Preferential adsorption coefficient of polymers

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The recent formulation of the preferential adsorption coefficient, λ, which takes into account differences in molecular contact surface and in free volume, is tested by comparing theoretical with experimental values of λ from the literature. Seven different systems containing polystyrene and poly(methyl methacrylate) are considered. Agreement between theory and experiment is reached by treating the contact surface of the polymer as a fitting parameters, *s*. The adjusted values of *s* are: (a) systematically higher than the ones calculated from chain geometry; (b) largest in systems containing specific interactions (methanol). The connection between this enhanced apparent contact surface of the polymer and the ternary interaction parameter of the classical theory of λ, is analysed.

Keywords Polymer; preferential adsorption; theory; Flory–Patterson–Prigogine theory; optimization

INTRODUCTION

In polymer-mixed solvent systems, the theoretical expression which is commonly used to interpret the experimental results of preferential sorption coefficient, λ, is that of Read[1]. This expression is derived from the Flory–Huggins (FH) thermodynamic theory of polymer solutions. According to a more recent thermodynamic theory (the so-called Flory–Patterson–Prigogine or FPP), the FH formalism is a simplification which neglects the differences in free volume and in molecular (contact) surface existing between high polymers and low molecular weight solvents. A theory of λ incorporating these effects of molecular surface and of free volume has been formulated recently[2]. It has been applied successfully to interpret preferential sorption of one of the cosolvent systems studied in our laboratory[3]. We extend here the application of such FPP theory of λ to other systems from the literature. Our aim is to test the applicability of this theory to a wide range of systems and, also, to compare it with the classical theory of Read.

Both the FH and FPP formalisms should be strictly valid for systems in which there are only weak interactions. For polar systems and for systems having specific interactions, it has been common practice to use a version of Read's formula which includes a ternary interaction parameter, χ_T. The value of χ_T is usually adjusted to fit the experiment. It has been suggested[2,4] that the effect of the ternary parameter in the classical formula is, in part, equivalent to the effects of molecular surface and of free volume in the new theory. To adjust the value of χ_T is, therefore, a compensation for the neglect of these effects. Polar and specific interactions are additional contributions important in many systems. However, their relative importance should be appreciated fully after the effects of free volume and molecular surface are correctly taken into account by means of the new theory.

The systems which we consider here for the comparison between theory and experiment include the polymers polystyrene (PS) and poly(methyl methacrylate) (PMMA). Some of the systems show an inversion in λ and some are cosolvent (at room temperature). By considering a variety of different behaviours we try to draw some general conclusions regarding the best way of describing λ. The use of just one property is only a partial characterization of a system and an insufficient test of the theory. Therefore, we focus mainly on λ, but we calculate another property, the total sorption function, Y, to make a parallel comparison with λ.

CALCULATION

The expression for λ derived from the FPP formalism is[2]:

$$\lambda = -v_3^0 \frac{\tilde{V}_1}{\tilde{V}_3} \frac{l - 1 + s(\varepsilon_{13} - l\varepsilon_{23}) + (s-\alpha)\varepsilon_{12}(\varphi_1 - \varphi_2)}{l\varphi_1 + \varphi_2 - 2\varepsilon_{12}\varphi_1\varphi_2} \varphi_1\varphi_2 \tag{1}$$

Here, v_3^0 is the specific volume of polymer, $\tilde{V}_i$ reduced volume of component i,φ_i volume fraction of i in the solvent mixture, $l = V_1/V_2$ is the ratio of solvent molar volumes, and s, α, and ε_{ij} are parameters of the theory defined in the following way:

$$s = S_3/S_1 \tag{2a}$$

S_i being the molecular surface to volume ratio of component i. The interaction parameters ε_{ij} are:

$$\varepsilon_{ij} = (-U_i/RT)\,X_{ij}/p_i^* \tag{2b}$$

U_i being the configurational energy, X_{ij} the binary interaction parameter defined by Flory[5], and p_i^* the characteristic reduction parameter for pressure. The

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Table 1 Magnitudes characteristic of the pure substances

Substance	v (cm^3 g^{-1})	α (10^3/K^{-1})	v^* (cm^3 g^{-1})	p^* (J cm^{-3})	T^* (K)	S (Å^{-1})	References
C_6H_6	1.1462	1.223	0.8873	628	4708	0.99	4,6
CCl_4	0.6304	1.229	0.4877	569	4697	0.96	4,6
c–C_6H_{12}	1.2946	1.217	1.0032	531	4719	0.93	4,6
CH_3–C_6H_{11}	1.3036	1.106	1.0292	450	4932	0.82	4,6,7
$CH_3\cdot OH$	1.2716	1.19	0.9893	500	4772	0.99	8
$(CH_3)_2CO$	1.2730	1.43	0.956	627	4349	1.14	9,10
PS	0.9336	0.572	0.8098	547	7420	0.47	4,11
PMMA	0.808	0.575	0.701	455	7380	0.53	3

function α is:

$$\alpha = \alpha_1 T(p_3^*/p_1^*)(1 - T_1^*/T_3^*) \tag{2c}$$

α_1 being the thermal expansion coefficient of the solvent and T_i^* the characteristic reduction parameter for temperature.

For practical purposes, equation 1 can be written in terms of the usual binary interaction parameters, χ_{ij}. According to a previous derivation[3], we can take:

$$\varepsilon_{12} \simeq \chi_{12} \tag{3a}$$

$$\varepsilon_{13} - l\varepsilon_{23} = \left\{\frac{1-l}{2}\left[1 - \left(\frac{\tilde{V}_3}{\tilde{V}_1}\right)^2\right] + \left(\frac{\tilde{V}_3}{\tilde{V}_1}\right)^2 (\chi_{13} - l\chi_{23})\right\} / s(s-\alpha) \tag{3b}$$

and convert equation (1) into the more useful form[3]:

$$\lambda = -v_3^0 \frac{H'(l-1) + H^{-1}(\chi_{13} - l\chi_{23}) + H\chi_{12}(\varphi_1 - \varphi_2)}{l\varphi_1 + \varphi_2 - 2\chi_{12}\varphi_1\varphi_2} \varphi_2\varphi_2 \tag{4a}$$

with

$$H \equiv (\tilde{V}_1/\tilde{V}_3)(s-\alpha) \tag{4b}$$

$$H' \equiv \tilde{V}_1/\tilde{V}_3 - [(\tilde{V}_1/\tilde{V}_3)^2 - 1]/2H \tag{4c}$$

The characteristic parameters and other magnitudes needed to calculate $\tilde{V}_i$, α, and s, in equations 4 are collected in *Table 1* for all the species studied[3,4,6–11]. In actual calculations, for the values of $\tilde{V}_1$, T_1^*, p_1^*, S_1, and α_1 to be used in equations 2 and 4, we take the mean values of the two liquids composing the solvent mixture.

The interaction parameters, χ_{ij}, used in our calculation, have been selected from the literature[1,7,12–20] and are given in *Table 2*. For the solvent–polymer pairs we use several sets of χ_{i3} values, denoted as A, B, C sets, in *Table 2*. For each ternary system, it is possible to decide which set best reproduces the experimental values of λ.

The molecular surface to volume ratio of the polymer, S_3, has a precise meaning in the theory and is obtained from the known geometry of the chain. The values for S_3 corresponding to the chain geometries of PS and PMMA are given in *Table 1*. However, S_3 is (usually) treated (also) as an adjustable parameter whose value is determined by fitting theory to experiment. Here we follow the same procedure and treat S_3 as variable, determining its value by optimization. The criterion followed to determine S_3 is that the sum of squared deviations between experimental and calculated λ's be a minimum. Since S_3 appears in equation 4 always in the form of $s-\alpha$, it is the value of $s-\alpha$ that is actually optimized, and from it the best value of S_3 is deduced making use of equations 2a and 2c. The calculation has been programmed in a general way such that, if desired, S_3 can be allowed to be a function of solvent composition. Our algorithm determines the coefficients a_0, a_1, a_2, ... such that the function:

$$|s-\alpha| = a_0 + a_1\varphi_2 + a_2\varphi_2^2 + \ldots \tag{5a}$$

produced the least sum-of-squared deviations in λ. Since α depends only on characteristic parameters of the pure substances, it is possible to convert the a_0, a_1, a_2, ..., coefficients into the expression:

$$S_3 = C_0 + C_1\varphi_2 + C_2\varphi_2^2 + \ldots \tag{5b}$$

giving the optimum $S_3(\varphi_2)$. The values of the coefficients $C_0, C_1, \ldots$, obtained when we let S_3 be a function of φ_2, are shown in *Table 2*. Also shown in *Table 2* are values of S_3 determined by this same optimization method but taking S_3 as constant, independent of φ_2. The consideration of S_3 as a function of φ_2 is an additional hypothesis, out of the theoretical considerations leading to equations 1 or 4, and should be looked on as a mere numerical fitting technique. As mentioned in the Introduction, in most of the systems the presence of polar and specific interactions renders the application of the theoretical expression, equation 4, approximate. The contributions of such interactions are, in some way, incorporated into the theory by substituting the interaction parameters χ_{ij} appearing in equation 4 for their experimental values, as discussed previously[3]. But even this procedure necessitates the use of an adjustable S_3 to compensate for the contributions not properly taken into account. As we shall discuss later, the difference between optimized and geometrical values of S_3 should be informative about the interactions in the system.

This idea of using an adjustable parameter to correct for the deficiencies of the theory, at least in what concerns its predictive capacity, is essentially the same as that which led to the extensive use of the ternary interaction parameter, χ_T, in the classical theory. An important difference is that here we resort to this procedure only after the effects of molecular surface and free volume are explicitly taken into account, while in the classical formula of λ:

$$\lambda = -v_3^0 \frac{l - 1 + \chi_{13} - l\chi_{23} + (\chi_{12} - \chi_T)(\varphi_1 - \varphi_2)}{l\varphi_1 + \varphi_2 - 2\chi_{12}\varphi_1\varphi_2} \varphi_1\varphi_2 \tag{6}$$

Table 2 Interaction parameters used in the calculation, and results obtained for the adjustable parameters S_3 and χ_T, by least squares analysis of the experimental λ (equation 4 for S_3 and equation 6 for χ_T)

								$S_3 = f(\varphi_2)$ (Å^{-1})			
Polymer	Solvent 1	Solvent 2	χ_{12}	χ_{13}	χ_{23}	Set	S_3 (Å^{-1})	C_0	C_1	C_2	χ_T
PS	C_6H_6	c–C_6H_{12}	$0.640^{a,b}$	0.444^{l}	0.534^{l}	A	0.653	0.444	0.311		0.334
								−0.737	5.539	-4.779^{p}	
				0.444^{l}	0.495^{h}	B	0.773	0.652	0.182		
								−1.824	9.231	-7.526^{q}	
	c–C_6H_{12}	$(CH_3)_2CO$	1.237^{18}	0.495^{h}	0.511^{i}	A	0.622	1.237	−2.976	3.273	0.760
				0.495^{h}	0.776^{h}	B	1.070	1.435	−2.749	4.050	
	CH_3–C_6H_{11}	$(CH_3)_2CO$	$1.37^{a,c}$	0.57^{j}	0.511^{i}	A	0.300	0.532	−0.593	0.311	−2.858
				0.57^{j}	0.776^{h}	B	0.474	0.820	−0.826	0.354	
				-4.11^{k}	-0.035^{k}	C	1.844	2.754	−6.864	10.026	
	C_6H_6	$CH_3 \cdot OH$	$2.70^{a,d}$	0.46^{e}	1.8^{f}	A	0.837	0.609	0.973	0.467	2.362
				0.24^{g}	1.8^{g}	B	0.869	0.628	1.017	0.518	
	CCl_4	$CH_3 \cdot OH$	$2.95^{a,d}$	0.46^{e}	1.8^{f}	A	0.726	0.530	1.214	−0.465	4.373
				0.24^{g}	1.8^{g}	B	0.750	0.545	1.267	−0.469	
PMMA	C_6H_6	$CH_3 \cdot OH$	$2.70^{a,d}$	0.42^{m}	0.93^{f}	A	0.831	0.898	−2.414	5.248	3.447
				0.42^{m}	1.19^{m}	B	1.028	1.113	−3.492	7.788	
	CCl_4	$CH_3 \cdot OH$	$2.95^{a,d}$	0.5^{n}	0.93^{f}	A	0.810	0.997	−2.723	5.420	3.701
				0.5^{n}	1.19^{m}	B	0.997	1.188	−3.552	7.443	

[a] χ_{12} dependent on φ_2; value shown is for $\varphi_2 = 0.5$
[b] $\chi_{12} = 0.303 + 0.704\,\varphi_2 - 0.057\,\varphi_2^2$, from ref. 12
[c] Linearly interpolated between $\chi_{12} = 1.48$ ($\varphi_1 = 0.21$) and 1.26 ($\varphi_1 = 0.88$), from ref. 13
[d] χ_{12} calculated from G^E reported in ref. 14
[e] From viscosity data of ref. 15
[f] Estimated from χ_{12}, χ_{23} and the solvent composition where $A_2 = 0$, as proposed by Dondos and Benoit[16]; data from refs. 16, 17
[g] Read[1]
[h] From solubility parameter[18]
[i] From the critical composition in the acetone + cyclohexanol mixture[19]
[j] Calculated from data in ref. 7
[k] From the critical composition in the acetone + methylcyclohexane mixture[13]
[l] Average of the values in ref. 12
[m] Average of the values in ref. 20
[n] Estimate based on the poor solubility of PMMA in CCl_4
[p] Range: $0.1842 < \varphi_2 < 0.9749$
[q] Range: $0.2702 < \varphi_2 < 0.9563$

everything is assigned to χ_T.

For the sake of comparison, we also use equation 6 to compare with the experimental data of the systems listed in *Table 2*. The value of χ_T is adjusted by optimization in the same way that is followed to determine constant S_3. The best values of χ_T constant thus determined in each system are shown in *Table 2*.

Our study is not limited to a single property. In addition to λ we also calculate ΔY, defined as the excess value of Y in the ternary system over its volume fraction average in the two binaries:

$$\Delta Y = Y - \varphi_1 Y_1 - \varphi_2 Y_2 \qquad (7)$$

According to the FPP formalism, ΔY is given by[4]:

$$\Delta Y = (\tilde{V}_1/\tilde{V}_3)^2(s^2 - s\alpha - \alpha')\chi_{12}\varphi_1\varphi_2 \qquad (8a)$$

where

$$\alpha' \equiv \alpha p_3^{*}/p_1^{*} \qquad (8b)$$

However, the FH formalism obtains for ΔY:[21]

$$\Delta Y = (\chi_{12} - 2\chi_T)\varphi_1\varphi_2 \qquad (9)$$

In each case, we calculate ΔY using the values of the adjusted parameters, S_3 or χ_T, deduced from the fit of λ data.

RESULTS AND DISCUSSION

The results of λ for the different systems are shown in *Figures 1–7*. Points correspond to experimental results[1,12,13,16–18,20,22–27] and curves to theoretical

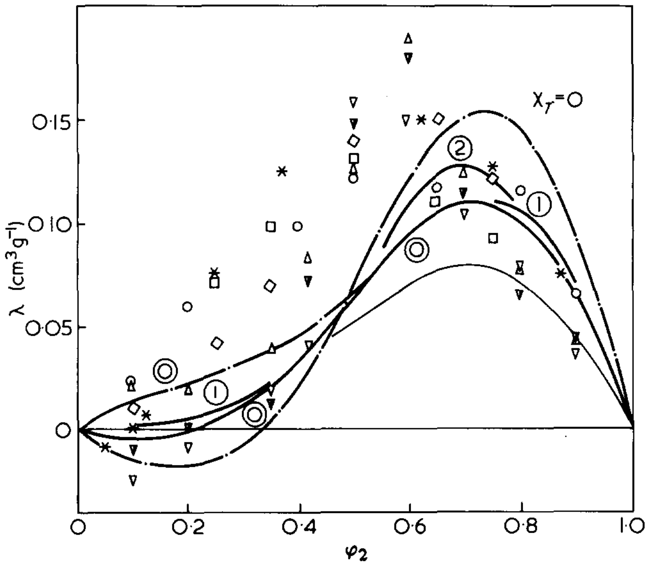

Figure 1 Preferential adsorption coefficient for the system benzene (1) + cyclohexane (2) + PS (3). Curves ———: calculated with equation 4 (0, 1, 2, denoting degree of polynomial in equation 5 used to optimize S_3); Curve ———: equation 4 with fixed geometrical value of S_3. Curves —·—: calculated with equation 6 (0 denoting optimization with χ_T constant). See also text. Experimental points: □ ref. 1; ○ ref. 22; ◇ ref. 23; △, ▽, ▼ ref. 12; ★ extrapolated to infinite molecular weight in ref. 16

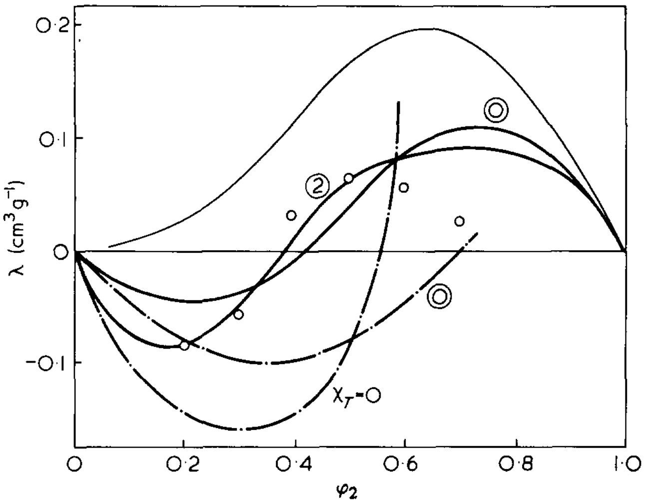

Figure 2 Preferential adsorption coefficient for the system cyclohexane (1) + acetone (2) + PS (3). Curves as in *Figure 1*. Experimental points extrapolated to infinite molecular weight, ref. 18

values. The continuous curves are calculated according to equation 4. The encircled numbers attached to these curves denote the degree of the polynomial in equation 5 used to optimize S_3 (O is for S_3 constant). The continuous curve carrying no number is for the fixed geometrical value of S_3. The broken curves are theoretical values from equation 6 calculated in two options: $\chi_T=0$ and optimization with a constant χ_T (broken curve 0). The curves represented correspond to the set of interaction parameters χ_{i3} giving the best fit of equation 4 in each system. Such a set is designated as A in *Table 2*.

Benzene (1)+cyclohexane (2)+PS (3): (Figure 1)

The consideration of a variable S_3 does not introduce an important improvement of the fit over the adoption of a constant S_3. A slight inversion shown by the experimental data extrapolated to $M\rightarrow\infty$[16] is described by equation 4 with S_3 constant but not by the classical theory with χ_T constant. The value of χ_T optimized with λ, when used in equation 9, predicts negative ΔY's for $\varphi_2<0.32$. However, the constant S_3 optimized with λ, when substituted in equation 8, predicts positive ΔY's, for the whole range of compositions, and a maximum in ΔY around $\varphi\simeq0.5$, which is in good agreement with the experimental results of intrinsic viscosity, $[\eta]$[28].

Cyclohexane (1)+acetone (2)+PS (3): (Figure 2)

The results from equation 4 are superior to the ones from the classical theory. The inversion is fairly well predicted by the optimized constant S_3. This system is cosolvent at room temperature. Its $[\eta]$ presents a maximum at $\varphi_2\simeq0.36$.[29] The optimized constant S_3 is

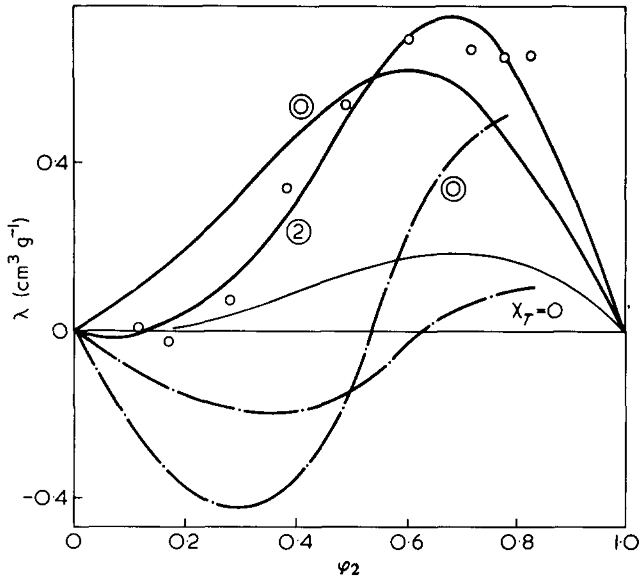

Figure 3 Preferential adsorption coefficient for the system methylcyclohexane (1) + acetone (2) + PS (3). Curves as in *Figure 1*. Experimental points, ref. 13

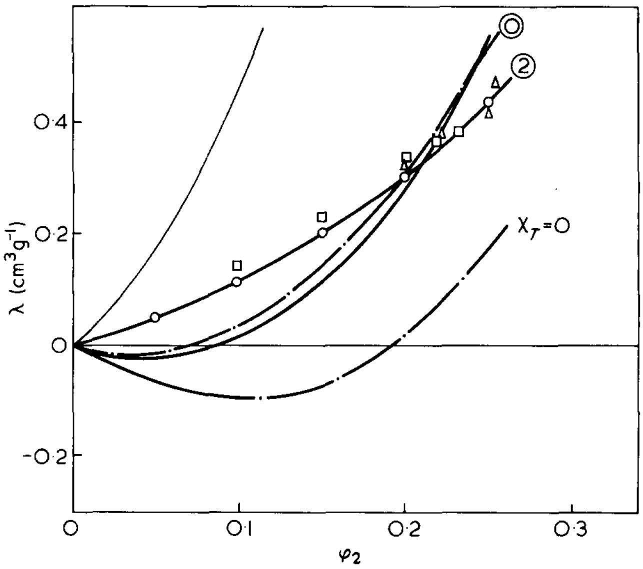

Figure 4 Preferential adsorption coefficient for the system benzene (1) + methanol (2) + PS (3). Curves as in *Figure 1*. Experimental points: □ ref. 25; △ ref. 24; ○ ref. 16 (extrapolated to infinite molecular weight)

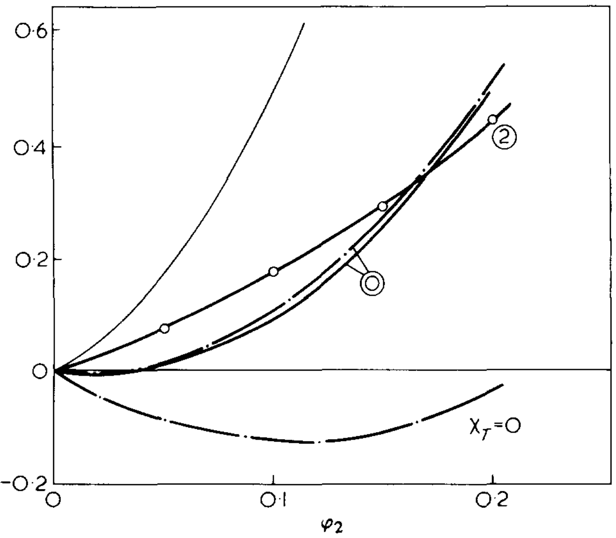

Figure 5 Preferential adsorption coefficient for the system carbon tetrachloride (1) + methanol (2) + PS (3). Curves as in *Figure 1*. Experimental points extrapolated to infinite molecular weight in ref. 16

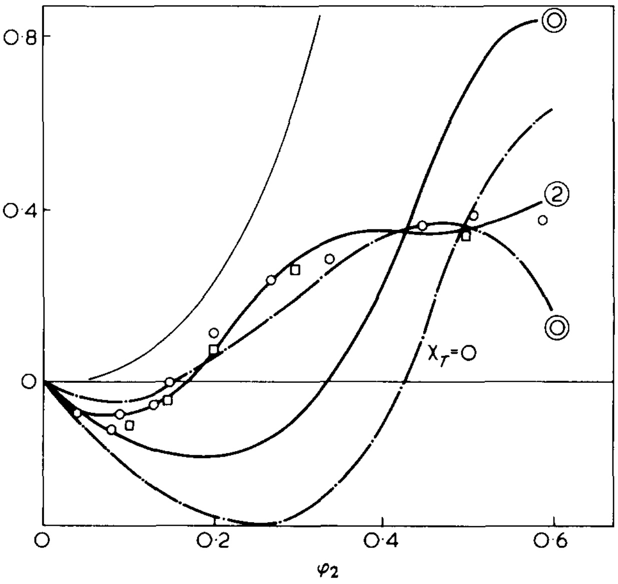

Figure 6 Preferential adsorption coefficient for the system benzene (1) + methanol (2) + PMMA (3). Curves as in *Figure 1*. Experimental points: ○ ref. 20 ($\lambda = v_3^0 A_1$); □ extrapolated to infinite molecular weight, ref. 27 (see also ref. 26)

satisfactory when used in equation 8 also, because it predicts a maximum in ΔY at $\varphi_2 \simeq 0.45$. However, the optimized χ_T which predicts negative ΔY's (equation 9), is inconsistent with the $[\eta]$ results. The use of a variable S_3 improves the fit of λ (curve 2 in *Figure 2*) at the expense of making the predicted ΔY values worse, which, although still positive, present two maxima and a local minimum. As mentioned before, the use of a variable $S_3(\varphi_2)$ is a numerical device rather than an improvement of the theory.

Methyl cyclohexane (1)+acetone (2)+PS (3): (Figure 3)

The curve for constant S_3 is superior to the classical curve with χ_T constant, in its description of the λ data. However, the opposite situation holds with respect to ΔY. The values of the second virial coefficient, A_2, indicate a large ΔY which passes through a maximum[13], and this is predicted by equation 9 with the χ_T fitted to λ. The results of ΔY from equation 8 are negative due to the very low value of S_3 obtained from λ (see *Table 2*). The fitted S_3 is even lower than the geometrical value shown in *Table 1*. This system is the only one for which the fitted S_3 is smaller than its geometrical value. It is also the only for which no experimental results extrapolated to $M \rightarrow \infty$ are available. Both facts may be correlated. Let us explore this possible correlation.

The molecular weight dependence of λ is of the form: $\lambda = \lambda_\infty + \beta M^{-1/2}$. The data in *Figure 3* are for [13] $M_w = 1.56 \times 10^5$. In the closely related system cyclohexane + acetone + PS, the term $\beta M^{-1/2}$ at $\varphi_2 \simeq 0.6$ (where λ is highest in *Figure 3*), corresponding to $M = 1.56 \times 10^5$, is larger than λ_∞. This means that if the present system (with methyl cyclohexane) shows a similar M dependence, on extrapolation to $M \rightarrow \infty$, λ could be reduced to less than half the value it shows in *Figure 3*. The use of non-extrapolated, large λ values, may be the cause of the anomalously low S_3 fitted value. The value of χ_T is also peculiar in that it is the only one found to be negative.

Benzene (1)+methanol (2)+PS (3): (Figure 4)

Only the data extrapolated to $M \rightarrow \infty$[16] have been used in the fit. Here fitting a constant S_3 or a constant χ_T leads to similar curves which describe the data fairly well. However, only the optimized constant S_3 gives satisfactory results for ΔY. The ΔY's from S_3 are positive and with a maximum at $\varphi_2 \simeq 0.14$, while the ΔY's from χ_T are negative for $\varphi_2 > 0.09$. The use of quadratic S_3 leads to a perfect fit of λ and positive ΔY's.

Carbon tetrachloride (1)+methanol (2)+PS (3): (Figure 5)

The results are very similar to the ones discussed in the preceding system. S_3 constant and χ_T constant produce equivalent fits of λ. S_3 quadratic gives a perfect fit. The comparison with ΔY is also analogous to the previous system. S_3 constant leads to a maximum in ΔY at $\varphi_2 \simeq 0.08$ while χ_T leads to negative ΔY's. The quadratic S_3 leads also to $\Delta Y < 0$. Therefore, S_3 constant is the best simultaneous description of λ and ΔY.

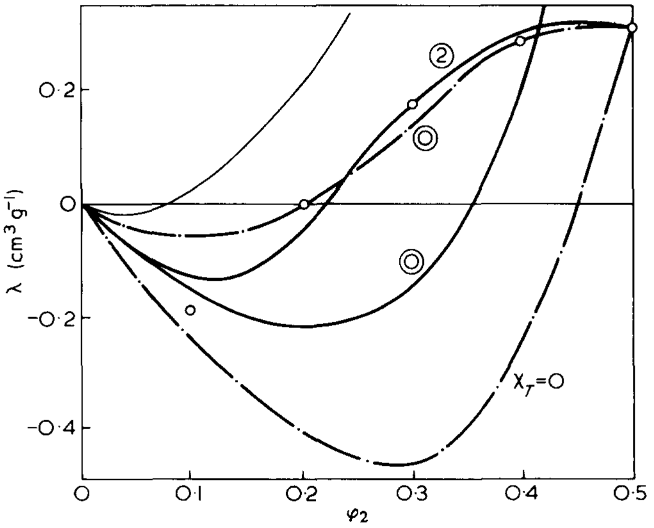

Figure 7 Preferential adsorption coefficient for the system carbon tetrachloride (1) + methanol (2) + PMMA (3). Curves as in *Figure 1*. Experimental points extrapolated to infinite molecular weight, ref. 17

Table 3 Description of preferential and total sorption using a constant adjustable parameter: S_3 in the FPP formalism and χ_T in the classical FH one. (Plus and minus signs indicate fair and poor description of the experimental results, respectively.)

		S_3 constant		χ_T constant	
		λ (eq. 4)	Δ*Y* (eq. 8)	λ (eq. 6)	Δ*Y* (eq. 9)
C_6H_6 + c–C_6H_{12}	PS	+	+	(+)	–
c–C_6H_{12} + $(CH_3)_2CO$		+	+	–	–
CH_3–c–C_6H_{11} + $(CH_3)_2CO$		+	–	–	+
C_6H_6 + CH_3OH		+	+	+	–
CCl_4 + CH_3OH		+	+	+	–
C_6H_6 + CH_3OH	PMMA	–	+	+	–
CCl_4 + CH_3OH		–	+	+	–

Benzene (1)+methanol (2)+PMMA (3): (Figure 6)

The description of λ by means of a constant S_3 is poor and quadratic S_3 is needed for a satisfactory fit. χ_T gives a very good fit, almost as good as the one with quadratic S_3. In contrast to the systems considered thus far, it is not possible to find a simultaneously good description of λ and ΔY with a single constant parameter, be it S_3 or χ_T. The description of λ is much better with χ_T constant than with S_3 constant, but the reverse is true with regard to ΔY. Constant χ_T gives $\Delta Y<0$, which contradicts experiments showing that $[\eta]$ passes through a maximum at $\varphi \simeq 0.18$[20]. The predictions with S_3 constant are, however, correct (at least qualitatively) because they give $\Delta Y>0$ with a maximum at $\varphi_2 \simeq 0.33$. The quadratic S_3 which gives a good fit of λ predicts a maximum in ΔY at $\varphi_2 \simeq 0.18$, but it is a local one, ΔY starting to rise again at $\varphi_2 \simeq 0.3$.

Carbon tetrachloride (1)+methanol (2)+PMMA (3): (Figure 7)

The results are analogous to those in the preceding system. Constant χ_T fits well with λ but produces negative ΔY. Constant S_3 fits poorly with λ but predicts $\Delta Y>0$ with a maximum at $\varphi_2 \simeq 0.35$, agreeing (at least qualitatively) with the experimental $[\eta]$, showing a maximum at $\varphi_2 \simeq 0.2$[17]. S_3 quadratic fits very well and predicts a maximum in ΔY at $\varphi_2 \simeq 0.23$, but it is a local one.

The summary of the systems studied is shown in *Table 3*, where the plus and minus signs denote fair and poor descriptions of the data, frespectively. As we can see, the PS systems are better described with the FPP formulas than with the classical ones. The two systems containing PMMA are not well described by either theory. However, previous analysis of the system acetonitrile (1)+chlorobutane (2)+PMMA (3) showed that S_3 constant gives good agreement both with λ and ΔY, while χ_T does not[3]. The simultaneous presence of PMMA and methanol renders the two systems more difficult to describe.

This type of analysis depends critically on the interaction parameters chosen and, to a certain degree, on the fitting procedure. In our work, λ is fitted directly; ΔY being calculated using the parameters obtained from λ. The direct fit of λ follows a least-squares criterion. In some work, the adjustable χ_T has been determined by solving $\lambda=0$ at the inversion point. This is simple, but overestimates the weight of such an inversion point. The least-squares criterion does not rely on any single point but considers all of them on the same basis.

The comparison established in *Table 3* between the FH and FPP formulas is for constant S_3 and χ_T parameters. It is sometimes found that a composition dependent χ_T is needed to describe experimental data. χ_{12} also varies with φ_2 in most systems. A formula for λ taking into account, explicitly, such φ_2 dependence has been developed in the FH scheme[21]. It should be a better description of λ to develop an equivalent formula in the FPP scheme by incorporating, explicitly, the derivatives of χ_{12} with respect to φ_2. Our present analysis is more crude, simply using equations 4 and 6 with $\chi_{12}(\varphi_2)$. This avoids the calculation of $d\chi_{12}/d\varphi_2$ and $d^2\chi_{12}/d\varphi_2^2$, which is impractical in many systems due to the uncertainty in the interaction parameter values.

CONTACT SURFACE AND TERNARY INTERACTIONS

The values of constant S_3 in *Table 2* are systematically larger than the geometrical values in *Table 1* (with the exception of methyl cyclohexane+acetone+PS, whose anomalous origin has been discussed previously. The value of S_3 obtained previously[3] for acetonitrile+chlorobutane+PMMA ($S_3=0.63$ Å^{-1}) is also higher than the geometrical one. The systems containing methanol have S_3 values in the range 0.73–0.84* which are higher than the values for the other systems, which have the range 0.62–0.65*. It seems, therefore, that for the systems having stronger specific interactions (alcohol), there is correspondingly a higher S_3. We are led to the conclusion that the strong interactions, which are not adequately taken into account by the thermodynamic theory, appear as a larger value of contact surface of the polymer. The effect of such interactions is, then, to produce an apparently larger exposure of the polymer molecular surface to solvents.

Consider, as a working hypothesis, the idea that strong interactions contribute to a larger S_3, and let us see what consequence this has on the solvation of the polymer chain. We write

$$s=s_g+\Delta s \tag{10}$$

with s_g meaning the geometrical value of s and Δs the difference between s_g and the empirically adjusted s. We substitute s given by equation 10 into the expression for total sorption (equation 8), and get:

$$\Delta Y=(s_g^2-s_g\alpha-\alpha')(\tilde{V}_1/\tilde{V}_3)^2\chi_{12}\varphi_1\varphi_2(1+\Delta s\cdot t) \tag{11a}$$

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* Set A

with

$$t \equiv (2s_g - \alpha + \Delta s)/(s_g^2 - s_g\alpha - \alpha') \qquad (11b)$$

In equation 11, ΔY is the result of two contributions. The first due solely to weak interactions ($s = s_g$), and the second (the one in Δs) is an additional contribution arising from the enhanced apparent molecular surface of the polymer, presumably due to stronger interactions. We can see that this additional contribution is positive and increases solvation of the polymer ($2s_g - \alpha + \Delta s$ is always found to be positive, of the order of unity). The actual total sorption is larger than that predicted for the same system having only weak, random interactions. This is an acceptable result.

Going back to *Table 2* we analyse what happens with the classical theory. We see that χ_T is larger in the systems containing methanol. The need of a non-zero χ_T has usually been interpreted as being due to the influence of ternary contacts, the non-random nature of the interactions, the gathering of solvent molecules around the polymer chain, etc. Intuitively, one would think these effects would be favourable to polymer solvation. However, the role played by χ_T in equation 8 is just the opposite to this intuitive expectation. χ_T appears in $\chi_{12} - \chi_T$ as a contribution opposing solvation. By writing $\chi_T = (\gamma/2)\chi_{12}$, we get from equation (8):

$$\Delta Y = \chi_{12}\varphi_1\varphi_2(1 - \gamma) \qquad (12)$$

which is of the same form as equation 11 but with the contribution from the ternary term paradoxically reducing total sorption.

We can now see that this paradoxical result happens because χ_T includes not only the effects of strong interactions but also the effects of contact surface and free volume. These two latter effects make ΔY much smaller than predicted by FH theory ($s_g^2 - s_g - \alpha'$ in equation 11 attains small values of the order of 0.1 or less). Once these are taken into account separately, the strong interactions can appear as a positive contribution to sorption ($\Delta s > 0$ in equation 11).

There are systems with favourable 1–2 interactions contributing negatively to ΔY, but none of the systems considered here fall in such a category. All of the liquid mixtures have $G^E > 0$ and solvation of the polymer coil is enhanced in the mixture.

The action of Δs on λ is more difficult to analyse because λ is a complex function of $s = s_g + \Delta s$ in equation 4. If we look solely at the term $(s - \alpha)\chi_{12}(\varphi_1 - \varphi_2)$, we see that Δs reinforces the adsorption of 1 for $\varphi_2 > 0.5$ and the adsorption of 2 for $\varphi_2 < 0.5$. That is, Δs favours the adsorption of the minor component in the liquid mixture thus giving a better solvent inside the coil, which is a reasonable result. However, the action of χ_T in the term $(\chi_{12} - \chi_T)(\varphi_1 - \varphi_2)$ of equation 6 is the opposite, because χ_T favours the adsorption of the major component.

Our discussion of Δs has been purely *ad hoc*. To take into account strong interactions in a proper way would require devising a model for such interactions, in the FPP formalism, and rederiving the equations for λ and ΔY.

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