Preferential Adsorption Determined by Specific Interactions. Poly(dialkyl itaconates)/1,4-Dioxane/Methanol[†]

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Received March 2, 1990; Revised Manuscript Received May 17, 1990

ABSTRACT: The variation of the preferential adsorption coefficient, λ, with the solvent composition, for a series of poly(dialkyl itaconates) is studied in the mixed solvent 1,4-dioxane/methanol. In these systems specific hydrogen bonding of methanol to 1,4-dioxane and to the polymer take place. Methanol is preferentially adsorbed at low methanol composition, but 1,4-dioxane is preferentially adsorbed at high compositions. All systems here studied show inverstion in λ. The variation of λ with solvent composition depends on the size of the side group of the polymer. In order to interpret the influence of hydrogen bonding on these systems, the recent theory of the association equilibria has been applied. According to the results of this theory, the inversion and extrema of λ come from a balance of effects: the high quality of 1,4-dioxane as solvent and the length of the chains of self-associated methanol, which are complexed with the polymer. It is possible to find a quantitative agreement between this theory and experimental results by using reasonable values for the association constants and interaction parameters of the theory.

Introduction

The study of dilute-solution properties of macromolecules in binary solvents has been a matter of current interest in different areas of polymer chemistry.[1] In these kinds of systems, preferential adsorption into a macromolecular coil plays an important role. In fact, there are a great variety of ternary systems where preferential adsorption has been studied from the experimental point of view.[1] The majority of data reported on preferential adsorption concerns systems containing at least one polar component.[1] Several attempts to offer an adequate and quantitative theoretical description of experimental data of preferential adsorption coefficient λ have been performed by several authors.[2–9] Classical thermodynamic theories[10–13] have been used for these purposes, which were later improved by Pouchlý et al.[14,15] and Horta et al.[6,7,16,17]

In the case of ternary systems containing polar components, specific interactions take place, and hydrogen bonds are often formed. Therefore, the applicability of the thermodynamic theories to such systems is limited. These are random-mixing theories, and specific interactions destroy randomness due to the existence of preferred contacts. It is therefore advisable to resort to other theories, which stress the effect of nonrandom mixing such as association equilibria theory,[5,18] as has been performed by Pouchlý et al.[5,18,19] Recently these authors have applied association equilibria theory to a particular ternary system, 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,[5] as is the case of the system poly(methyl methacrylate)/benzene (inert)/methanol (self-associates).

In a recent paper,[9] we have extended the same treatment of Pouchlý et al.[5] to a more complicated system, in which one of the two liquids in the mixed solvent, besides self-associating and interacting with the polymer, also interacts specifically with the other solvent, which cannot be considered as inert. A quantitative agreement was found betwen theory and the experimental results dealing with the dependence of the preferential adsorption coefficient λ with the composition, in the cases that were chosen as examples: poly(alkyl methacrylates)/1,4-dioxane/methanol.[9] On the other hand, in these systems, the experimental results indicate that the preferential adsorption is markedly influenced by the size of the side groups attached to the polymer backbone,[20] as has been reported for other related ternary systems.[21,22] In fact, the adsorption of methanol diminishes as the size of the side group increases and finally disappears when the lateral group is bulky enough. These results can be qualitatively described by the theory through the comparison of the association constants used in the association equilibria theory, as was reported in the previous paper;[9] i.e., the association constant decreases as the lateral group increases.

It seems interesting to extend the same theoretical treatment to other closely related systems, in order to lend confidence about the real validity of the parameters used by this extended theory.

The aim of this work was to determine experimentally the preferential adsorption of a family of poly(dialkyl itaconates) [poly[1-(alkoxycarbonyl)-1-[(alkoxycarbonyl)-methyl]ethylene]; see Chart I] in 1,4-dioxane/methanol, to apply our theoretical framework of association equilibria theory in order to interpret the experimental results, and also to compare the interpretation given previously to that of the preferential adsorption of poly(alkyl methacrylates) in the same mixed solvent. In the poly(diitaconates) studied here it is expected that the effect of the side chain on the preferential adsorption should be similar to that of poly(methacrylates), but since in the poly(itaconate) chain there are two lateral groups per monomer unit, the steric hindrance is higher; therefore, this effect should be reflected in the association constant of methanol to the polymer. Also, the specific binding of methanol to the polymer should be affected by the presence of the two carbonyl groups in the monomer unit of the poly(diita-

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[†] Dedicated to Prof. G. M. Guzmán on the occasion of his appointment as Professor Emeritus.

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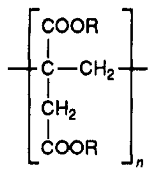
Chart I



R = –CH$_3$ (PDMI)
–CH$_2$CH$_3$ (PDEI)
–(CH$_2$)$_2$CH$_3$ (PDPI)
–(CH$_2$)$_3$CH$_3$ (PDBI)

conates) as compared to only one carbonyl in poly(methacrylates).

Experimental Part

Monomer and Polymer Preparation. Diitaconates were prepared by conventional acid-catalyzed esterification of itaconic acid (1 mol) with the corresponding alcohols (3–4 mol), using *p*-toluensulfonic acid in toluene.[23] The pure monomers were obtained by repeated distillation of the crude product under reduced pressure; purity was confirmed by ^{1}H NMR and IR spectroscopy.

Free-radical polymerization of monomers was carried out in bulk at 323 K using α,α'-azobis(isobutyronitrile) (0.2–0.4 mol %) as initiator under N$_2$ (polymerization time, 48 h; conversion, 71%). The reaction mixture was dissolved in chloroform, and the polymer was isolated by precipitation. Polymers were purified by repeated dissolution and reprecipitation before drying in vacuo at 323 K.

Fractionation and Characterization. Polymers were partially fractionated by solubility using benzene/methanol as the solvent precipitant pair. Three fractions were obtained, and in all cases the second was selected for the present work with polydispersity indices (M_w/M_n) of 1.2–1.3. All samples have molecular weights higher than 10^5. Molecular weights of the samples were estimated by size-exclusion chromatography (SEC) in THF, using a Perkin-Elmer high-performance liquid chromatograph (HPLC) with a 6000-psi pump, a Perkin-Elmer differential refractometer Model LC-25, an injector of 175 μL, and three Waters Associated UltraStyragel columns (10^3 Å, 10^4 Å, and 10^5 Å) in series.

Equilibrium Dialysis. Equilibrium dialysis measurements were performed in a dialyzer of a total volume of 15 mL at 298 K. The dialytic equilibrium is reached after 6 h.

Refractometric Measurements. The refractive index increment (d*n*/d*c*) of the solutions before and after the dialytic equilibrium were measured in a Brice Phoenix BP 2000 differential refractometer.

The preferential adsorption coefficient, λ, was determined by means of the equation

$$\lambda = (\mathrm{d}n/\mathrm{d}c)_\mu - (\mathrm{d}n/\mathrm{d}c)_k/(\mathrm{d}n/\mathrm{d}k) \qquad (1)$$

where $(\mathrm{d}n/\mathrm{d}c)_\mu$ and $(\mathrm{d}n/\mathrm{d}c)_k$ are the refractive index increment of the polymer solution after and before the dialytic equilibrium, respectively, and d*n*/d*k* is the refractive index increment of the solvent mixture.

Results and Discussion

Experimental Results of λ. The dependence of the preferential adsorption coefficient, λ, for PDMI, PDEI, PDPI, and PDBI (see Chart I) in 1,4-dioxane (A)/methanol (B) mixtures, as a function of the methanol volume fraction in the mixed solvent, u_{B0} ($u_{A0} = 1 - u_{B0}$), is shown in Figure 1. As can be seen, at low u_{B0}, methanol is preferentially adsorbed by the polymer, and also in all cases there is an inversion in solvation (λ = 0). These results are very similar to those of poly(alkyl methacrylates) in the same binary solvent previously reported.[20] In fact, in the case of poly(dialkyl itaconates) as well as poly(alkyl methacrylates) the adsorption of methanol at low u_{B0} and of 1,4-dioxane at higher u_{B0} decreases as the size of the lateral group of the polymer chain increases, as can be seen in Figure 1. The main differences between these two ternary systems seem to be that the adsorption of methanol as well as the composition of the inversion $(u_{B0})_{\lambda=0}$ is slightly higher in poly(dialkyl itaconates) than in poly(alkyl methacrylates). This behavior could be due to the fact that in the former systems there are two ester groups per repeat unit; therefore, if specific interactions are the main reasons for the adsorption of methanol, as has been demonstrated,[5,9,20] it would be expected to find, in this case, a stronger adsorption of methanol. However, the adsorption of methanol is only slightly higher, as was mentioned above. This result could be due to differences in the steric hindrance between poly(itaconate) and poly(methacrylate) chains, which in a certain form exert an opposed effect to that of specific interactions. On the other hand, we have not found linear relationships between the nature of the lateral groups and the preferential adsorption coefficient, λ, or inversion composition $(u_{B0})_{\lambda=0}$, as in the case of poly(alkyl methacrylates).[20] Therefore, from the experimental point of view only qualitative agreement is found between the preferential adsorption behavior of both systems.

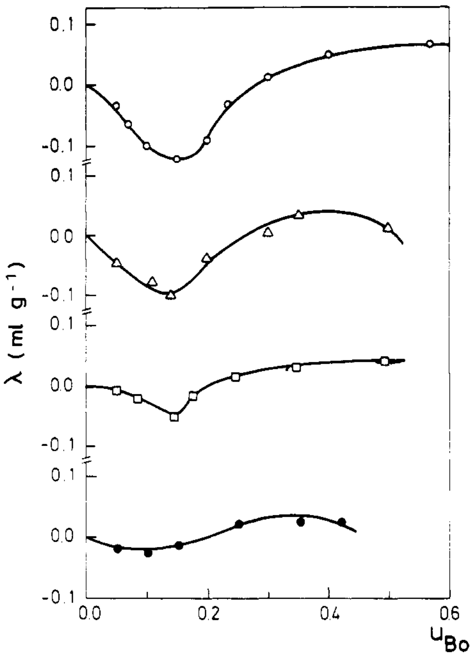


Figure 1. Variation of preferential adsorption coefficient, λ, as function of methanol volume fraction u_{B0}, for PDMI (○), PDEI (△), PDPI (□), and PDBI (●), at 298 K.

Theoretical Interpretation of λ. In order to give a quantitative description of the variation of λ and its dependence with the nature of the side groups of the polymer in these systems, we have attempted to perform a theoretical interpretation by applying classical thermodynamic theories[2] and the association equilibria theory.[5,18]

According to the thermodynamic theories, it is possible to define appropriate variables *X* and *Y*, as proposed by Pouchlý and Zivný[2]

$$X = -\frac{\mathrm{d}}{\mathrm{d}u_{B0}}(u_{A0}u_{B0}g_{BA}) \qquad (2)$$

$$Y = \frac{\lambda}{v_C}\,\frac{r_A u_{B0} + u_{A0} + u_{A0}u_{B0}\dfrac{\mathrm{d}^2}{\mathrm{d}u_{B0}^{\,2}}(u_{A0}u_{B0}g_{BA})}{u_{A0}u_{B0}} \qquad (3)$$

from which the representation of preferential adsorption

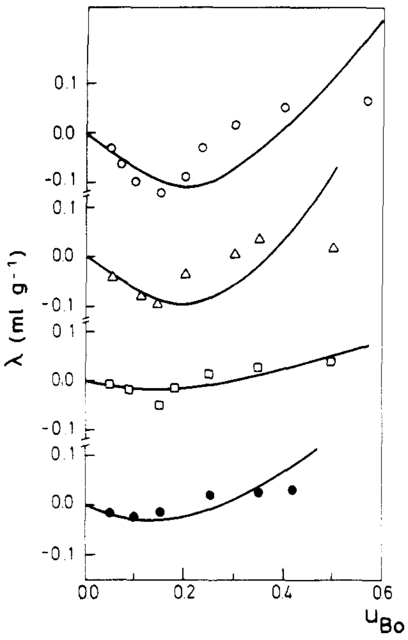


Figure 2. Comparison between theory and experiment for the preferential adsorption coefficient, λ, by using classical thermodynamic theories.[2] Points: experimental result of λ. Curves: classical thermodynamic theories.[2]

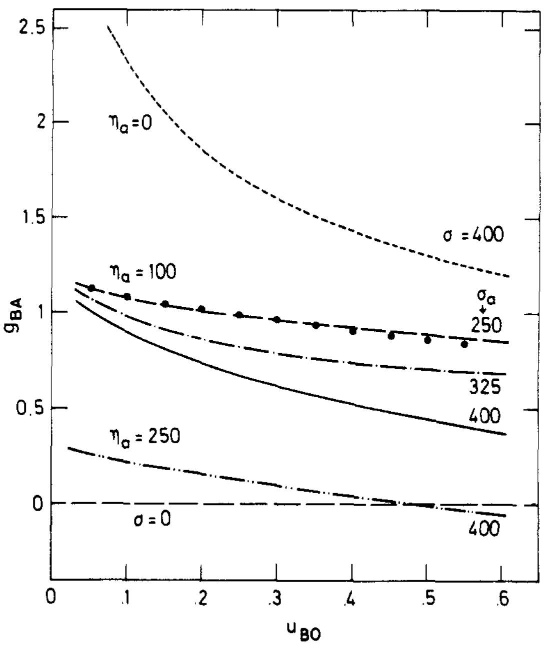


Figure 3. Fit of the theoretical Flory–Huggins interaction parameter, g_{BA}, for the liquid mixture 1,4-dioxane (A)/methanol (B). Points: experimental data = mean g_{BA} values at 298 K, calculated from the data of the Wilson and NRTL equations.[9] Curves: $\sigma = 0$ (– –); all other curves calculated with $\sigma = 400$ and $\eta_a = 0$, $\sigma_a = 400$ (- - -); $\eta_a = 100$, $\sigma_a = 250$ (– –); $\eta_a = 100$, $\sigma_a = 325$ (– · –); $\eta_a = 100$, $\sigma_a = 400$ (—); $\eta_a = 250$, $\sigma_a = 400$ (– · · –). $g_{BA} = 0$ in all cases.

in the form Y vs X should be linear. Here, C denotes the polymer, g_{ij} is the liquid–liquid concentration-dependent inteaction parameter for the pair i,j, v_C is the polymer specific volume, and r_A is the ratio of molar volumes, V_A/V_B. However, the experimental results for the systems studied here, as in the case of poly(alkyl methacrylates),[9] do not follow a linear Y vs X variation. Figure 2 shows the fit of the experimental results of λ by using this thermodynamic criterion. Bad fits are obtained as it can be seen in Figure 2, where the theoretical curves tend to ever increasing λ values at high u_{B0} and do not reproduce appropriately the experimental variation of λ. Following the same scheme used for poly(alkyl methacrylates),[9] we could explain this behavior considering specific interactions among the components of the ternary system. Therefore, we should apply the association equilibria theory developed in the previous paper,[9] in order to obtain the theoretical description of the preferential adsorption coefficient λ, for these kinds of polymer systems.

Basically, there are three kinds of constants in the theory previously reported:[9] (a) equilibrium constants for the association of a methanol molecule to a site in 1,4-dioxane (A), η_a, and to a site in the polymer (C), η_c; (b) constants for the self-association of methanol in chain-like complexes; i.e., an equilibrium constant for the joining of one additional B molecule to a chain of self-associated B (self-association of free B molecules) (σ), an equilibrium constant for the self-association of B molecules when the first B is associated with a site in A (σ_a), and an equilibrium constant for the self-association of B molecules when the first B is associated with a site in C (σ_c); (c) constant parameters for nonspecific interaction i–j (g'_{ij}); also, the number of sites in the 1,4-dioxane molecule (m_A) and in the polymer (m_C).

Input Parameters for the Liquid Mixture. Following the same notation and theoretical procedure of ref 9, first we assign values to the parameters σ, η_a, σ_a, m_A, and g'_{BA}, calculating the interaction parameter of the liquid mixture, g_{BA}, according to eq 19 of ref 9 and comparing the results with the experimental g_{BA}. The parameters are adjusted to give the least-squares deviation from g_{BA} computed at intervals of 0.05 of u_{B0} in the range u_{B0} = 0–0.57, which is the one covered by our experimental results of λ. The details of the calculation of g_{BA} are given in ref 9. It is necessary to take into account that the data for the liquid mixtures, i.e., the coefficients of the Wilson and NRTL equations, are the same as those reported previously,[9] but the range of compositions used here is more extended.

We take $m_A = 1$ and $\sigma = 400$ as the best values, for the reasons discussed in previous analysis.[2,9] In our previous fit of the liquid mixture 1,4-dioxane + methanol, we used the approximation $\sigma_a = \sigma$ in order to reduce the number of adjustable parameters. This simplification implies that the formation of chains of self-associated methanol is not hindered when the first molecule of the chain is associated with 1,4-dioxane. Let us explore now the more general case in which σ_a as well as η_a can be varied. The results are shown in Figures 3 and 4. In Figure 3 we show the interaction parameter g_{BA}, calculated by taking the constant term g'_{BA} equal to zero. The effect of considering a nonzero g'_{BA} is just to shift the curves parallel to the ones drawn. In Figure 4 we show the length of the chains of self-associated methanol in free methanol and in complexes with 1,4-dioxane molecules, j_w is the length of the chains (number of methanol molecules forming a self-associated chain) of free methanol, and j_a is the length of the chains attached to a 1,4-dioxane segment. In fact, j_w/u_{B0} and j_a/u_{B0} are the magnitudes plotted.

We start the discussion with g_{BA} (Figure 3). The curve $\sigma = 0$ is for an ideal mixture. The curve $\sigma = 400$ with $\eta_a = 0$ is considering the self-association of methanol ($\sigma = 400$) but no complexes with 1,4-dioxane ($\eta_a = 0$). This gives too large g_{BA} values compared with experiment. The mixing of self-associated methanol with 1,4-dioxane would give too large positive deviation from ideality if 1,4-dioxane were inert, but the specific interassociation methanol/1,4-dioxane opposes this effect and brings the actual g_{BA} to lower values.

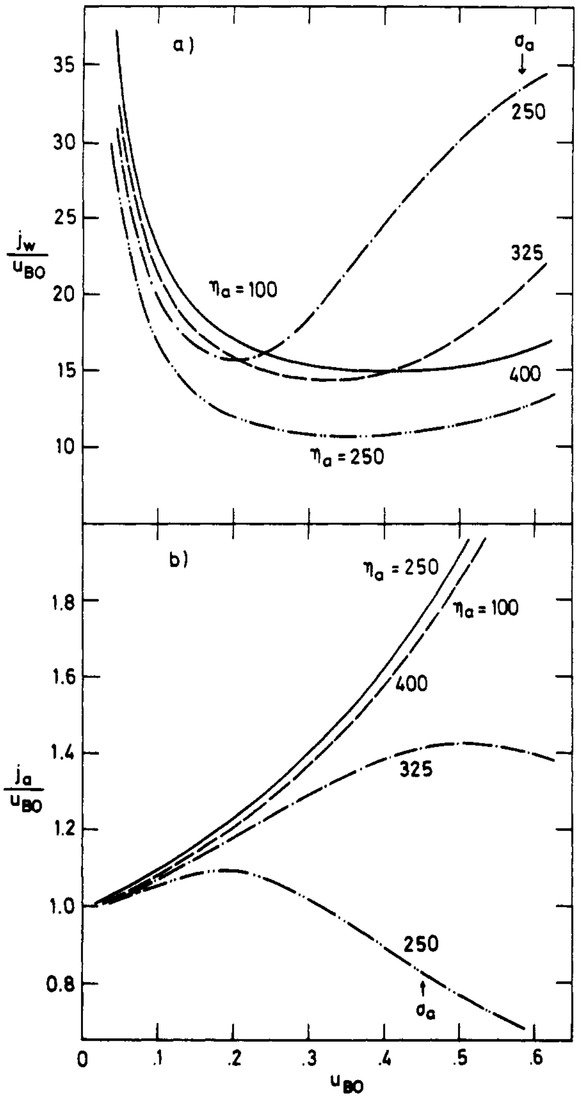


Figure 4. (a) Variation of the length of the free methanol chains, j_w/u_{B0} against u_{B0}, for the following: $\eta_a = 100$, $\sigma_a = 250$ (–·–); $\eta_a = 100$ $\sigma_a = 325$ (– –); $\eta_a = 100$, $\sigma_a = 400$ (—); $\eta_a = 250$, $\sigma_a = 400$ (–···–). (b) Variation of the length of the methanol chains complexed with dioxane, j_a/u_{B0} against u_{B0}, for the following: $\eta_a = 250$, $\sigma_a = 400$ (—); $\eta_a - 100$, $\sigma_a = 400$ (– –); $\eta_a = 100$, $\sigma_a = 325$ (–·–); $\eta_a = 100$, $\sigma_a = 250$ (–···–).

If we increase η_a above zero, the curve g_{BA} vs u_{B0} shifts to lower values. Let us consider the curves $\eta_a = 100$ and $\eta_a = 250$, both for $\sigma_a = \sigma = 400$. With $\eta_a = 100$ we are already close to experiment, and only a small shift $g'_{BA} = 0.3$ is required for coincidence. The higher value of $\eta_a = 250$ brings the curve down to the region of the ideal mixture and requires a much higher shift of $g'_{BA} = 0.85$ for coincidence. With this higher η_a, the fit of g_{BA} results is better than that with $\eta_a = 100$ (lower standard deviation), but it has the disadvantage that we are attributing then the largest part of the observed g_{BA} to nonspecific forces ($g_{BA} \cong g'_{BA}$).

Let us discuss now the length of the methanol chains in the complexes (Figure 4). As we have already seen, the effect of increasing η_a is the lowering of g_{BA}. This is achieved by the following molecular mechanism. The length of chains of free methanol decreases because methanol molecules complex with 1,4-dioxane. Thus compare the curves of j_w for $\eta_a = 100$ and $\eta_a = 250$ (both with $\sigma_a = \sigma = 400$). The length of the methanol chains complexed with 1,4-dioxane (j_a) does not change very much with η_a. The length j_a depends strongly on η_a only for η_a below 50, but for η_a above 50 (where the values useful to describe g_{BA} of the mixture are found), η_a has little influence on the length of the methanol chains associated with a 1,4-dioxane molecule. See j_a curves for $\eta_a = 100$ and $\eta_a = 250$ (both with $\sigma_a = \sigma = 400$). So, increasing η_a in this range produces an increase in the proportion of 1,4-dioxane molecules complexed with methanol, but the length of the methanol chains in these complexes remains relatively stable.

Let us consider now the effect of σ_a being different from σ. In Figure 3 the curves for $\eta_a = 100$ with $\sigma_a = 400$, 325, and 250 show the typical behavior. If we consider σ_a lower than σ, then the variation of g_{BA} vs u_{B0} becomes less steep. For $\eta_a = 100$ this is useful because the curve $\eta_a = 100$ with $\sigma_a = \sigma = 400$ has a slope larger than that described by the experimental points. Thus the best fit of experiment with $\eta_a = 100$ is achieved for $\sigma_a = 275$ (and $g'_{BA} = 0.04$). Let us see what happens at the molecular level with the chains of methanol (Figure 4). When σ_a is decreased below σ (for a given η_a), the effect is to cut the length of the chains of methanol complexes with 1,4-dioxane. Compare the curves of j_a for $\eta_a = 100$, with $\sigma_a = 400$, 325, and 250. This effect is not of equal magnitude at all methanol concentrations; it depends very much on u_{B0}. For u_{B0} concentrations below 0.2, we can see that the curves corresponding to different σ_a values differ only slightly, but for u_{B0} values above 0.2, the j_a and j_w curves corresponding to different σ_a values separate widely. In this region of $u_{B0} \geq 0.2$ the effect of decreasing σ_a on the length of the methanol chains complexed with 1,4-dioxane is most important.

The region $u_{B0} \sim 0.2$ is also where the inversion in λ appears, so that the effect of $\sigma_a < \sigma$ should be especially delicate for the range where λ is positive, namely for the preferential adsorption of 1,4-dioxane. As we shall see later, the experimental results of λ require a high value of σ_a to describe the preferential adsorption of 1,4-dioxane, so that we shall be forced to choose again $\sigma_a = \sigma$ in spite of the better description of g_{BA} values that can be achieved by $\sigma_a < \sigma$.

Ternary System. We calculate λ according to the association equilibria theory, by means of eqs 4–17 of ref 9. Following the same procedure as for poly(alkyl methacrylates),[9] we use as fitting criterion for λ the minima in the standard deviation (δ) between the calculated and the experimental λ. We maintain fixed the selected parameters obtained to fit the liquid mixture (discussion above) and calculate λ by assigning values to the remaining parameters of the theory. Our strategy is as follows.

We have to determine the values of three parameters for the ternary system. These are η_c, σ_c, $g'_{AC} - r_A g'_{BC}$. A first approximation would be to consider $\sigma_c = \sigma$, which means that the formation of chains of self-associated methanol is the same in the methanol complexed to the polymer as it is in free methanol. Since intuitively one expects the polymer to pose some hindrance to such methanol chain formation, we choose as trial values for σ_c the following: $\sigma_c = 375$, 275, and 100, thus, one value very close to $\sigma_c = \sigma = 400$ and two lower values. With such trial values we obtain η_c and $g'_{AC} - r_A g'_{BC}$ by finding the minimum standard deviation (δ) between the calculated and experimental λ. Since the poly(itaconates) have two ester groups per repeat unit, the number of sites for the association of methanol can be two per monomer. Thus, we use $m_C = 2$ and $m_C = 1$ as trial values.

The results that are obtained for the minimum standard deviation in each case are shown in Table I. We show only the results obtained with the methyl polymer, PDMI, as a typical example of the behavior. They have been calculated by using two possible combinations of parameters for the liquid mixture, which have been

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

σ	σ_a	η_a	g'_{BA}	m_C	σ_c	η_c	$g'_{AC} - r_A g'_{BC}$	$\delta \times 10^2$	curve in Figure 5A
400	400	100	0.30	1	375	412	−0.70	2.26	b
				2	375	243	−1.61	2.08	a
				2	275	161	−0.25	2.56	c
	275	100	0.04	1	275	372	0.13	2.73	
				1	100	559	0.31	2.70	
				2	375	150	−0.50	3.02	
				2	275	151	0.04	2.86	d
				2	100	225	0.25	2.65	e

discussed above, namely, one with $\sigma_a = \sigma$ and another with $\sigma_a < \sigma$. From the results shown in Table I we can extract the following conclusions. First, the choice $\sigma_a = \sigma$ for the liquid mixture is always better than $\sigma_a < \sigma$. Second, the choice $m_C = 2$ gives more reasonable values of η_c than $m_C = 1$. Thus, with $m_C = 1$ one finds extremely high values of η_c, even larger than σ. With $m_C = 2$, on the other hand, the range of values found ($\eta_c = 150$–250) is similar to the one previously found for PMMA ($\eta_c = 195$–243), which is reasonable if η_c is to represent the association of a methanol molecule to one ester carbonyl of the polymer, and in both cases we are comparing a methyl ester group. Third, the lower value of σ_c does not improve the agreement. In fact, the best fit is obtained with $\sigma_c = 375$, $m_C = 2$, $\sigma_a = 400$, and $\eta_a = 100$ (second row in Table I).

In order to obtain a molecular picture of the association of methanol to the polymer in each one of the choices tested, we show in Figure 5A the length of the methanol chains complexed with each repeat unit in PDMI, as a function of u_{B0}. j_c is the length or number of methanol molecules forming a self-associated chain when the first methanol molecule is attached to a polymer segment (in fact, the quantity plotted is j_c/u_{B0}). The curves are designated with letters to match the row designation in Table I, in order to identify the set of parameter values to which each curve corresponds. The value of the standard deviation of λ corresponding to each set is also shown on the curves of j_c. We can see that those sets of parameter values that give shorter chains of methanol associated to the polymer (values of j_c/u_{B0} below 2) are the ones having the highest δ values (curves c–e). In order to obtain lower standard deviations, it is necessary to use sets of parameter values giving longer methanol chains attached to the polymer: thus, curve b with a j_c/u_{B0} of around 2, and especially curve a, which gives the best fit (lowest δ) and for which j_c is largest ($j_c/u_{B0} \simeq 3$).

What is very important is not only that j_c should have a higher value but that it should increase proportionally to u_{B0}, in order to obtain a good description of the λ data. Curve a shows j_c/u_{B0} approximately constant in the range of u_{B0} covered; hence, the length of the chains of methanol complexed to the polymer increases continuously with u_{B0}. λ reaches an inversion at $u_{B0} \simeq 0.2$–0.3, and for higher u_{B0} the liquid preferentially adsorbed is 1,4-dioxane. In spite of this, the theoretical results inform us that methanol continues to be adsorbed, even for liquid mixture compositions where the net preferential adsorption is of 1,4-dioxane. This is the reason why the preferential adsorption of 1,4-dioxane does not grow more and more but levels off and suggests a maximum in λ. Without this ever-increasing complexation of methanol to the polymer, the curve of λ would be more like the one predicted by conventional thermodynamic theory (Figure 2).

Let us consider now the influence of the lateral group on λ; namely, let us compare the results for the methyl, ethyl, propyl, and butyl poly(diitaconates). To compare the different polymers, we show only the results obtained with the set of parameter values that give the best fit in Table I, that is, with $m_C = 2$, $\sigma_a = \sigma = 400$, and $\sigma_c = 375$. Again, we determine σ_c and $g'_{AC} - r_A g'_{BC}$ for each polymer by looking for the minimum deviation δ. The results obtained are shown in Table II. We can see that the constant for the association of methanol to a polymer site, η_c, decreases as the size of the lateral group increases, in accordance with the results previously reported for poly(alkyl methacrylates).[9] This result can be interpreted in

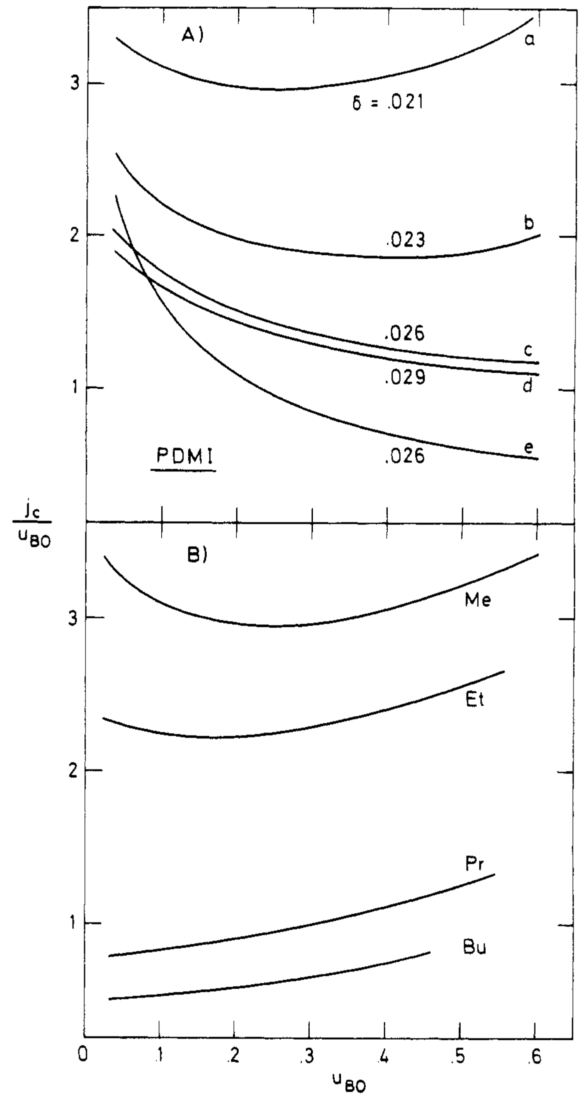


Figure 5. (A) Variation of the length of the methanol chains associated to the polymer, j_c/u_{B0} against u_{B0}, for different sets of parameter values (denoted as a–e in Table I) and the standard deviation (δ) obtained in each case for the calculated λ. (B) Variation of the length of the methanol chains associated to the polymer, j_c/u_{B0} against u_{B0}, for the different polymers.

Table II
Parameter Values Giving the Minimum Deviation (δ) between Theory and Experiment for the Preferential Adsorption Coefficient (λ) of PDMI, PDEI, PDPI, and PDBI, Calculated According to the Association Equilibria Theory and Using $\sigma = \sigma_a = 400$, $\eta_a = 100$, $g'_{BA} = 0.30$, $m_A = 1$, $\sigma_c = 375$, and $m_C = 2$

	η_c	$g'_{AC} - r_A g'_{BC}$	$\delta \times 10^2$
PDMI	243	−1.61	2.08
PDEI	185	−1.02	2.22
PDPI	67	−0.12	1.40
PDBI	49	0.15	1.05

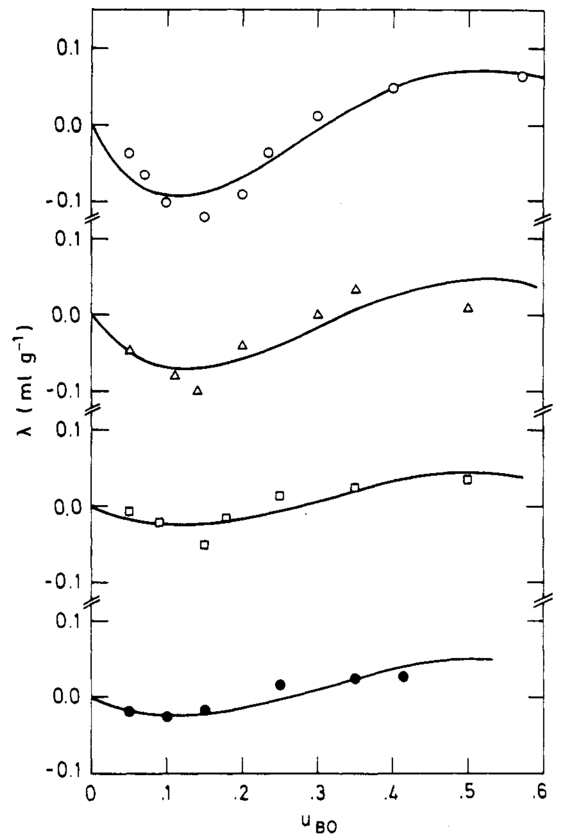


Figure 6. Comparison of theory and experiment for the preferential adsorption coefficient, λ, of poly(dialkyl itaconates) in 1,4-dioxane/methanol (u_{B0} = methanol volume fraction). Points: experimental results for PDMI (○), (alkyl = Me); PDEI (△) (Et); PDPI (□) (nPr); PDBI (●) (nBu). Curves: Association equilibria theory calculated with the set of parameter values shown in Table II.

terms of the different steric hindrances to complex formation imposed by the side groups.

The molecular representation of j_c for these polymers is shown in Figure 5B. A strong decrease in the number of methanol molecules attached to the polymer is suffered as the size of the substituent increases: from $j_c/u_{B0} \simeq$ 3.0–3.3 for Me, to $\simeq$2.2–2.5 for Et, to $\simeq$0.8–1.2 for Pr, and $\simeq$0.5–0.8 for Bu. The largest jump occurs from Et to Pr.

In Figure 6 we show the results of λ calculated with the theory of association equilibria using the parameter values shown in Table II. As we can see, they give a very good description of the experimental results. According to these results, it is possible to conclude that the association equilibria theory of preferential adsorption, in systems such as those here described, represents in a quantitative way the variation of the preferential adsorption coefficient, λ, with the solvent composition. In view of the association constant values (η_c and σ_c) that are needed for this quantitative description of λ, we can conclude that (a) the poly(dialkyl itaconates) bind methanol through their two ester groups, in each one with a strength similar to that of the ester group of poly(alkyl methacrylates), (b) the formation of methanol chains is not very much hindered by the polymer and not more in the doubly substituted poly(dialkyl itaconates) than in the poly(alkyl methacrylates), and (c) the size of the lateral group is a factor having great influence on the association of methanol to the polymer.

Besides these conclusions regarding the association constants, there are also some comments to be made about the magnitude of the parameters for physical interactions, g'_{ij}, that are of interest. Regarding the parameter for the liquid mixture, g'_{BA}, the value that has to be used in order to obtain the best fit of the experimental results of λ is lower than the g'_{BA} that woud be obtained by a best fit of the G_m^E of the mixture. This result has been discussed in the previous paper.[9] With regard to the polymer–solvent parameter for nonspecific interactions given by the term $g'_{AC} - r_A g'_{BC}$, we can see that these interaction parameters are reasonably low, as would be expected for systems whose specific interactions are the most important.

Finally, we can conclude that the association equilibria theory of preferential adsorption in systems with solvent–solvent and solvent–polymer interactions describes in a quantitative way the experimental results of λ. Although the systems in which the theory has been applied are closely related and the experimental results are also similiar, it seems reasonable to think that this kind of theoretical treatment is appropriate for the description of highly polar ternary systems. On the other hand, in the systems here studied it is possible to reach a good description of experiment with a set of parameters physically probable, although there remain several weaknesses in the theoretical framework that should be improved.

Acknowledgment. We thank Dr. J. Pouchlý, Prague, for his very helpful comments. Our thanks to the "Ministerio de Educación y Ciencia" for financial help through a cooperation grant between the UNED and PUC. D.R. and L.G. express their thanks to the DIUC, Universidad Católica de Chile, and to the FONDECYT for partial financial support.

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