decrease in $N\chi_{\text{blend}}$ in order to satisfy the inequality on the left side of eq 36, as well as the inequality in eq 37. Thus, as more copolymer is added, the compatibility between copolymer–homopolymer may also need to be increased.)

In summary, we have generated new phase diagrams for ternary blends of the type A/B/AB. The diagrams show that miscibility in these systems is extremely sensitive to the value of θ or the copolymer sequence distribution. Also evident is the fact that the block copolymer does not always act as the best bulk agent in creating a completely miscible A/B/AB blend. This observation concurs with recent experimental findings.[13] We hope our predictions concerning the complicated phase diagrams that can be obtained with this model will encourage new experimental efforts in this area. We conclude by noting that our future work will examine the compatibilizing efficiency of block copolymers in microphase-separated systems. In this regime, the entropy term in our model (ΔS) must be modified. Specifically, the theory must reflect the reduction in ΔS when block copolymers undergo microphase separation.

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Association Equilibria Theory of Preferential Adsorption in Systems with Solvent–Solvent and Solvent–Polymer Interactions

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ABSTRACT: The theory of association equilibria is used to derive the amount of preferential adsorption for polymer–mixed solvent systems in which one of the two liquids in the mixed solvent (B) autoassociates and interacts specifically with the polymer and with the other liquid (A). The model takes into account the constants for the association of one molecule of B to one site in A and of one molecule of B to one site in the polymer and also the corresponding constants for the multiple self-association of B for the case where the first B molecule is associated either with A or with the polymer or is free. The theoretical results are applied to the systems poly(alkyl methacrylate)s, alkyl = Me, Et, iBu, in the mixed solvent methanol (B) + 1,4-dioxane (A). The experimental results of these systems can be quantitatively well reproduced by the theory.

Introduction

Preferential or selective adsorption is a very common phenomenon in ternary systems composed of a polymer and a binary solvent mixture. There is a great variety of ternary systems that have been studied, mainly those containing at least one polar component.[1] In many cases, specific interactions between polar groups are important, and the formation of hydrogen bonds have to be taken into account. This is the case, especially, when alcohols are components of the system.

In systems with specific interactions random mixing cannot be assumed. Hence, the thermodynamic theories traditionally used to interpret ternary system properties, such as the Flory–Huggins formalism or the equation-of-state theory of Flory,[2] are expected not to apply to such systems.

For systems showing strong specific effects such as hydrogen bonding, Pouchlý et al.[3-5] have developed a theoretical framework that is based on the theory of association equilibria.[4] The existence of associated complexes formed by association of individual molecules is explicitly recognized in such theory, and the thermodynamic properties are derived from the equilibrium constants for association. This type of formalism is expected to be useful in the interpretation of systems having complexation by hydrogen bonding, such as those containing alcohols or water, which are liquids frequently found in studies of polymers in mixed solvents.

The treatment in such theory of association equilibria, although straightforward, is more difficult to develop in detail than the usual random thermodynamic treatment. As far as we know, the theory of association equilibria has

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been fully developed and applied only for the particular case in which one of the two liquids in the mixed solvent self-associates and interacts specifically with the polymer while the other solvent is inert (Pouchlý and Živný).[3]

Extending the same treatment to other closely related systems is desirable, because comparison among systems could lend confidence to the validity of the parameters used in the theory.

Here, we extend the theoretical treatment to the case in which one of the liquids self-associates, interacts specifically with the polymer, and also interacts specifically with the molecules of the other liquid. This case is thus somewhat more general, and the theoretical results obtained for it include the previous case of one liquid being inert as a particular case.

Our first task in the present paper is to develop such a theoretical scheme for the preferential adsorption coefficient, λ. Later we apply these equations to experimental results of λ for the systems poly(alkyl methacrylate)–1,4-dioxane–methanol,[6] which are expected to be good examples of systems having the type of interactions assumed in the theory. Namely, one of the mixed liquids (here methanol) self-associates, and hydrogen bonds are formed to the polar groups of the polymer (ester carbonyl), as well as to the other liquid (here 1,4-dioxane), which is a hydrogen bond acceptor (through the ether oxygen).

Theory

Ternary System Polymer–Mixed Solvent. The components of the mixed solvent will be identified as B (for the self-associated liquid) and A, and the polymer, as C.

In the ternary system there are different specific interactions. We assume self-association of B, which is open and uniform; i.e., chainlike complexes of any length are formed. The joining of each additional B molecule to the associated chain is characterized by self-association constant σ. B interacts specifically with sites along the polymer chain. Therefore, we have to consider association constants of B with C. Following the scheme of ref 3, we assume that the polymer molecule has m_C sites for specific interactions with B, that the constant for such specific interaction between one B and one site in C is η_c, and that the self-association of B when the first B is associated with a site in C is characterized by the constant σ_c. This σ_c is expected to have a smaller value than σ due to some hindrance of the polymer chain, and it is also expected that η_c or σ_c, or both, will vary from polymer to polymer depending on the size of the alkyl substituent.

In addition to considering the association constants of B with C (η_c, σ_c), we have to postulate also association constants of B with A. These are η_a and σ_a. The number of sites on A is called m_A. The constant for the association of one B with one site in A is η_a, and the self-association of B when the first B is associated with a site in A is σ_a.

Considering independent behavior of the m_C sites in the polymer, we deduce for the ternary system

$$\sum_s \nu_s = P_A\left(1 + \frac{\eta_a P_B}{1 - \sigma_a P_B}\right)^{m_A} + \frac{P_B}{1 - \sigma P_B} + P_C\left(1 + \frac{\eta_c P_B}{1 - \sigma_c P_B}\right)^{m_C} \quad (1)$$

where ν_s is the amount of substance in moles of the s complex per 1 mol of sites of the Flory–Huggins lattice, and P_K are concentrations of molecules not involved in the complexes. The symbol $\sum_s$ means summation over all coexisting species of complexes, including free unimers, following the notation of ref 3.

From the $\sum_s \nu_s$ of eq 1, we can obtain ν_A, ν_B, and ν_C, i.e., the nominal concentration of components in moles per moles of sites, according to:[3]

$$\nu_K = \frac{\partial \sum_s \nu_s}{\partial \ln P_K} \qquad K = \text{A, B, C} \quad (2)$$

If we call r_K the ratio of molar volumes, $r_K = V_K/V_B$, then $\Phi_K = r_K\nu_K$, where Φ_K is the volume fraction of component K.

The Gibbs mixing function per lattice site, ΔG_N, for the ternary system is[3]

$$\frac{\Delta G_N}{RT} = \sum_K^3 \left[\nu_K \ln \frac{P_K}{P_K{}^0} + \Phi_K(\sum_s \nu_s)_K{}^0\right] - \sum_s \nu_s + \sum_{K<J}\sum^3 \nu_K \Phi_J g_{KJ}{}' \quad (3)$$

where the double index K^0 is related to the pure component K and $g_{KJ}{}'$ is the constant parameter for nonspecific interactions K–J.

From this ΔG_N, we have to calculate the preferential adsorption coefficient λ. According to Pouchlý et al.,[3] it is given by

$$\lambda = -\bar{v}_C{}^0 \frac{M_{AC}}{M_{AA}} \quad (4)$$

where $\bar{v}_C{}^0$ is infinite dilution partial specific volume of polymer and M_{KJ}'s are the second derivatives of $G_u{}^*$ defined as

$$M_{KJ} = \left(\frac{\partial^2 G_u{}^*}{\partial u_K \partial u_J}\right)^0 \quad (5)$$

with

$$G_u{}^* = (1 + u_C)\frac{RT}{V_B}\left(\frac{\Delta G_N}{RT} - \frac{\Phi_C}{r_C} \ln \Phi_C\right) \quad (6)$$

where u_K is volume fraction referred to the volume occupied by the liquid mixture: $u_K = \Phi_K(1 + u_C)$, and superscript zero means the limit $u_C \rightarrow 0$.

The derivatives M_{AA} and M_{AC} are obtained theoretically by finding the corresponding second derivatives of $G_u{}^*$, with ΔG_N given by the association equilibria theory (eq 3). These theoretical M_{AA} and M_{AC} are used in eq 4 to obtain λ.

We define the weight average degree of self-association of B in the solvent mixture, j_w, the average number of B molecules bound by specific forces to one segment of C in an infinitely dilute solution, j_c, and the average number of B bound by specific forces to one segment of A in the liquid mixture, j_a.

They are given in terms of $\sum_s \nu_s$ as

$$\frac{r_K j}{P_{B0}} = \left(\frac{\partial^2 \sum_s \nu_s / \partial P_B \partial P_K}{\partial \sum_s \nu_s / \partial P_K}\right)^0 \quad (7)$$

with $j = j_a$, j_w, and j_c, for K = A, B, and C, respectively. Subscript zero in P_{B0} or in other concentration variables denotes the liquid mixture outside the polymer coils.

Using the equivalences

$$P_K = \frac{\Phi_K}{r_K}\left(\frac{\partial \sum_s \nu_s}{\partial P_K}\right)^{-1} \quad (8)$$

we can write $G_u{}^*$ as

$$\frac{V_A}{RT}G_u{}^* = u_A \ln \Phi_A + r_A u_B \ln \Phi_B + \frac{1}{1+u_C}(u_A u_B g_{AB}' + u_A u_C g_{AC}' + r_A u_B u_C g_{BC}') - u_A \ln\left(\frac{\partial \sum_s \nu_s}{\partial P_A}\right) - r_A u_B \ln\left(\frac{\partial \sum_s \nu_s}{\partial P_B}\right) - \frac{r_A}{r_C}u_C \ln\left(\frac{\partial \sum_s \nu_s}{\partial P_C}\right) - r_A(1+u_C)\sum_s \nu_s + r_A u_A(\sum_s \nu_s)_A{}^0 + r_A u_B(\sum_s \nu_s)_B{}^0 + r_A u_C(\sum_s \nu_s)_C{}^0 - r_A u_B \ln (P_B{}^0) \quad (9)$$

Using the form of $\sum_s \nu_s$ appropriate for the type of association equilibria, we are considering, namely, eq 1, we finally obtain

$$\frac{V_A}{RT}M_{AC} = \frac{-1 - r_A\frac{u_{A0}}{u_{B0}}\frac{j_a}{j_w} + \frac{r_A j_a + r_A}{j_w}\left(1 + \frac{j_c}{u_{B0}}\right)}{1 - \frac{u_{A0}}{u_{B0}}\frac{r_A j_a{}^2}{j_w}} + g_{AC}' - r_A g_{BC}' + (u_{A0} - u_{B0}) r_A g_{BA}' \quad (10)$$

and

$$\frac{V_A}{RT}M_{AA} = \frac{\frac{1}{u_{A0}} + \frac{r_A + 2r_A j_a}{j_w}\frac{1}{u_{B0}}}{1 - \frac{u_{A0}}{u_{B0}}\frac{r_A j_a{}^2}{j_w}} - 2r_A g_{BA}' \quad (11)$$

with

$$j_a = \frac{m_A}{r_A}\frac{\eta_a P_{B0}}{(1 - \sigma_a P_{B0})[1 + (\eta_a - \sigma_a)P_{B0}]} \quad (12)$$

$$j_c = \frac{m_C}{r_C}\frac{\eta_c P_{B0}}{(1 - \sigma_c P_{B0})[1 + (\eta_c - \sigma_c)P_{B0}]} \quad (13)$$

$$j_w = \left\{\frac{1}{(1 - \sigma P_{B0})^2} + m_A \eta_a P_{A0}\frac{[1 + (\eta_a - \sigma_a)P_{B0}]^{m_A - 1}}{(1 - \sigma_a P_{B0})^{m_A + 1}}\right\}^{-1} \times \left\{\frac{1}{(1 - \sigma P_{B0})^2}\frac{1 + \sigma P_{B0}}{1 - \sigma P_{B0}} + m_A \eta_a P_{A0}\frac{[1 + (\eta_a - \sigma_a)P_{B0}]^{m_A - 1}}{(1 - \sigma_a P_{B0})^{m_A + 1}} \times \frac{1 + \sigma_a P_{B0} + \frac{(m_A - 1)\eta_a P_{B0}}{1 + (\eta_a - \sigma_a)P_{B0}}}{1 - \sigma_a P_{B0}}\right\} \quad (14)$$

In these equations, P_{B0} is related to the liquid mixture composition, u_{B0}, through

$$P_{B0} = (1 - \sigma P_{B0})^2 \hat{u}_{B0} \quad (15)$$

with

$$\hat{u}_{B0} = u_{B0}\left\{1 + \frac{m_A}{r_A}\frac{\eta_a u_{A0}(1 - \sigma P_{B0})^2}{(1 - \sigma_a P_{B0})[1 + (\eta_a - \sigma_a)P_{B0}]}\right\}^{-1} \quad (16)$$

Equation 15 can be considered as second degree in P_{B0} and solved formally as

$$P_{B0} = \frac{1 + 2\sigma\hat{u}_{B0} - (1 + 4\sigma\hat{u}_{B0})^{1/2}}{2\sigma^2\hat{u}_{B0}} \quad (17)$$

obtaining P_{B0} from u_{B0} by iteration.

The equations for j_w and $\hat{u}_{B0}$ are simplified when we introduce the assumption $\sigma_a = \sigma$. They are further simplified when using $m_A = 1$.

Binary Liquid Mixture. The expression for the Gibbs mixing function per lattice site, ΔG_N, for the binary mixture, according to the association equilibria theory, is given by eq 3 with $\Phi_C = 0$, $\sum \nu_s$ having the same meaning as in eq 1, but with $P_C = 0$, and ν_A and ν_B being obtained from $\sum \nu_s$ through eq 2. P_A and P_B refer now to the A + B mixture.

According to the Flory–Huggins model, we can write the binary ΔG_N as

$$\frac{\Delta G_N}{RT} = \nu_A \ln \Phi_A + \nu_B \ln \Phi_B + \nu_A \Phi_B r_A g_{BA} \quad (18)$$

where g_{BA} is the Flory–Huggins interaction parameter. This interaction parameter is used as a phenomenological coefficient whose value is determined from the experimental values of ΔG_N for the mixture. Its results thus are composition dependent, in contrast with g_{BA}', which by definition of the model is constant (recall that g_{BA}' is the interaction parameter for nonspecific effects). For the binary liquid mixture Φ_B is equivalent to the previously used u_{B0}.

Comparing eq 3 ($\Phi_C = 0$) and eq 18, we obtain for the Flory–Huggins interaction parameter g_{AB}, as given by the association equilibria theory

$$g_{BA} = g_{BA}' + \frac{1}{\Phi_A}\ln\frac{\hat{\Phi}_B}{\Phi_B} + \frac{2}{\Phi_A}\ln(1 - \sigma P_B) - \frac{m_A}{r_A\Phi_B}\ln\left(1 + \frac{\eta_a P_B}{1 - \sigma_a P_B}\right) - \frac{1}{\Phi_A}\left(\ln P_B{}^0 - \frac{P_B{}^0}{1 - \sigma P_B{}^0}\right) - \frac{1}{\Phi_A\Phi_B}\frac{P_B}{1 - \sigma P_B} \quad (19)$$

with $\hat{\Phi}_B$ ($\equiv\hat{u}_{B0}$) given by eq 16 and P_B ($\equiv P_{B0}$) given by eq 17 and $P_B{}^0 = P_B$ ($\hat{\Phi}_B = 1$). Since P_B is s function of $\hat{\Phi}_B$ and $\hat{\Phi}_B$ is a function of P_B, eq 17 has to be solved by iteration.

Application

The systems to which we apply now the theory are the methyl, ethyl, and isobutyl methacrylate polymers (PMMA, PEMA, PiBMA, respectively), all in the mixed solvent 1,4-dioxane (A) + methanol (B). It is supposed that methanol associates with the carbonyl of the polymer ester group and with the ether oxygens of 1,4-dioxane. The experimental results of λ for these systems are from ref 6.

Binary Liquid Mixture. We first determine the parameters of the theory corresponding to the liquid mixture 1,4-dioxane + methanol by comparison with the experimental results of the molar excess function, $G_m{}^E$, of this mixture. Such experimental $G_m{}^E$ is reduced to the form of empirical value of g_{BA} through

$$g_{BA} = \frac{1}{X_B\Phi_A}\left[\frac{G_m{}^E}{RT} + X_A \ln\frac{X_A}{\Phi_A} + X_B \ln\frac{X_B}{\Phi_B}\right] \quad (20)$$

with X_K = mole fraction.

The experimental g_{BA}'s at the temperature 298 K, at which λ was determined, were calculated from $G_m{}^E$ data in the literature at other temperatures. In ref 7 we find $G_m{}^E$ values for 1,4-dioxane + methanol in the form of Wilson and NRTL equations. Two sets of coefficients for these equations are given: one obtained from experimental data determined at 293 K, the other from experimental data determined at 303 K. They conveniently bracket our working temperature of 298 K. To obtain g_{BA}, we put T = 298 K in the Wilson and NRTL equations and use both sets of coefficients. The values thus calculated for g_{BA}

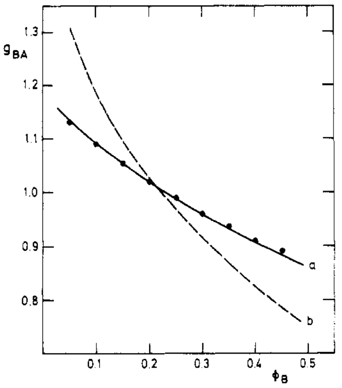

Figure 1. Fit of the theoretical Flory–Huggins interaction parameters, g_{BA} for the liquid mixture 1,4-dioxane (A)–methanol (B). Points: Experimental data = mean g_{BA} values at 298 K, calculated from data of Wilson and NRTL equations at 293 and 308 K from ref 7. Curve a: calculated for $g_{BA}' = 0.85$, $\sigma = 400$, $\eta_a = 244$, $m_A = 1$. Curve b: calculated for $g_{BA}' = 0.30$, $\sigma = 400$, $\eta_a = 100$, $m_A = 1$.

depend slightly on the type of equation chosen and on the set of coefficients used in it. However, for a given Φ_B, differences in the g_{BA} calculated are small (within 2% of the mean value). We take for g_{BA} the average of all four calculations (Wilson, 293 and 308 K; NRTL, 293 and 308 K). These mean values are shown in Figure 1.

Now, the fitting criterion, in order to determine the parameters σ, η_a, σ_a, m_A, and g_{BA}', is to obtain the least-squares deviation in the range $\Phi_B = 0$–0.45 between these experimental g_{BA} and the ones calculated from the association equilibria theory as explained before.

Since we have too many parameters, we try to simplify. First, we take $\sigma_a = \sigma$, under the assumption that the self-association of B would not be hindered by A if B is already associated with a site of A. The molecule of A is small enough not to restrict appreciably the accessibility of other B molecules to the one attached to one site. Also, for m_A we taken only two possible values: $m_A = 1$ or 2, corresponding to a saturation of the acceptor capacity of dioxane when one proton of the donor is attached or to independent capacity of donor–acceptor exchange for both oxygen atoms of the dioxane molecule, respectively.

We also have as a guide the previous results obtained for the benzene–methanol mixture in which it was found $\sigma = 400$.[3] Since σ refers to the self-association of pure methanol, independent of the companion liquid, we take here $\sigma = 400$ also, for consistency with previous results.

Presumably, η_a for the heterocontact methanol–dioxane should be smaller than σ for the self-contact of methanol ($\eta_a < \sigma$).

Also, it is reasonable to expect that g_{BA}' should be only a fraction of the experimental g_{BA} ($g_{BA}' < g_{BA}$).

Input Parameters for the Liquid Mixture. With $\sigma = 400$ and $m_A = 1$, the minimum deviation is found for $g_{BA}' = 0.85$ and $\eta_a = 244$. The fit of the experimental g_{BA} by theory using these parameter values is perfect (standard deviation of 0.3%), as it can be seen in Figure 1, curve a.

In order to obtain a set of parameters involving lower values of η_a (the association constant of B with A), in curve b of Figure 1, we have represented the fit of experimental g_{BA} by theory using $\sigma = 400$, $m_A = 1$, $\eta_a = 100$, and $g_{BA}' = 0.3$. This g_{BA}' value corresponds to a minimum in the standard deviation (9%) for $\eta_a = 100$. This set of parameters has been selected because, as we will see in the following section, it is the set that gives the best fit for experimental λ values.

When $m_A = 2$ (maintaining $\sigma = 400$) is used, the fit of g_{BA} results is always worse than using $m_A = 1$. Therefore, from now on we concentrate on presenting the results for the $m_A = 1$ case only.

Table I
Parameter Values Giving the Minimum Deviation (δ) between Theory and Experiment,[6] for the Preferential Adsorption Coefficient, λ, Calculated According to the Association Equilibria Theory

	polymer	σ	g_{BA}'	η_a	σ_c	$g_{AC}' - r_A g_{BC}'$	η_c	δ
1	PMMA	400	0.85	244	400	0.0	5.7	0.034
2	PEMA	400	0.85	244	400	−1.2	59.3	0.028
3	PiBMA	400	0.85	244	400	−2.3	129.5	0.018
4	PMMA	400	0.30	100	400	−3.4	243.2	0.013
5	PEMA	400	0.30	100	400	−2.75	169.2	0.014
6	PiBMA	400	0.30	100	400	−1.6	88.2	0.009
7	PMMA	400	0.85	244	375	−0.1	11.2	0.034
8	PEMA	400	0.85	244	375	−2.2	145.4	0.028
9	PiBMA	400	0.85	244	375	−1.6	100.7	0.035
10	PMMA	400	0.30	100	375	−2.45	195.5	0.013
11	PEMA	400	0.30	100	375	−1.75	125.0	0.016
12	PiBMA	400	0.30	100	375	−0.5	45.6	0.016

Preferential Adsorption Coefficient. Parameters for the Ternary System. We calculate λ according to the association equilibria theory, by means of eq 4–17. The values of the parameters σ, η_a, g_{BA}', and m_A are fixed from the comparison with the experimental g_{BA}. For the remaining parameters η_c, σ_c, and $g_{AC}' - r_A g_{BC}'$, we have the previous study of the system PMMA (C)–benzene (A)–methanol (B) as a guide.[3] In that system, parameters η_c and σ_c refer to the specific interaction of methanol with the polymer PMMA. Here, in one of our systems, we have this same polymer–solvent pair, so we expect η_c and σ_c to have the same values as found before.[3] These were $\sigma_c = 375$ and $\eta_c = 6.5$. But the theoretical λ calculated for PMMA in the mixture 1,4-dioxane–methanol using these same parameter values for the interaction PMMA–methanol and different trial values for $g_{AC}' - r_A g_{BC}'$, either with $\eta_a = 244$, $g_{BA}' = 0.85$ or with $\eta_a = 100$, $g_{BA}' = 0.3$, gives an unacceptable representation of the experimental λ. We are forced to change the values of η_c and σ_c altogether. This represents a weakness of the theory, since a unique value is not found for each type of interaction irrespective of the system studied.

Then, we proceed to vary all three parameters σ_c, η_c, and $g_{AB}' - r_A g_{BC}'$, looking for a minimum in the standard deviation, δ:

$$\delta = \left[\frac{1}{n} \sum_{i=1}^{n} (\lambda_i^{\mathrm{calc}} - \lambda_i^{\mathrm{exptl}})^2 \right]^{1/2} \tag{21}$$

In this search, the values of σ_c, η_c, and $g_{AC}' - r_A g_{BC}'$ have been scanned at intervals of 25 in σ_c, 0.1 in η_c, and 0.05 in $g_{AC}' - r_A g_{BC}'$. The lowest δ's have been found for the sets of parameter values that are summarized in Table I. In this table we also collect the different sets of parameters selected for the liquid mixture in the preceding section of the paper. The theoretical curves calculated with the sets of parameter values giving lowest δ are shown in Figure 2. We can see that they reproduce the main features of the experimental variation of λ.

Discussion

Although we obtain a good agreement between theory and experiment, it is necessary to discuss the numerical values found for the parameters. Let us see first whether these values are reasonable. For the self-association of methanol, $\sigma = \sigma_a = \sigma_c = 400$ agrees well with the known data for hydrogen bonding in methanol. Thus, an equilibrium constant for 400 corresponds to a Gibbs energy for hydrogen bond formation of −15 kJ·mol^{-1}, which is the value found for methanol.[8] For the association of methanol

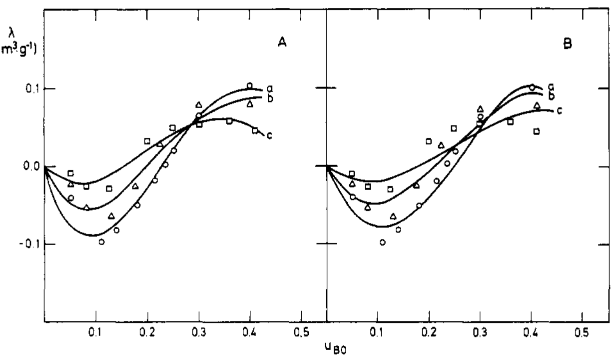

Figure 2. Comparison of theory and experiment for preferential adsorption coefficient, λ, of poly(alkyl methacrylate)s in 1,4-dioxane–methanol. (u_{B0} = methanol volume fraction). Points: Experimental results from ref 6. (○) PMMA (alkyl = Me); (△) PEMA (Et); (□) PiBMA (iBu). Association equilibria theory. (2-A) Calculated with the parameter values shown in Table I and numbered as 4–6. Curves: (a) PMMA; (b) PEMA; (c) PiBMA. (2-B) Calculated with the parameter values shown in Table I and numbered as 10–12. Curves: (a) PMMA; (b) PEMA; (c) PiBMa.

to dioxane or to the carbonyl of polymer we have as a guide studies of liquid mixtures composed of a hydrogen bonding self-associated liquid and a hydrogen bond acceptor, such as methanol + methyl acetate and H_2O + THF.[9] The heat capacity of these mixtures has been interpreted using an association equilibria model. The equilibrium constant for proton donor–proton acceptor complex formation was found lower than that of the proton donor self-association, but not very different from it.[9] Thus, our use of $\eta_a = 100$ and 244 and η_c in a wide range of values up to 243 is reasonable. (For the polymer we are using the approximation $m_C/r_C = 1$, so variations in the value of η_c reflect changes in site–segment ratios besides differences in the strength of the polymer–methanol complex.)

Let us discuss now the consequences and physical meaning of the different values found for η_a and η_c. We divide this discussion into two points: first, the influence of η_a and η_c on the length of the methanol chains (associated to polymer, associated to dioxane, or free); second, how η_a and η_c influence the shape of the preferential adsorption curve (λ vs u_{B0}, with its minimum, inversion, and maximum points).

We start with the influence of η_a and η_c on the length of methanol chains. j_a and j_w depend only on η_a, while j_c depends simultaneously on η_a and η_c. $\eta_a = 0$ means no association of methanol to dioxane. For $\eta_a = 0$ the length of the free methanol chains varies with u_{B0} from $j_w = 9.0$ ($u_{B0} = 0.05$) to $j_w = 26.9$ ($u_{B0} = 0.45$; $\sigma_a = \sigma = 400$). When the association with dioxane takes place ($\eta_a > 0$), the chains of methanol become much shorter. The association of methanol to dioxane effectively cuts the chains by a factor of 4–7. Thus, $j_w = 1.7$ ($u_{B0} = 0.05$) and 6.7 ($u_{B0} = 0.45$), for $\eta_a = 100$, and $j_w = 1.3$ ($u_{B0} = 0.05$) and 5.0 ($u_{B0} = 0.45$), for $\eta_a = 244$. The methanol–dioxane complexes that are formed are even shorter. This can be seen from the very low values of j_a compared with j_w. For example, $j_a r_A = 0.11$ ($u_{B0} = 0.05$); 1.6 ($u_{B0} = 0.45$), either for $\eta_a = 100$ or $\eta_a = 244$ (j_a changes very little with η_a for η_a values above 50). Therefore, dioxane cuts the length of free methanol chains and forms methanol–dioxane complexes, which contain much shorter chains.

The association of methanol to polymer is gauged by η_c. For $\eta_c = 0$ there is no such association. As η_c increases, j_c also increases. For $\eta_a = 100$, $\eta_c = 243$ (case 4 in Table I), the j_c values are $j_c r_C/m_C = 0.24$ ($u_{B0} = 0.05$) and 2.5 ($u_{B0} = 0.45$). Thus, larger methanol chains associate to the polymer site than to the dioxane molecule. But still, these methanol–polymer site complexes are much shorter than the self-complexes of free methanol. So the length of the methanol chains in the complexes are in the order methanol–dioxane < methanol–polymer < methanol–methanol (in dioxane) < methanol–methanol (in an inert solvent).

By comparing the three polymers (with the set of parameter values giving the best fit of experimental λ: cases 4–6 in Table I), we see that the value of η_c decreases with increasing size of the lateral substituent. This is reasonable if we believe that the bulkiness of the substituent poses steric hindrance to the formation of methanol–carbonyl complexes.

At infinite dilution of polymer, there are no free polymer sites; all are in the form of complexes with methanol. The length of the methanol chains in these complexes is a growing function of u_{B0}. This has important consequences for the shape of the preferential adsorption curve. We take now this second point of the discussion: the influence of η_a and η_c on the form of λ vs u_{B0}. We have to distinguish three zones or ranges of u_{B0}. The range where methanol is preferentially adsorbed (λ < 0), the inversion point (λ = 0), and the range where dioxane is preferentially adsorbed (λ > 0).

The preferential adsorption of methanol is determined both by η_c and η_a. Since the association of methanol to a polymer site is gauged by η_c, it is natural that large values of η_c give increased preferential adsorption of methanol (more negative λ). j_c in M_{AC} (eq 10) is responsible for this effect, but η_a has also some influence. Large values of η_a disfavor the adsorption of methanol to polymer because dioxane is competing for complex formation. The influence of η_a is exerted through j_a, j_w in M_{AC} (eq 10) and in M_{AA} (eq 11).

At the inversion point, the number of methanol molecules associated with a polymer site are 1.1 (PMMA), 0.7 (PEMA), 0.35 (PiBMA) (cases 4–6 of Table I). So, zero preferential adsorption does not mean that methanol is not associated to polymer but rather a compensation of effects.

After the inversion, dioxane is preferentially adsorbed (λ > 0). In spite of this, methanol continues to be associated with the polymer in this range. Then, what are the factors determining an overall preferential adsorption of dioxane? In M_{AC} (eq 10) there are three contributions. One comes from specific interactions (the fraction in eq 10). This gives always a negative contribution to λ (for the sets of parameter values being used). The other two are from nonspecific effects. One is due to the interaction between liquids (the term containing g_{BA}' in eq 10). This also gives a negative contribution to λ (in the range of u_{B0} where the polymers are soluble). The only term left for dioxane to be preferentially adsorbed is the one related to the balance of solvent–polymer nonspecific interactions ($g_{AC}' - r_A g_{BC}'$ in eq 10).

The preferential adsorption of dioxane is thus attributed in the theory to the difference in solvent quality of the two liquids. If dioxane is a better solvent of the polymers (for reasons other than the associating capacity of methanol), then $g_{AC}' - r_A g_{BC}' < 0$, and this term gives a positive contribution to λ. This contribution is not influenced by the value of η_c, but it is influenced by the value of η_a through M_{AA}. In the range where λ > 0, M_{AA}^{-1} is larger for higher η_a's. Therefore, the preferential adsorption of dioxane is favored by large η_a's (the formation of methanol–dioxane complexes acts in favor of the preferential adsorption of dioxane).

We mentioned before that the length of the methanol chains associated to polymer, j_c, is an increasing function of u_{B0}. In fact, j_c increases faster than u_{B0} (for the parameter values being used), so that j_c/u_{B0} in M_{AC} (eq 10) still grows with u_{B0}. This means that in the range of large u_{B0}'s the preferential adsorption of dioxane is opposed by an ever increasing length of the methanol–polymer complexes. These two opposing effects finally reach a compensation that is responsible for the appearance of a maximum in λ. After this maximum, the growing methanol–polymer complexes dominate and λ starts to decrease.

This is exactly the behavior suggested by the experimental points. Its prediction is one of the successes of the theory. Any other theory not taking into account association equilibria would miss this maximum and yield a continuous increase of λ after the inversion point (in the range of u_{B0} accessible to experiment).

Let us finally comment on the values of the parameters for nonspecific interactions. We notice that the $-(g_{AC}' - r_A g_{BC}')$ values required are very large. If dioxane were an athermal solvent ($g_{AC}' = 0$) and methanol would have a g_{BC}' value similar to the g interaction parameter of poor solvents in systems with no specific interactions ($g_{BC}' \simeq 0.8$),[10] then $g_{AC}' - r_A g_{BC}'$ would be around -1.7. Our values are not too far from this situation. However, the polymer–solvent parameters for physical interactions, g_{AC}' and g_{BC}', are assumed constant in the theoretical model applied here. This could be a simplification that is more important in the case of g_{BC}'.

Regarding the parameter for the liquid mixture, g_{BA}', the value that best fits the experimental results of λ is lower than the g_{BA}' obtained from G_m^E of the mixture. This is similar to the case of ternary systems when they are analyzed in terms of the Flory–Huggins model. In fact, the binary parameter g_{BA} necessary to fit λ is lower than that of the mixture, which is usually represented by a ternary contribution g_T, and then in the expression of λ, g_{BA} is expressed as a difference $g_{BA} - g_T$.

Finally, we can conclude that the association equilibria theory of preferential adsorption applied to systems with solvent–solvent and solvent–polymer interactions results in a good description of the experimental data on the poly(alkyl methacrylate)–1,4-dioxane–methanol systems. A quantitative agreement between theory and experiment is found.

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Registry No. PMMA, 9011-14-7; PEMA, 9003-42-3; PiBMA, 9011-15-8; methanol, 67-56-1; 1,4-dioxane, 123-91-1.

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