Interaction parameters in the n-undecane/butanone/poly(dimethyl siloxane) system

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Intrinsic viscosities, $[\eta]$, second virial coefficients, A_2, preferential solvation coefficients, λ, and binary interaction potential as measured by light scattering, g_{12}, for the system n-undecane(1)/butanone(2)/poly(dimethylsiloxane)(3) have been determined at 20.0°C. The system shows cosolvent character, as the inversion in λ and the maxima in A_2 and in $[\eta]$, at $\phi_{10} \simeq 0.65$, seem to indicate. $(g_{13} - sg_{23})$ and the ternary interaction potential, g_T, and its derivatives on system composition, $(\partial g_T/\partial u_1)_{\phi_3 \to 0}$ and $(\partial g_T/\partial \phi_3)_{u_1,\phi_3 \to 0}$, have been evaluated. Global interaction parameters, χ_{m3}, have also been evaluated and a critical analysis on the approximations usually followed for χ_{m3} calculations is undertaken.

(Keywords: intrinsic viscosities; second virial coefficients; preferential solvation coefficients; binary interaction potential; light scattering; n-undecane(1)/butanone(2)/poly(dimethylsiloxane)(3); global interaction parameters)

INTRODUCTION

To interpret experimental data on ternary solvent(1)/solvent(2)/polymer(3) systems two theoretical formalisms are usually followed. The first is based on the Flory–Huggins (FH)[1] equation for binary solvent/polymer solutions and the other is based on the Flory–Prigogine–Patterson (FPP)[2,3] equation. When applying the FH equation, two methods are usually followed: the single liquid approach and the generalization of the FH equation to ternary systems[1]. With the single liquid approach, transport properties (through some excluded volume see for example the Stockmayer–Fixman equation) as well as thermodynamic properties, may be defined in terms of a global interaction parameter between solvent mixture and polymer; the evaluation of this parameter from thermodynamic or transport measurements is the main task.

The generalization of the FH equation as modified by Pouchlý[5] to ternary systems permits the definition of the above global interaction parameter in terms of the corresponding binary (g_{ij}) and ternary (g_T) interaction potentials. Because the scarcity of reliable data on binary interaction potentials and the inherent difficulties in the evaluation of ternary ones, many approximations are usually made in the equations yielding the global parameter (χ_{m3}). As a result, a fair agreement between experimental and calculated χ_{m3} values is not reached, therefore limiting its potential applicability.

A critical analysis on the above points is undertaken in this paper. As a test, and following a systematic study that we are carrying out on n-alkane(1)/butanone, MEK, (2)/poly(dimethyl siloxane), PDMS, (3) ternary systems, the n-undecane, UND, (1)/MEK(2)/PDMS(3) system has been chosen for study.

Data on intrinsic viscosities, $[\eta]$, on second virial coefficients, A_2, on preferential solvation coefficients, λ, as well as on g_{12} potential are reported for the UND/MEK/PDMS system, which happens to be a stronger cosolvent system than the n-hexane/MEK/PDMS and n-heptane/MEK/PDMS systems previously reported[6].

EXPERIMENTAL

PDMS's were commercial samples kindly provided by Siliconas Hispania S.A. (Rhodorsil). Their molecular weights were determined by light scattering in benzene and their polydispersity indices (1.15–1.20) by independent g.p.c. measurements. Intrinsic viscosities were measured with a slightly modified Ubbelhode viscometer.

Refractive index increments of polymers in solution at 633 nm were measured with a Waters R-401 differential refractometer especially equipped for static measurements, to which a Chem-Anal Monochromator with its light source was adapted.

Apparent molecular weights and second virial coefficients were measured with a Chromatix KMX-6 low angle laser light scattering photometer.

g_{12} interaction parameters were also evaluated from light scattering measurements with unpolarized and polarized (vertically and horizontally) incident light[6-8].

All the measurements were made at 293 K.

RESULTS AND DISCUSSION

Throughout the text, the following nomenclature will be used to define ternary system compositions. ϕ_{i0} ($i = 1, 2$) gives the volume fraction of component i in the bulk solvent. ϕ_i ($i = 1,2,3$) stands for volume fraction of component i in the domain of the coil. u_i ($i = 1,2$) is the volume fraction of the liquid mixture of components 1 and 2 inside the coil.

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In *Table 1*, apparent (A_2^*) and real (A_2) second virial coefficients and apparent molecular weights (M_3^*) for PDMS samples with nominal (M_3) molecular weights 31 500, 80 500, 125 000 and 150 000 at several compositions of the binary solvent mixture are given. *Table 2* shows the variation of the refractive index increments $\nu_3 = (dn/dc_3)$ and $\nu_1 = (dn/d\phi_{10})_{c3=0}$ with the polymer concentration and the solvent mixture composition. They are necessary for the evaluation of M_3^* and λ.

In *Figure 1*, the $[\eta]$ dependence on mixture composition (ϕ_{10}) is shown for the above PDMS samples and for a polymer with molecular weight 185 000. A maximum in $[\eta]$ appears at $\phi_{10} = 0.65$–0.67 for all the polymers except for the lowest molecular weight sample. The higher the molecular weight, the sharper the maximum.

In a binary solvent/polymer solution, the thermodynanic quality of solvent is defined by the interaction parameter between the solvent and the polymer. When the measured property is one of equilibrium, the classical Flory's parameter, χ, appears. If a transport property such as $[\eta]$ is measured, it is related to the B parameter. Both parameters are defined in terms of their respective properties with the FH equation.

$$A_2 = \frac{\bar{v}^2}{V}\left(\frac{1}{2} - \chi\right) \qquad (1)$$

Table 1 Nominal (M_3) and apparent (M_3^*) molecular weights and real (A_2) and apparent (A_2^*) second virial coefficients for UND/MEK/PDMS system at several mixture compositions at 20.0° C

M_3 (g. mol^{-1})	ϕ_{10}	M_3^* (g. mol^{-1})	$A_2 \times 10^4$ (ml. mol g^{-2})	$A_2^* \times 10^4$ (ml. mol g^{-2})
31500	0.00	–	0.04	0.04
	0.20	35100	2.62	2.35
	0.30	35400	4.10	3.61
	0.40	37000	4.94	4.21
	0.50	37600	5.60	4.69
	0.60	33200	6.08	5.77
	0.90	41500	4.65	3.53
	0.95	35800	3.80	3.34
	1.00	–	2.52	2.52
80500	0.00	–	0.12	0.12
	0.20	88900	2.28	2.06
	0.30	91500	3.25	2.86
	0.40	94100	4.20	3.59
	0.50	94400	4.82	4.11
	0.60	81600	5.00	4.93
	0.90	100500	3.66	2.93
	0.95	89700	3.20	2.87
	1.00	–	1.77	1.77
125000	0.00	–	0.09	0.09
	0.20	135500	2.14	1.97
	0.30	139600	3.10	2.78
	0.40	142400	3.95	3.48
	0.50	142100	4.40	3.87
	0.60	127800	4.65	4.58
	0.90	151900	3.41	2.81
	0.95	135400	3.00	2.77
	1.00	–	1.62	1.62
150000	0.00	–	0.10	0.10
	0.20	163000	2.00	1.84
	0.30	170000	2.92	2.58
	0.40	172400	3.74	3.25
	0.50	169000	4.19	3.72
	0.60	155700	4.50	4.33
	0.90	192600	3.30	2.57
	0.95	161300	2.95	2.74
	1.00	–	1.49	1.49

Table 2 Variations with polymer concentration (ν_3) and with solvent mixture composition (ν_1) of refractive index increments for the UND/MEK/PDMS system at several mixture compositions (at 20.0°C)

ϕ_{10}	ν_1	ν_3 (ml g^{-1})
0.00	0.0280	0.0295
0.20	0.0320	0.0226
0.30	0.0340	0.0200
0.40	0.0360	0.0160
0.50	0.0381	0.0115
0.60	0.0401	0.0086
0.90	0.0461	−0.0098
0.95	0.0472	−0.0130
1.00	0.0481	−0.0161

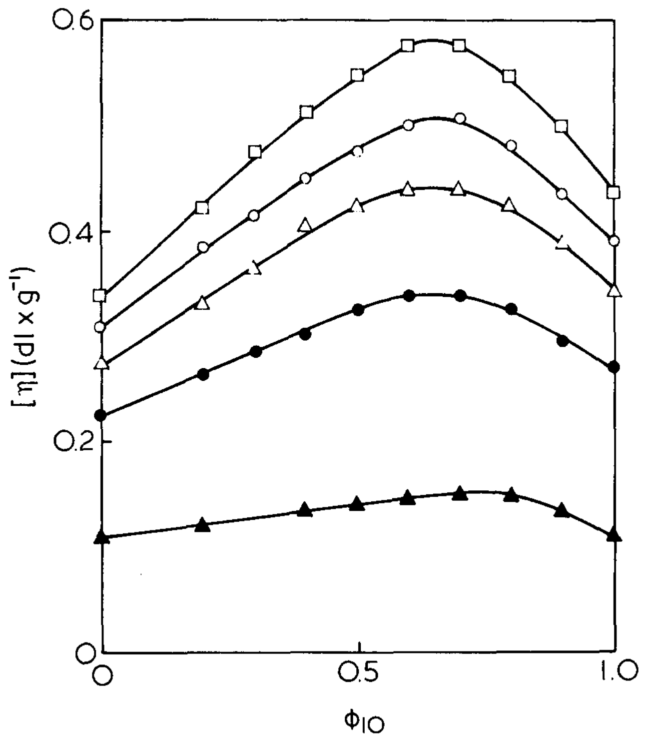

Figure 1 Dependences of intrinsic viscosities at 20.0°C on volume fraction of component 1 for the UND(1)/MEK(2)/PDMS(3) system. $\bar{M}_w$ of PDMS samples: (▲) 31 500; (●) 80 500; (△) 125 000; (○) 150 000 and (□) 185 000

and with the Stockmayer–Fixman[4] equation as modified by Yamakawa[10] we obtain

$$[\eta]M^{-1/2} = K_\theta + 0.346\phi_0 BM^{1/2} \qquad (2)$$

where $\bar{v}$ is the partial specific volume of polymer, V is the solvent molar volume, K_θ is a function of the dimensions of the chain statistical elements at θ conditions and ϕ_0 is Flory's universal constant ($\phi_0 = 2.5 \times 10^{21}$, when $[\eta]$ is given in dl g^{-1}).

The parameters B and χ are related by

$$B = \frac{2\bar{v}^2}{N_0 V}\left(\frac{1}{2} - \chi\right) \qquad (3)$$

where N_0 is Avogadro's number.

Equations (1) and (3) may be extended to ternary systems if it is assumed that a mixture of two solvents behaves just like a single solvent with the mean properties of both solvents[11–13]:

$$A_2=\frac{\bar{v}_3^2}{V_m}\left(\frac{1}{2}-\chi_{m3}\right) \tag{4}$$

$$B=\frac{2\bar{v}_3^2}{N_0 V_m}\left(\frac{1}{2}-\chi_{m3}\right) \tag{5}$$

where V_m is the molar volume of solvent mixture, $V_m=V_1V_2/(\phi_{10}V_2+\phi_{20}V_1)$,$\bar{v}_3$ the partial specific volume of polymer and χ_{m3} the new interaction parameter of the solvent–polymer mixture.

χ_{m3} evaluation following this single liquid model may be undertaken from equilibrium properties (equation (4)) as well as from transport properties (equations (2) and (5)). The Stockmayer–Fixman equation is represented in *Figures 2* and *3*. Good fits are accomplished with all the polymer samples, an exception is shown again with the lowest molecular weight polymer. The difficulties inherent to the characterization by light scattering and by viscometry of low molecular weight polymers may be responsible for this exception. K_θ and B values are obtained from the intercepts and slopes respectively of the straight lines in *Figures 2* and *3*. For the pure solvents $K_\theta(\text{UND})=7.95\times10^{-4}$ dl g$^{-3/2}$ mol$^{1/2}$ and $K_\theta(\text{MEK})=7.85\times10^{-4}$ dl g$^{-3/2}$ mol$^{1/2}$, this last value being in fair agreement with literature data[14].

In *Figure 4*, the dependences on solvent mixture composition of χ_{m3} values from second virial coefficients (equation (4)) and from B values (equation (5)) are shown. There is a point that deserves some comment. B is independent of polymer molecular weight and therefore χ_{m3}, evaluated from B, is also molecular weight independent. χ_{m3} values evaluated from second virial coefficients are, however, molecular weight dependent. Of course, the interaction parameter is defined for infinite molecular weight and in *Figure 4* it is clearly seen how χ_{m3}'s obtained from A_2's approach the χ_{m3} curve from $[\eta]$, as the molecular weight of polymers increases. Moreover, in the same Figure χ_{m3} values from A_2^∞ (second virial coefficients at infinite molecular weight) are also represented. A_2^∞ values have been obtained as the intercepts of plots A_2 vs. $M^{-1/2}$.[15] Fair agreement between χ_{m3} values from $[\eta]$ and from A_2^∞ is observed along the mixture composition up to $\phi_{10}\simeq0.80$, slight deviations occurring in the range $0.80\leqslant\phi_{10}\leqslant1.0$.

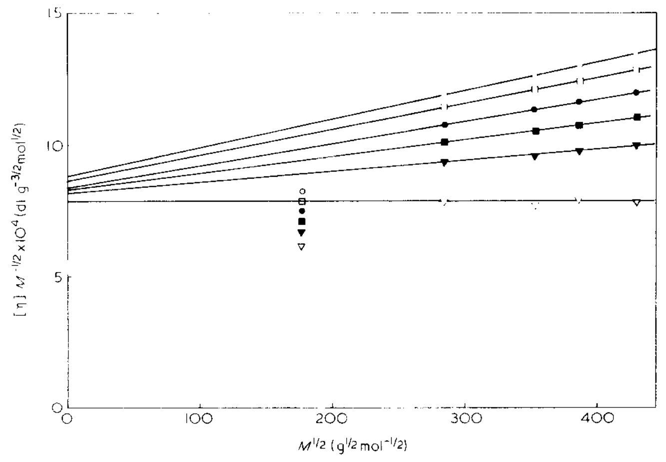

Figure 2 Stockmayer–Fixman plots at several compositions of the binary solvent mixture for the UND(1)/MEK(2)/PDMS(3) system: (▽) $\phi_{10}=0.00$; (◆) $\phi_{10}=0.20$; (■) $\phi_{10}=0.30$; (●) $\phi_{10}=0.40$; (□) $\phi_{10}=0.50$; (○) $\phi_{10}=0.60$

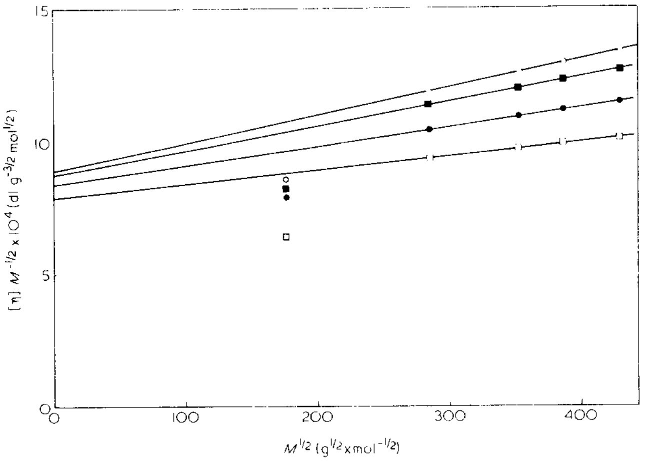

Figure 3 Stockmayer–Fixman plots at several compositions of the binary solvent mixture for the UND(1)/MEK(2)/PDMS(3) system: (○) $\phi_{10}=0.70$; (■) $\phi_{10}=0.80$; (●) $\phi_{10}=0.90$; (□) $\phi_{10}=1.00$

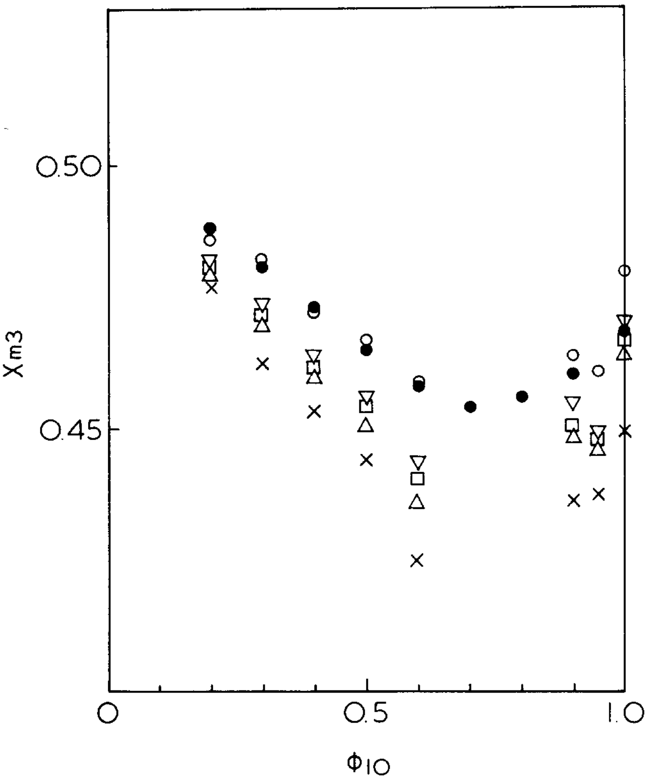

Figure 4 Dependences of experimental global interaction parameters on binary solvent mixture composition for the UND/MEK/PDMS system. ●, χ_{m3} from $[\eta]$ (equation (5)). The remaining symbols for χ_{m3} from A_2 (equation (4)). (○) $\bar{M}_w=\infty$; (▽) $\bar{M}_w=150\,000$; (□) $\bar{M}_w=125\,000$; (△) $\bar{M}_w=80\,5000$; (×) $\bar{M}_w=31\,500$

The generalization to ternary systems of the FH equation[11] has been made among others by Pouchly *et al.*[5]. The second virial coefficient, according to Pouchly's formalism, is given by

$$A_2=\frac{\bar{v}_3^2}{2RT}\left(M_{22}-\frac{M_{13}^2}{M_{11}}\right) \tag{6}$$

where M_{ij}, the second derivatives of the Gibbs energy of mixing with respect to u_i and u_j at polymer infinite dilution, are given by

$$M_{11}=\frac{RT}{V_1}\left[\left(\frac{1}{\phi_{10}}\right)+\left(\frac{s}{\phi_{20}}\right)-2g_{12}+2(\phi_{20}-\phi_{10})\left(\frac{\mathrm{d}g_{12}}{\mathrm{d}\phi_{10}}\right)+\phi_{10}\phi_{20}\left(\frac{\mathrm{d}^2g_{12}}{\mathrm{d}\phi_{10}^2}\right)\right] \qquad (7)$$

$$M_{13}=\frac{RT}{V_1}\left[s-1+g_{13}-sg_{23}+(\phi_{10}-\phi_{20})(g_{12}-g_{\mathrm{T}})-\phi_{10}\phi_{20}\left(\frac{\mathrm{d}g_{12}}{\mathrm{d}\phi_{10}}\right)+\phi_{10}\phi_{20}\left(\frac{\partial g_{\mathrm{T}}}{\partial u_1}\right)_{\phi_3\to 0}\right] \qquad (8)$$

$$M_{33}=\frac{2RT}{V_1}\left[\frac{1}{2}(\phi_{10}+s\phi_{20})+(g_{12}-2g_{\mathrm{T}})\phi_{10}\phi_{20}-\left(g_{13}-\frac{\mathrm{d}g_{13}}{\mathrm{d}\phi_3}\right)\phi_{10}-s\left(g_{23}-\frac{\mathrm{d}g_{23}}{\mathrm{d}\phi_3}\right)\phi_{20}+\left(\frac{\partial g_{\mathrm{T}}}{\partial\phi_3}\right)_{\substack{u_1\\ \phi_3\to 0}}\right] \qquad (9)$$

where $s=V_1/V_2\cdot g_{ij}$ and g_{T} are binary and ternary concentration-dependent interaction potentials. The conceptual differences between interaction potentials, g, and interaction parameters, χ, have recently been discussed by Pouchly *et al.*[16].

In equation (6) the term M_{33} accounts for global sorption and the term M_{13}^2/M_{11} for preferential sorption. Comparison between equations (4) and (6) would, of course, allow calculation of χ_{m3} from interaction potentials data. It would therefore be possible to predict the equilibrium as well as the transport properties of ternary systems. Unfortunately, this clear statement becomes, in practice, an almost impossible task. First of all, because of the scarcity of reliable literature data on binary interaction potentials. While on the other hand, the evaluation of g_{T} and their derivatives from system composition requires detailed experimental measurements on total and preferential sorption coefficients but the evaluation is still not an easy task. Of course, the first objection can be overcome by detailed experimental studies on the corresponding binary systems. A contradiction, however, arises in the second point, where the potential applicability of χ_{m3} in order to predict experimental properties is hindered, because for X_{m3} calculation, g_{T} values are needed, which, in turn, must be evaluated from experimental data. This point will be discussed later.

Because of the above difficulties many approximations have been introduced for χ_{m3} calculations. The most commonly used, will be discussed in an increasing order of complexity.

The approach pioneered by Dondos and Patterson[12] neglects preferential sorption effects against global sorption ($M_{33}-M_{13}^2/M_{11}\simeq M_{33}$). Moreover, if in M_{33} (equation (9)) the ternary potential and its dependence on polymer concentration are also neglected, and the equation of Koningsveld and Kleitjens[17] relating χ_{ij} and g_{ij} is recalled, comparison of equations (4) and (6) yields

$$\chi_{m3}=\frac{V_m}{V_1}(\chi_{13}\phi_{10}+\chi_{23}s\phi_{20}-\chi_{12}\phi_{10}\phi_{20}) \qquad (10)$$

which is a simple equation relating χ_{m3} with binary interaction parameters and it has been widely used to get information on ternary systems. So, χ_{m3}'s from binary parameters through equation (10) and from viscosities (equation (5)) have been compared by Strazielle *et al.*[13] (for carbon tetrachloride/methanol/poly(oxyethyleneglycol) and benzene/methanol/polystyrene systems), and by Maillols *et al.*[18] (for acetone/cyclohexane/-polystyrene). Dondos and Benoit[19] calculated χ_{ij}'s from experimental χ_{m3}'s for the benzene/cyclohexane/poly(2 vinyl piridine), benzene/methanol/polystyrene, carbon tetrachloride/methanol/polystyrene and chloroform/-methanol/poly(2 vinyl piridine) systems; χ_{ij}'s so evaluated were later used to predict preferential sorption coefficients by means of the simplified Read's expression[20]. λ's were also theoretically evaluated from Read's equation[20] by Deb *et al.*[21] for the acetone/cyclohexane/polystyrene system. They calculated χ_{m3} from χ_{ij}'s, using in equation (10) Scott's approximation[22] ($V_1=V_2=V_m$), and arbitrarily assigned to χ_{T}'s the calculated χ_{m3} values.

Serious discrepancies arise, in general, between above calculated χ_{m3}'s or λ's and the respective experimental values, as also happens with the UND/MEK/PDMS system. Applicability of equation (10) is tested for the last system in *Figure 5*, in which χ_{m3}'s from binary interaction parameters are represented vs. ϕ_{10}. Three sets of χ_{ij} values

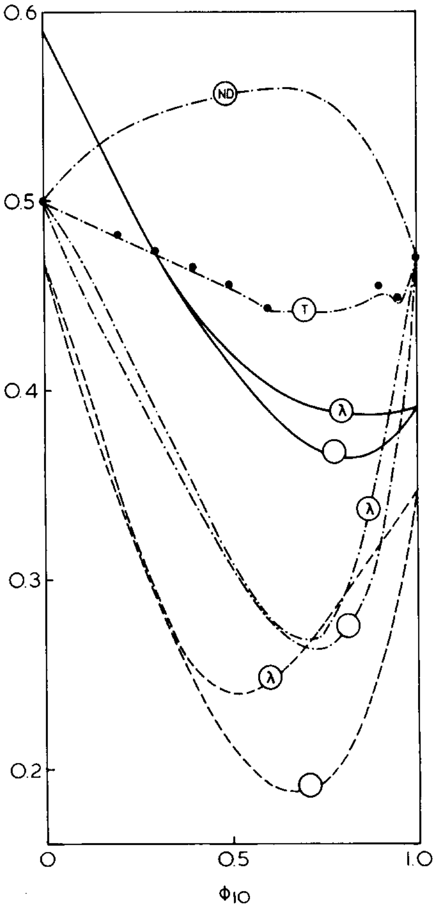

Figure 5 Comparison between experimental (full points) and calculated (lines) global interaction parameters for the UND/MEK/PDMS ($\bar{M}_w=150\,000$) system. (———), Hildebrand–Scatchard χ_{ij}'s; (– – –), Branks–Prausnitz χ_{ij}'s; (–·–·–), experimental χ_{ij}'s. χ_{m3} from equation (10), ○; from equation (11), (λ); from equation (13), Ⓣ; from equation (13) neglecting $(\partial g_t/\partial\phi_3)_{u_1,\phi_3\to 0}$, (ND)

have been used to calculate χ_{m3}: those evaluated in a rough approximation from solubility parameters through the Hildebrand–Scatchard approach[23] with values $\chi_{13}=0.39$, $\chi_{23}=0.59$ and $\chi_{12}=0.79$, those calculated through the more refined Branks–Prausnitz method[24] with values $\chi_{13}=0.35$, $\chi_{23}=0.49$ and $\chi_{12}=1.48$ and finally the experimental ones. Solubility parameters (δ_i) and molar volumes used for the above χ_{ij} approximate evaluations were from refs. 24–27; ψ_{ij} data from Figure 2 in ref. 24 and Λ and τ values from refs. 24 and 25.

Experimental χ_{13}'s, from A_2 values in *Table 1*, range from 0.438 for the lowest molecular weight sample ($M=31\,500$) to 0.450 for the highest ($M=150\,000$) one. χ_{23} dependence on molecular weight is negligible and in the molecular weight range so far studied χ_{23} may be defined by a unique value, $\chi_{23}=0.499$. $\chi_{12}=g_{12}$, in this context, as evaluated from light scattering measurements, obeys the equation

$$g_{12}=1.201+0.542(\phi_{10}-\phi_{20})+0.478(\phi_{10}-\phi_{20})^2$$

Figure 5 shows that χ_{m3}'s from equation (10) differ from experimental values (although adequate χ_{ij} parameters are used). Caution is then required when applying equation (10). The discrepancies between calculated by equation (10) and experimental χ_{m3}'s must be due to neglecting preferential sorption effects and/or g_T depending terms. If the term accounting for preferential sorption is added, χ_{m3} will be given by

$$\chi_{m3}=\frac{V_m}{V_1}\Bigg[\chi_{13}\phi_{10}+\chi_{23}s\phi_{20}-\chi_{12}\phi_{10}\phi_{20}+\phi_{10}\phi_{20}$$

$$\frac{[1-s+g_{12}(\phi_{20}-\phi_{10})-(g_{13}-sg_{23})+\phi_{10}\phi_{20}(\mathrm{d}g_{12}/\mathrm{d}\phi_{10})]^2}{2\Big\{s\phi_{10}+\phi_{20}+\phi_{10}\phi_{20}\Big(2(\phi_{20}-\phi_{10})\Big(\frac{\mathrm{d}g_{12}}{\mathrm{d}\phi_{10}}\Big)-2g_{12}}$$

$$+\phi_{10}\phi_{20}\Big(\frac{\mathrm{d}^2g_{12}}{\mathrm{d}\phi_{10}^2}\Big)\Big)\Big\}\Bigg] \qquad (11)$$

where besides binary parameters, the first and second derivatives of g_{12} with respect to the solvent mixture composition and the difference $(g_{13}-sg_{23})$ appear. Application of equation (11) for the three sets of χ_{ij}'s is also represented in *Figure 5*. The approximation $g_{13}=\chi_{13}$ and $g_{23}=\chi_{23}$ has been followed when using χ_{ij} approximate values. When testing experimental χ_{ij}'s, a value $(g_{13}-sg_{23})=-1.326$ (also experimental as will be later commented) has been used. No appreciable improvement is attained by adding the preferential sorption term and at least for this system an immediate conclusion may be drawn: χ_{m3} values calculated only from binary interaction parameters are far from experimental ones. g_T depending terms cannot then be omitted.

g_T parameters have been evaluated from preferential sorption coefficients according to Munk's equation[28]

$$g_T=g_{12}-\frac{1}{\phi_{20}}\int_{\phi_{10}}^{1}L(\phi_{10})N_{11}\mathrm{d}\phi_{10}+\frac{1}{\phi_{10}}\int_0^{\phi_{10}}L(\phi_{10})N_{11}\mathrm{d}\phi_{10} \qquad (12)$$

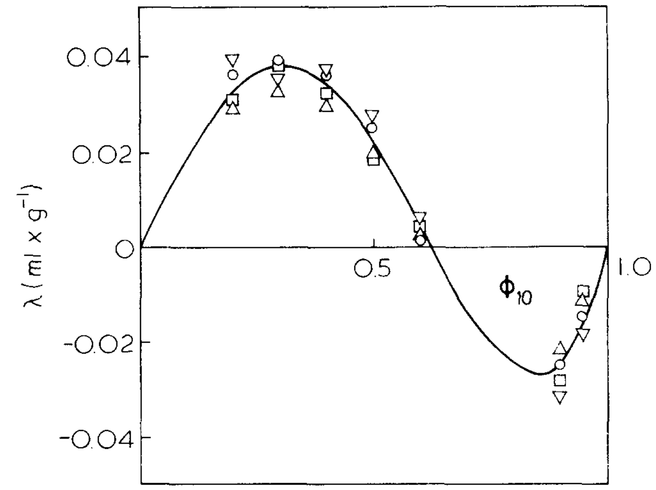

Figure 6 Dependence of preferential solvation coefficients on solvent mixture composition for the UND/MEK/PDMS system. $\bar{M}_w$ of PDMS samples: (▽) 31 500; (○) 80 500; (△) 125 000 and (□) 150 000

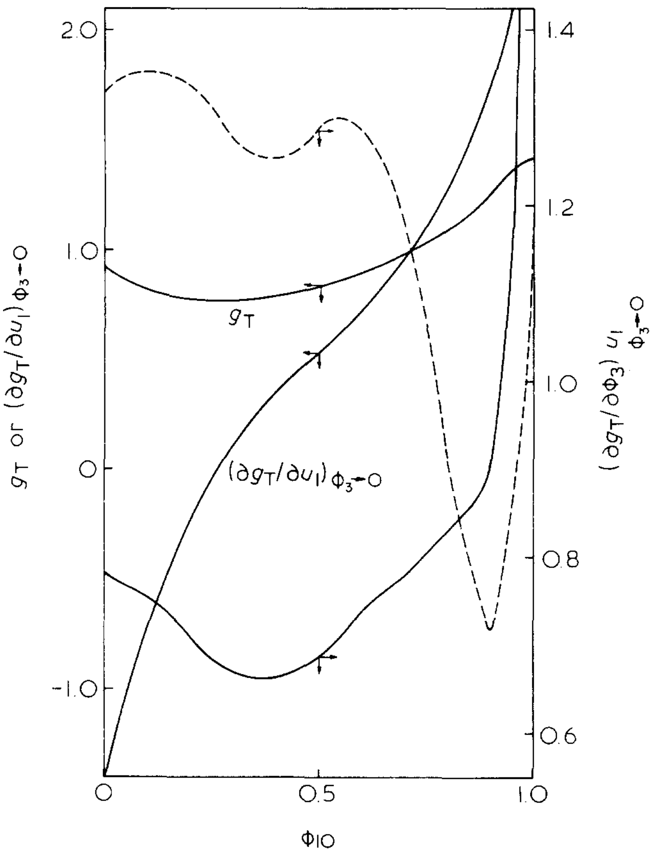

Figure 7 Ternary potential function and its derivatives with system composition for (———) UND/MEK/PDMS ($\bar{M}_w$=150 000) and (- - -) n-hexane/MEK/PDMS ($\bar{M}_w$=150 000)

with $L(\phi_{10})=-\lambda/\bar{v}_3$ and $N_{11}=M_{11}V_1/RT$. In *Figure 6*, λ values are represented vs. solvent mixture composition for four polymer samples. The continuous line depicted in *Figure 6* represents smoothed λ values used for g_T calculations through equation (12). In *Figure 7* g_T's vs. binary solvent composition are represented. From it $(\partial g_T/\partial u_1)_{\phi_3\to 0}$ is evaluated, being also depicted in the same Figure. Munk's method[28] also allows $(g_{13}-sg_{23})$ evaluation through the following equation.

$$g_{13}-sg_{23}=(1-s)+\int_0^1 L(\phi_{10})N_{11}\mathrm{d}\phi_{10}$$

a value $(g_{13}-sg_{23})=-1.326$ being obtained. Finally, $(\partial g_T/\partial \phi_3)_{u_1,\phi_3\to 0}$ remains as the only unknown in equation (6) and can be evaluated from it. In this context, $(\partial g_T/\partial \phi_3)_{u_1,\phi_3\to 0}$ looks like an adjustable parameter fitting λ and A_2 experimental values. In *Figure 7*, $(\partial g_T/\partial \phi_3)_{u_1,\phi_3\to 0}$ dependence on binary solvent composition for the polymer with molecular weight 150 000 is also represented.

Returning to χ_{m3} calculation, if preferential sorption effects are neglected, comparison of equations (4) and (6), recalling M_{33} definition through equation (11), yields for χ_{m3}

$$\chi_{m3}=\frac{V_m}{V_1}\left[\chi_{13}\phi_{10}+\chi_{23}s\phi_{20}-\phi_{10}\phi_{20}\left\{\chi_{12}-2g_T+\left(\frac{\partial g_T}{\partial \phi_3}\right)_{\substack{u_1\\ \phi_3\to 0}}\right\}\right] \quad (13)$$

where χ_{m3} not only depends on binary interaction parameters, but also on ternary potentials. Application of the above equation is again represented in *Figure 5*. A good fit is obtained between calculated and experimental χ_{m3}'s, in spite of preferential sorption effects being neglected. Of course, in the present system, preferential sorption effects are negligible. This is shown by the low λ values in *Figure 6*. However, for those systems with appreciable preferential solvation effects it must be expected that such a coincidence between the calculated values from equation (13) and the experimental χ_{m3}'s will not occur. This is illustrated in *Figure 8* for the n-hexane/MEK/PDMS system. A good fit between the calculated values from equation (13) and experimental χ_{m3}'s is not obtained, because preferential sorption effects are much higher in this system than in the UND/MEK/PDMS system. This is shown by a comparison between λ values for both systems (see Figure 4(a) in ref. 6 and *Figure 6* in the present paper). In *Figure 8*, χ_{m3}'s calculated for the n-hexane (1)/MEK(2)/PDMS(3) system in a parallel form to that made for the UND(1)/MEK(2)/PDMS(3) system are represented vs. ϕ_{10}. χ_{ij}, g_{12} and their dependences on system composition, $(g_{13}\ldots sg_{23})$, g_T and its dependence on solvent mixture composition, necessary to calculate χ_{m3}'s for the n-hexane system were from ref. 6 and in *Figure 7* is represented $(\partial g_T/\partial \phi_3)_{u_1,\phi_3\to 0}$ vs. ϕ_{10} for this system and for the polymer with molecular weight 150 000.

A partial and indirect use of equation (13) was made by Horta *et al.*[29] to theoretically predict preferential sorption parameters for a acetonitrile/1-chloro-n-butane/poly(methylmethacrylate) system. They compared calculated $(Y\simeq V_1M_{33}/2RT)$ and experimental $(Y=V_1A_2/\bar{v}_3^2)$ total sorption parameters, in the former neglecting preferential sorption contributions as done in equation (13). Neglecting also in M_{33} the $(\partial g_T/\partial \phi_3)_{u_1,\phi_3\to 0}$ term, they obtain g_T values at different system compositions, and hence $(\partial g_T/\partial u_1)_{\phi_3\to 0}$, therefore being able to predict theoretical λ's $(\lambda=-\bar{v}_3M_{13}/M_{11})$. The neglecting of $(\partial g_T/\partial \phi_3)_{u_1,\phi_3\to 0}$ contribution to χ_{m3} in equation (13), in a parallel form to that followed by Horta *et al.*[29] is illustrated in *Figures 5* and *8* for UND/MEK/PDMS and n-hexane/MEK/PDMS systems, respectively. As can be seen in these Figures, the trend followed by χ_{m3}'s so calculated is inverse to that followed by experimental values, high numerical differences arising between calculated and experimental χ_{m3}'s.

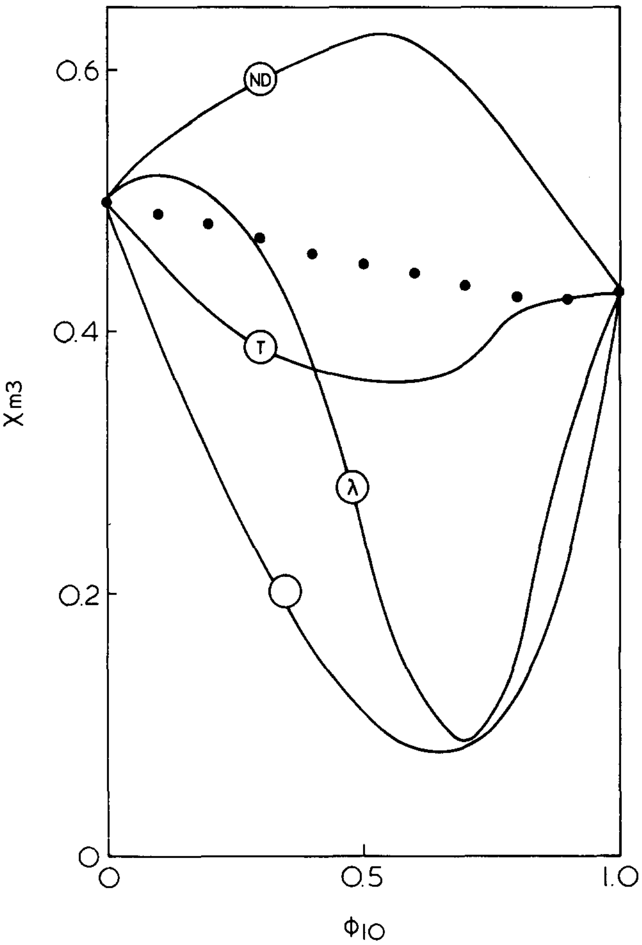

Figure 8 Comparison between experimental (full points) and calculated (lines) global interaction parameters for n-hexane/MEK/PDMS ($\bar{M}_w$=150000) system. Symbols as in *Figure 5*

Throughout this paper a conclusion is evident that all simplifications introduced in order to calculate χ_{m3}'s yield results greatly different from experimental ones. This occurs chiefly when the ternary parameter or its dependences on system composition are omitted. The application of χ_{m3}'s calculated only with binary parameters for the prediction of total sorption (or A_2) or preferential sorption parameters seems useless. At this point a paradox appears. The accurate prediction of χ_{m3} (or A_2 or Y) needs g_T and $(\partial g_T/\partial \phi_3)_{u_1,\phi_3\to 0}$ values. g_T's, however, can only be evaluated if λ values along the whole composition range of the binary solvent mixture are known, and the evaluation of $(\partial g_T/\partial \phi_3)_{u_1,\phi_3\to 0}$, this point being the most important, demands the joint knowledge of λ and A_2, in this context $(\partial g_T/\partial \phi_3)_{u_1,\phi_3\to 0}$ being a parameter adjusting at once λ and A_2 experimental data. On these grounds, the FH equation extended to ternary systems either in the single liquid approach or in the generalized version seems unable to predict appropriate total sorption effects (or A_2) from measured preferential sorption coefficients or *vice versa*, even if binary interaction parameters and potentials are accurately known.

Two ways are suggested as possible solutions for the above problem. The first, an experimental method, could be based on the observed λ dependence on polymer concentration[30-32]. λ's evaluation at different polymer concentrations (ϕ_3) along the whole composition range of the binary solvent mixture would yield $g_T(\phi_3)$ and hence $(\partial g_T/\partial\phi_3)_{u_1,\phi_3\to 0}$ values at any ϕ_{10}. Therefore total sorption effects could be predicted from experimental preferential solvation coefficients. This way could also serve, by comparing measured and 'adjustable' $(\partial g_T/\partial\phi_3)_{u_1,\phi_3\to 0}$'s, as an autoconsistency test of the generalized FH formalism. The second suggested method could consist of the evaluation of M_{33} through a different formalism. This can be done using the FPP equation or by introducing a simplification in M_{33} (similar that suggested by Pouchly *et al.*[16] for the evaluation of M_{14}. The parameter $(\partial g_T/\partial\phi_3)_{u_1,\phi_3\to 0}$ could thus be eliminated or independently evaluated.

REFERENCES

1 Flory, P. J. 'Principles of Polymer Chemistry', Cornell University Press, Ithaca, New York, 1953
2 Flory, P. J. *Discuss. Faraday Soc.* 1970, **49**, 7
3 Patterson, D. and Delmas, G. *Discuss. Faraday Soc.* 1970, **49**, 98
4 Stockmayer, W. H. and Fixman, M. *J. Polym. Sci. Part C* 1963, **1**, 127
5 Pouchly, J., Zivny, A. and Solc. K. *J. Polym. Sci. Part C* 1968, **23**, 245
6 Campos, A., Celda, B., Tejero, R. and Figueruelo, J. E. *Europ. Polym. J.* (in press)
7 Volatie, P., Giurgea, M. and Sandulescu. D. *Z. Phys. Chem. Leipzig* 1978, **259**, 139
8 Fernandez-Pierola, I. and Horta, A. *J. Chem. Phys.-Chem. Phys. Biol.* 1980, **77**, 271
9 Strazielle, C. and Benoit, H. *J. Chem. Phys.* 1961, **38**, 675
10 Yamakawa, H. *Pure Appl. Chem.* 1972, **31**, 179
11 Shultz, A. R. and Flory, P. J. *J. Polym. Sci.* 1955, **15**, 231
12 Dondos, A. and Patterson, D. *J. Polym. Sci. Part A2* 1969, **7**, 209
13 Maldovan, L. and Strazielle, C. *Makromol. Chem.* 1970, **140**, 201
14 Mark, J. E., Flory, P. J. and Crescenci, V. *J. Amer. Chem. Soc.* 1964, **86**, 138
15 Kurata, M., Fukatsu, M., Sotobayashi, H. and Yamakawa, H. *J. Chem. Phys.* 1964, **41**, 139
16 Pouchly, J. and Zivny, A. *Makromol. Chem.* 1982, **183**, 3019
17 Koningsveld, R. and Kleitjens, L. A. *Macromolecules* 1971, **4**, 637
18 Maillols, H., Bardet, L. and Grom. S. *Europ. Polym. J.* 1978, **14**, 1015
19 Dondos, A. and Benoit, H. *Makromol. Chem.* 1978, **179**, 1051
20 Read, B. E. *Trans. Faraday Soc.* 1960, **56**, 382
21 Deb, P. C., Prasad, J. and Chatterjee, S. R. *Makromol. Chem.* 1977, **178**, 1455
22 Scott, L. R. *J. Chem. Phys.* 1949, **17**, 268
23 Hildebrand, J. J. 'The Solubility of Nonelectrolytes', Reinhold Publishing Corp., New York, 1950
24 Blanks, R. F. and Prausnitz, J. M. *Ind. Eng. Chem.* 1964, **3**, 1
25 Hansen, C. M. *J. Paint. Technol.* 1967, **39**, 104
26 Burrel, H. 'Polymer Handbook' (Ed. J. Brandrup and H. Immergut), John Wiley and Sons, 2nd Edn., 1975, p. IV-337
27 Campos, A. and Strazielle, C. *Europ. Polym. J.* 1978, **14**, 517
28 Chu, S. G. and Munk, P. *Macromolecules* 1978, **11**, 879
29 Horta, A. and Fernández-Piérola, I. *Macromolecules* 1981, **14**, 1519
30 Hert, M. and Strazielle, C. *Intern. J. Polym. Mater.* 1976, **4**, 195
31 Hert, M., *Ph.D. Thesis*, Université L. Pasteur, Strasbourg, 1974
32 Zivny, A. and Pouchly, J. *J. Polym. Sci. Part A-2* 1972, **10**, 1467