A. *Makromol. Chem.* **1981**, *182*, 1705.
(13) Fernández-Martin, F.; Fernández-Piérola, I.; Horta, A. *J. Polym. Sci., Polym. Phys. Ed.* **1981**, *19*, 1353.
(14) Prolongo, M. G.; Masegosa, R. M.; Hernández-Fuentes, I.; Horta, A. *J. Phys. Chem.* **1984**, *88*, 000.
(15) Carr, C. J.; Zimm, B. H. *J. Chem. Phys.* **1950**, *18*, 1616.
(16) Huglin, M. B. "Light Scattering from Polymer Solutions"; Huglin, M. G., Ed.; Academic Press: London, 1972.
(17) Fernández-Piérola, I.; Horta, A. *J. Chim. Phys. Phys.-Chim. Biol.* **1980**, *77* (4), 271.
(18) Okita, K.; Teramoto, A.; Kawahara, K.; Fujita, H. *J. Phys. Chem.* **1968**, *72*, 278.
(19) Prolongo, M. G.; Masegosa, R. M.; Hernández-Fuentes, I.; Horta, A. *Polymer*, in press.
(20) Prolongo, M. G.; Masegosa, R. M.; Hernández-Fuentes, I.; Horta, A. *Macromolecules* **1981**, *14*, 1526.
(21) Masegosa, R. M.; Prolongo, M. G.; Hernández-Fuentes, I.; Horta, A. *Ber. Bunsenges. Phys. Chem.* **1984**, *88*, 103.
(22) Mehling, I. G.; Onken, U.; Arlt, W. "Vapor-Liquid Equilibrium Data Collection"; Dechema: 1978, Vol. I, Part 2b.
(23) Horta, A.; Prolongo, M. G.; Masegosa, R. M.; Hernández-Fuentes, *Polymer* **1981**, *22*, 1147.
(24) Read, B. E. *Trans. Faraday Soc.* **1960**, *56*, 382.
(25) Živný, A.; Pouchlý, J.; Šolc, K. *Collect. Czech. Chem. Commun.* **1967**, *32*, 2753.
(26) Katime, I.; Campos, A.; Teijón, J. M. *Eur. Polym. J.* **1979**, *15*, 291.
(27) Pouchlý, J.; Živný, A.; *J. Polym. Sci., Part A-2* **1972**, *10*, 1467.
(28) Tuzar, Z.; Bohdanecký, M. *Collect. Czech. Chem. Commun.* **1969**, *34*, 284.
(29) Horta, A.; Fernández-Piérola, I. *Polymer* **1981**, *22*, 783.
(30) Pouchlý, J.; Živný, A. *J. Polym. Sci., Part A* **1972**, *10*, 1481.
(31) Pouchlý, J.; Patterson, D. *Macromolecules* **1976**, *9*, 574.
(32) Horta, A. *Macromolecules* **1979**, *12*, 785.
(33) Flory, P. J. *Discuss. Faraday Soc.* **1970**, *49*, 7.
(34) Bondi, A. "Physical Properties of Molecular Crystals Liquid and Glasses"; Wiley: London, 1968.

# Analysis of Stress-Induced Phase Separations in Polymer Solutions

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ABSTRACT: The free energy of polymer solutions must depend upon the conformation of the macromolecules, and hence upon the deformation state imposed on the system, as well as upon the more familiar thermodynamic state variables of temperature and composition. As one consequence of the importance of this additional thermodynamic state variable, the precipitation temperature (cloud point) of polymer solutions may be increased by several tens of degrees Centigrade by imposition of steady shearing at low deformation rates. As a second consequence, the precipitated phase is sometimes found to be a solid of new morphology, and one which is quite refractory to re-solution. In this work a quantitative theoretical analysis of solubility phenomena in deforming solutions is given. The free energy of macromolecules in stagnant solutions is obtained from the Flory–Huggins theory, and changes with deformation state are computed from Marrucci's analysis for dilute solutions of elastic dumbbells. The parameters in the theoretical analysis were evaluated, using solutions of polystyrene in dioctyl phthalate, by measurements of the thermodynamic interaction parameter and of the rheological properties. The theory, which contains no adjustable parameters, was used to make a priori predictions of the change in cloud point with deformation state. The experimentally observed changes, of 3–28 °C, were predicted with a mean deviation of about 3 °C.

## Introduction

Simple shear, when applied to materials, imparts both extension and rotation to a fluid element, under the influence of which polymer molecules will be oriented and stretched. In this way the distribution of the orientation and the end-to-end distance of the macromolecular coils will be modified, and such modifications may result in drastic changes of the behavior of the material: it may lead to precipitation of polymer aggregates, as found by Joly,[1] to fiber formation,[2-5] or to formation of a second fluid phase.[6,7] A more complete review of the literature is given in Table I, which summarizes published studies of phase separation during mechanical deformation. In addition, we call attention to the excellent reviews of fiber formation in deforming solutions published by McHugh and Forrest[3] and by Peterlin.[4]

A cursory examination of Table I reveals that in many instances mild deformations are sufficient to create phase changes. The formation of aggregates occurs in many flow geometries (cone and plate, concentric cylinders, tube flow, and converging and extensional flows). Its occurrence is quite general for a variety of both polar and nonpolar polymers of high molecular weight in a broad range of concentration (including melts), of temperature, and of solvent type. Dunlop and Cox[30] have additionally considered the importance of aggregate formation in very dilute solutions such as those encountered in turbulent drag reduction.

Several specific examples of the studies cited in Table I illustrate the diversity and permanence of the new phases formed by the deformation of a fluid. Laufer et al.[23] found, using a cone-and-plate viscometer, that polymer particles had precipitated during the shearing process; these re-

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