

# Quantitative relationship between total and preferential sorption coefficients in polymer cosolvent systems

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Second virial ( $A_2$ ) and preferential solvation ( $\lambda$ ) coefficients, as well as binary interaction potentials ( $g_{12}$ ), as measured by light scattering, for the ternary systems n-dodecane/butanone (MEK)/poly(dimethylsiloxane) (PDMS) and n-hexadecane/MEK/PDMS have been determined at 20.0°C. An inversion of  $\lambda$  and a maximum in coefficient  $A_2$ , at  $\phi_{10} \approx 0.57$  in the n-dodecane/MEK/PDMS system and at  $\phi_{10} \approx 0.40$  in the n-hexadecane/MEK/PDMS system, take place, both systems displaying cosolvent character. The coincidence in solvent composition at which  $A_2$  is maximum and  $\lambda = 0$  can, in light of the Flory-Huggins-Pouchly formalism, be used to predict the total sorption parameter  $Y$  from experimental  $\lambda$  values and vice versa. The developed formalism is proven to hold for the above ternary systems as well as for n-nonane/MEK/PDMS, n-decane/MEK/PDMS and n-undecane/MEK/PDMS.

(Keywords: second virial coefficients; preferential solvation coefficients; binary interaction potentials; ternary interaction potentials; cosolvent systems; n-alkane/butanone/poly(dimethylsiloxane) systems)

## INTRODUCTION

The Flory-Huggins (FH) formalism, as generalized by Pouchly<sup>1</sup> to ternary solvent (1)/solvent (2)/ polymer (3) systems, describes sorption equilibrium properties (total,  $Y$ , and preferential,  $\lambda$ , solvation coefficients) in terms of binary,  $g_{ij}$ , and ternary,  $g_T$ , interaction potentials as well as some derivatives with system composition of both kinds of interaction potentials. The complex dependence of the sorption coefficients on the function  $g_T$  and its derivatives may be simplified by changing the above functions by the approximate concentration-independent  $a_g$  and  $a_\lambda$  parameters<sup>2,3</sup>. Since the evaluation of  $g_T$  and its derivatives<sup>4,5</sup>, or of  $a_g$  and  $a_\lambda$  in the approximate alternative, demands known values of both  $Y$  and  $\lambda$  data, the generalized formalism seems unable not only to predict any sorption equilibrium property but to establish a relationship between both equilibrium properties.

In this paper, the above problem is partially overcome. It is shown in which manner, for those systems with an inversion in  $\lambda$  and without specific interactions,  $Y$  values can be predicted from known  $\lambda$  values or vice versa. As test systems, n-alkane (1)/butanone (MEK) (2)/poly(dimethylsiloxane) (PDMS) (3) ternary systems, with the n-alkane being n-nonane (NON), n-decane (DEC), n-undecane (UND), n-dodecane (DOD) and n-hexadecane (HED), have been chosen. Moreover, following a systematic study on the above systems, carried out in this laboratory, data on  $A_2$ ,  $\lambda$  and  $g_{12}$  are reported for the DOD/MEK/PDMS and HED/MEK/PDMS systems, which show a similar behaviour to the ones previously reported<sup>6-9</sup>.

## EXPERIMENTAL

Characterization of polymer samples and experimental techniques and conditions have been described elsewhere<sup>6,7</sup>.

## THEORY

A dilute solvent (1)/solvent(2)/polymer (3) solution may be considered as being formed by two phases coexisting in equilibrium: the bulk solvent and the domain of the coil, binary and ternary, respectively. Throughout the text the following nomenclature will be used to define the composition in both phases:  $\phi_{i0}$  ( $i=1,2$ ) is the volume fraction of component  $i$  in the bulk solvent and it is assumed to be equal to the composition of the solvent mixture prior to polymer solution;  $\phi_i$  ( $i=1,2,3$ ) is the volume fraction of component  $i$  in the domain of the coil and  $u_i$  ( $i=1,2$ ) the volume fraction of the solvent mixture inside the coil, so<sup>2</sup>

$$u_i = \phi_i / (1 - \phi_3)$$

From a phenomenological point of view, two quantities define the sorption equilibrium in ternary systems, coefficients  $Y$  and  $\lambda$ :  $\lambda$  is directly accessible from experiment, whereas  $Y$  is not. However  $Y$  is related to the experimental quantity  $A_2$ , through

$$Y = (V_1/\bar{v}_3^2)A_2/F(x)$$

where  $\bar{v}_3$  is the partial specific volume of polymer,  $V_1$  the molar volume of component  $i$  ( $i=1,2$ ) and  $F(x)$  a function of the excluded volume. In the following, the

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approximation  $F(x)=1$  is used, as usual<sup>10-12</sup>. Also  $Y$  is indirectly related, through some excluded-volume theory, to another experimental quantity like  $[\eta]$  (intrinsic viscosity)<sup>3,13</sup>. According to the FH formalism, as generalized by Pouchlý,  $\lambda$  and  $A_2$  are respectively defined by

$$\lambda = -\frac{M_{13}}{v_3 M_{11}} \quad (1)$$

$$A_2 = \frac{\bar{V}_3^2}{2RT} \left( M_{33} - \gamma \frac{M_{13}^2}{M_{11}} \right) \quad (2)$$

where  $\gamma=1$  when preferential sorption effects are taken into account, and  $\gamma=0$  when they are not ('single liquid' approach). The  $M_{ij}$ , the limits at infinite polymer dilution of the second derivatives of the Gibbs energy of mixing with respect to  $u_i$  and  $u_j$ , are not simple functions of system composition. They depend on binary,  $g_{ij}^\circ$ , and ternary,  $g_T^\circ$ , interaction parameters at infinite polymer dilution and on some derivatives of both kinds of potentials with system composition<sup>1,7</sup>.

$M_{13}$  can be calculated experimentally as a function of  $\phi_{10}$  through equation (1) from  $\lambda(\phi_{10})$  and  $g_{12}(\phi_{10})$  experimental data, since  $M_{11}(\phi_{10})$  can be evaluated unequivocally when  $g_{12}(\phi_{10})$  is known. However, the theoretical expression for  $M_{13}$ , as given by Pouchlý *et al.*<sup>1</sup>, depends on  $g_T^\circ(u_1)$  and  $(\partial g_T / \partial u_1)_{\phi_i \rightarrow 0}$ , which are unknown. To overcome this situation and reproduce  $\lambda$  from only  $g_{12}(\phi_{10})$  data, or to look for a correlation between experimental  $\lambda$  data, Pouchlý<sup>2</sup> assumes that

$$g_T^\circ(u_1) = a_g g_{12}(\phi_{10}) \quad (3)$$

$a_g$  being a constant at any composition.

The substitution of equation (3) into the corresponding  $M_{13}$  expression<sup>1,5</sup> allows us to define an approximate  $M_{13}$ ,  $M_{13}^p$ , as

$$N_{13}^p = \frac{M_{13}^p V_1}{RT} = (s-1 + g_{13}^\circ - s g_{23}^\circ) + (1-a_g) \times \left( g_{12}(\phi_{10} - \phi_{20}) - \frac{dg_{12}}{d\phi_{10}} \phi_{10} \phi_{20} \right) \quad (4)$$

where  $s=V_1/V_2$  and the  $g_{ij}^\circ$  parameters are related to  $\chi_{ij}^\circ$  through the Koningsveld and Kleitsjens equation<sup>14,15</sup>. Rearranging terms in equation (2), after substituting the  $M_{11}$  expression<sup>7</sup> and the above approximate  $M_{13}^p$ , a linear correlation between  $\lambda$  and  $g_{12}$  is obtained. From its intercept and slope, the values of the constants  $(g_{13}^\circ - s g_{23}^\circ)$  and  $(1-a_g)$  can respectively be evaluated and, of course, may be used to recalculate  $\lambda$ .

In the case of the global sorption term,  $M_{33}$ , the unknown variables are  $g_T^\circ(u_1)$  and  $(\partial g_T / \partial \phi_3)_{u_i, \phi_i \rightarrow 0}$  and  $M_{33}(\phi_{10})$  can only be evaluated through equation (2) from experimental  $A_2(\phi_{10})$  and  $g_{12}(\phi_{10})$  data. In a second approach<sup>3</sup>, looking for correlations between  $[\eta]$  data, Pouchlý assumes that

$$\chi_T^\circ(u_1) = a_\chi g_{12}(\phi_{10}) \quad (5)$$

where  $a_\chi$  is a constant at any composition and  $\chi_T^\circ(u_1)$  is

related to  $g_T^\circ(u_1)$  by

$$\chi_T^\circ(u_1) = g_T^\circ(u_1) - \frac{1}{2} \left( \frac{\partial g_T}{\partial \phi_3} \right)_{u_i, \phi_i \rightarrow 0} \quad (6)$$

With this assumption, the new global sorption term, namely  $M_{33}^p$ ,

$$\frac{M_{33}^p V_1}{RT} = \phi_{10} + s \phi_{20} - 2\chi_{13}^\circ \phi_{10} - 2s\chi_{23}^\circ \phi_{20} + 2(1-2a_\chi)g_{12}\phi_{10}\phi_{20} \quad (7)$$

no longer depends on  $g_T^\circ(u_1)$  nor on  $(\partial g_T / \partial \phi_3)_{u_i, \phi_i \rightarrow 0}$ . Substituting  $M_{33}^p$  in equation (2), together with  $M_{13}^p$  and  $M_{11} V_1 / RT = N_{11}$  yields  $A_2$  as a function of  $g_{12}(\phi_{10})$ . Rearranging terms in the new defining  $A_2$  equation, two possible linear correlations can be obtained, namely:

$$Z = \frac{1}{2s\phi_{20}} \left( \frac{A_2 2V_1}{\bar{v}_3^2} + \gamma \frac{(N_{13}^p)^2}{N_{11}} - \phi_{10} - s\phi_{20} + 2s\chi_{13}^\circ \phi_{10} \right) = -\chi_{23}^\circ + (1-2a_\chi) \frac{g_{12}\phi_{10}}{s} \quad (8)$$

or

$$Z = \frac{1}{2\phi_{10}} \left( \frac{A_2 2V_1}{\bar{v}_3^2} + \gamma \frac{(N_{13}^p)^2}{N_{11}} - \phi_{10} - s\phi_{20} + 2s\chi_{23}^\circ \phi_{20} \right) = -\chi_{13}^\circ + (1-2a_\chi)g_{12}\phi_{10} \quad (9)$$

From the slope and intercept of equation (8),  $(1-2a_\chi)$  and  $\chi_{23}^\circ$  may respectively be calculated, whereas from the slope and intercept of equation (9),  $(1-2a_\chi)$  and  $\chi_{13}^\circ$  can be obtained. In any case, as occurs with  $g_T^\circ(u_1)$  and  $(\partial g_T / \partial \phi_3)_{u_i, \phi_i \rightarrow 0}$  evaluation, application of (4) on the one hand or of (8) or (9) on the other, demands experimental  $\lambda$  and  $A_2$  data<sup>2,3</sup> over a broad range of solvent mixture composition.

## RESULTS AND DISCUSSION

Throughout the text, the ternary systems will be named by reference to the n-alkane. Thus, DOD system will mean n-dodecane/MEK/PDMS ternary system.

Apparent ( $A_2^*$ ) and real ( $A_2$ ) second virial coefficients and apparent molecular weights ( $M_3^*$ ) for PDMS samples with nominal ( $M_3 = \bar{M}_w$ ) molecular weights 68 000, 80 500, 125 000 and 150 000, at several compositions of the ternary solvent mixtures, are respectively given for DOD and HED systems in Tables 1 and 2. In the HED system, the polymer sample with the lowest molecular mass was not measured. Tables 3 and 4 show the variation of the refractive index increments  $v_3 = (dn/dc_3)_{u_i}$  and  $v_1 = (dn/d\phi_{10})_{c_3=0}$  for the DOD and HED systems respectively. They are necessary for the evaluation of  $M_3^*$ ,  $A_2^*$  and  $\lambda$  (ref. 7).

From a qualitative point of view, the dependences of  $A_2$  and  $\lambda$  on mixture composition,  $\phi_{10}$ , and on  $\bar{M}_w$  for both systems, are similar to those previously reported for HEX, HEP, NON, DEC and UND systems<sup>6-9</sup>. So,  $A_2$  dependence on  $\phi_{10}$  shows a maximum, and the sharper the maximum the lower the molecular weight of the polymer, as commented earlier<sup>6-9</sup>. Likewise, the  $\lambda$  values

**Table 1** Nominal ( $M_3$ ) and apparent ( $M_3^*$ ) molecular weights, real ( $A_2$ ) and apparent ( $A_2^*$ ) second virial and preferential solvation coefficients ( $\lambda$ ) for DOD/MEK/PDMS system at several mixture compositions at 20.0°C

$M_3$ (g mol <sup>-1</sup> )	$\phi_{10}$	$M_3^*$ <sup>a</sup> (g mol <sup>-1</sup> )	$A_{10}^2 \times 10^4$ <sup>a</sup> (ml mol g <sup>-2</sup> )	$A_2 \times 10^4$ (ml mol g <sup>-2</sup> )	$\lambda$ <sup>b</sup> (cm <sup>3</sup> g <sup>-1</sup> )
68 000	0.00		0.08	0.08	
	0.10	72 500	0.94	1.00	0.022
	0.20	76 900	1.49	1.69	0.034
	0.30	78 000	2.33	2.68	0.032
	0.40	81 300	2.97	3.55	0.032
	0.50	71 300	3.61	4.31	0.007
	0.55	65 900	4.34	4.32	-0.003
	0.60				-0.017 <sup>c</sup>
	0.70				-0.044 <sup>c</sup>
	0.85	102 900	1.66	2.51	-0.044
	0.90	91 900	1.66	2.23	-0.034
0.95	78 000	1.47	1.69	-0.019	
1.00		1.37	1.37		
80 500	0.00		0.12	0.12	
	0.10	86 600	0.86	0.92	0.025
	0.20	89 100	1.43	1.58	0.028
	0.30	94 300	2.21	2.59	0.037
	0.40	93 100	3.04	3.52	0.026
	0.50	86 000	4.01	4.29	0.008
	0.55	81 300	4.13	4.17	0.001
	0.85	120 800	1.58	2.37	-0.043
	0.90	107 100	1.59	2.11	-0.033
	0.95	93 300	1.45	1.68	-0.020
	1.00		1.22	1.22	
125 000	0.00		0.09	0.09	
	0.10	131 700	0.82	0.86	0.018
	0.20	139 300	1.32	1.47	0.030
	0.30	144 000	1.92	2.21	0.033
	0.40	144 800	2.52	2.92	0.026
	0.50	139 100	3.11	3.47	0.013
	0.55	122 500	3.46	3.39	-0.002
	0.60				-0.021 <sup>c</sup>
	0.70				-0.045 <sup>c</sup>
	0.85	178 200	1.42	2.02	-0.037
	0.90	159 400	1.53	1.95	-0.029
0.95	140 400	1.21	1.35	-0.026	
1.00		1.16	1.16		
150 000	0.00		0.10	0.10	
	0.10	158 500	0.79	0.83	0.019
	0.20	167 800	1.24	1.39	0.031
	0.30	176 400	1.74	2.05	0.038
	0.40	175 600	2.31	2.71	0.028
	0.50	159 000	2.79	2.96	0.011
	0.55	150 000	3.08	3.08	0.000
	0.85	215 600	1.36	1.95	-0.038
	0.90	201 900	1.32	1.78	-0.036
	0.95	174 400	1.12	1.30	-0.021
	1.00		1.05	1.05	

<sup>a</sup>Uncertainties on  $M_3^*$  and  $A_2^*$  are about 4–5%.

<sup>b</sup>Mean deviation of  $\lambda$  values is  $\pm 0.007$ 
<sup>c</sup>From steric exclusion chromatography measurements<sup>6</sup>

and the range of solvent mixture composition in which  $\lambda$  values are positive (i.e. in which PDMS is preferentially solvated by n-alkane) follow a similar trend to the corresponding ones for the systems previously studied. So, solvation by MEK ( $\lambda$  negative values) is higher than in the other n-alkane systems, as expected<sup>8</sup>.

Both DOD and HED systems seem to obey both Pouchlý's approaches as expressed by equations (3) and (5), as shown in Figure 1, as also happened with the remaining studied n-alkane/MEK/PDMS systems<sup>6–9</sup>. Similarly, the solvent composition at which  $A_2$  attains its maximum value coincides with the  $\lambda$  inversion point ( $\lambda = 0$ ). This fact, in accordance with the thermodynamic

theory<sup>16,17</sup> for cosolvent systems, deserves detailed discussion.

Let us call  $\phi_{10}^i$  the solvent mixture composition at the inversion point. At that composition,  $\lambda = 0$ , and the preferential sorption term in  $A_2$ , ( $M_{13}^2/M_{11}$ ) = 0; therefore

**Table 2** Nominal ( $M_3$ ) and apparent ( $M_3^*$ ) molecular weights, real ( $A_2$ ) and apparent ( $A_2^*$ ) second virial and preferential solvation coefficients ( $\lambda$ ) for HED/MEK/PDMS system at several mixture compositions at 20.0°C

$M_3$ (g mol <sup>-1</sup> )	$\phi_{10}$	$M_3^*$ <sup>a</sup> (g mol <sup>-1</sup> )	$A_2^* \times 10^4$ <sup>a</sup> (ml mol g <sup>-2</sup> )	$A_2 \times 10^4$ (ml mol g <sup>-2</sup> )	$\lambda$ <sup>b</sup> (cm <sup>3</sup> g <sup>-1</sup> )
80 500	0.00		0.12	0.12	
	0.10	82 600	1.03	1.06	0.008
	0.20	84 400	1.59	1.67	0.010
	0.24	84 400	1.70	1.78	0.009
	0.30	84 700	2.07	2.18	0.007
	0.35	83 800	2.32	2.42	0.004
	0.40	79 900	2.51	2.49	0.000
	0.55				-0.039 <sup>c</sup>
	0.68	121 300	0.83	1.25	-0.034
	0.70	118 000	0.55	0.80	-0.034
	0.75	109 250	0.15	0.20	-0.031
0.80	106 400	0.01	0.01	-0.033	
125 000	0.00		0.09	0.09	
	0.10	128 400	0.90	0.92	0.008
	0.20	130 800	1.50	1.57	0.009
	0.24	130 600	1.51	1.58	0.008
	0.30	131 800	1.84	1.94	0.007
	0.35	129 400	2.03	2.10	0.004
	0.40	125 800	2.13	2.14	0.000
	0.68	184 000	0.75	1.11	-0.032
	0.70	185 600	0.48	0.72	-0.035
	0.75	174 000	0.04	0.06	-0.034
	0.80	159 300	0.00	0.00	-0.029
150 000	0.00		0.10	0.10	
	0.10	154 900	0.76	0.79	0.010
	0.20	156 500	1.23	1.28	0.009
	0.24	156 200	1.38	1.44	0.007
	0.30	159 200	1.74	1.85	0.008
	0.35	154 200	1.96	2.01	0.003
	0.40	149 500	2.10	2.09	0.000
	0.68	224 300	0.80	1.20	-0.033
	0.70	211 000	0.73	1.02	-0.030
	0.75	214 300	0.20	0.29	-0.037
	0.80	185 000	0.00	0.00	-0.024

<sup>a</sup>Uncertainties on  $M_3^*$  and  $A_2^*$  are about 4–5%.

<sup>b</sup>Mean deviation of  $\lambda$  values is  $\pm 0.007$ 
<sup>c</sup>From steric exclusion chromatography measurements<sup>6</sup>
**Table 3** Variations with polymer concentration ( $v_3$ ) and with solvent mixture composition ( $v_1$ ) of refractive index increments for DOD/MEK/PDMS system at several mixture compositions at 20.0°C

$\phi_{10}$	$v_1$	$v_3$ <sup>a</sup> (ml g <sup>-1</sup> )
0.00	0.0356	0.0295
0.10	0.0369	0.0250
0.20	0.0383	0.0206
0.30	0.0396	0.0178
0.40	0.0410	0.0140
0.50	0.0423	0.0100
0.55	0.0430	0.0085
0.60	0.0437	0.0030
0.70	0.0451	0.0015
0.80	0.0464	-0.0065
0.85	0.0471	-0.0084
0.90	0.0478	-0.0100
0.95	0.0484	-0.0128
1.00	0.0491	-0.0150

<sup>a</sup>Mean deviation of  $v_3$  values is  $\pm 0.0002$

$M_{13}^i(\phi_{10}^i) = 0$ . Recalling the definition of  $M_{13}$  given by (4) and for those systems obeying Pouchlý's approach (3), the following equality holds at  $\phi_{10}^i$ :

$$0 = (s - 1 + g_{13}^0 - sg_{23}^0) + (1 - a_g) \times \left( g_{12}(\phi_{10}^i)(\phi_{10}^i - \phi_{20}^i) - \frac{dg_{12}(\phi_{10}^i)}{d\phi_{10}} \phi_{10}^i \phi_{20}^i \right) \quad (10)$$

On the other hand, the application of the condition for a maximum of the total sorption term, at  $\phi_{10}^i$ , yields, for the system obeying Pouchlý's second approach (equation (5)):

$$\frac{dM_{33}(\phi_{10}^i)}{d\phi_{10}} = \frac{1}{2}(1 - s) - \chi_{13}^0 + s\chi_{23}^0 + (1 - 2a_\chi) \times \left( \phi_{10}^i \phi_{20}^i \frac{dg_{12}(\phi_{10}^i)}{d\phi_{10}} + (\phi_{20}^i - \phi_{10}^i)g_{12}(\phi_{10}^i) \right) = 0 \quad (11)$$

From the above expression, the following equation yields

**Table 4** Variations with polymer concentration ( $v_3$ ) and with solvent mixture composition ( $v_1$ ) of refractive index increments for HED/MEK/PDMS system at several mixture compositions at 20.0°C

$\phi_{10}$	$v_1$	$v_3^a$ (ml g <sup>-1</sup> )
0.00	0.0354	0.0295
0.10	0.0392	0.0240
0.20	0.0429	0.0170
0.30	0.0467	0.0130
0.40	0.0505	0.0080
0.60	0.0580	-0.0020
0.65	0.0599	-0.0080
0.70	0.0618	-0.0100
0.75	0.0637	-0.0120
0.80	0.0656	-0.0145
0.90	0.0694	
1.00	0.0732	

<sup>a</sup> Mean deviation of  $v_3$  values is  $\pm 0.0002$

the value of  $a_\chi$  in terms of  $\chi_{ij}^0$  binary interaction parameters and the composition at the inversion point:

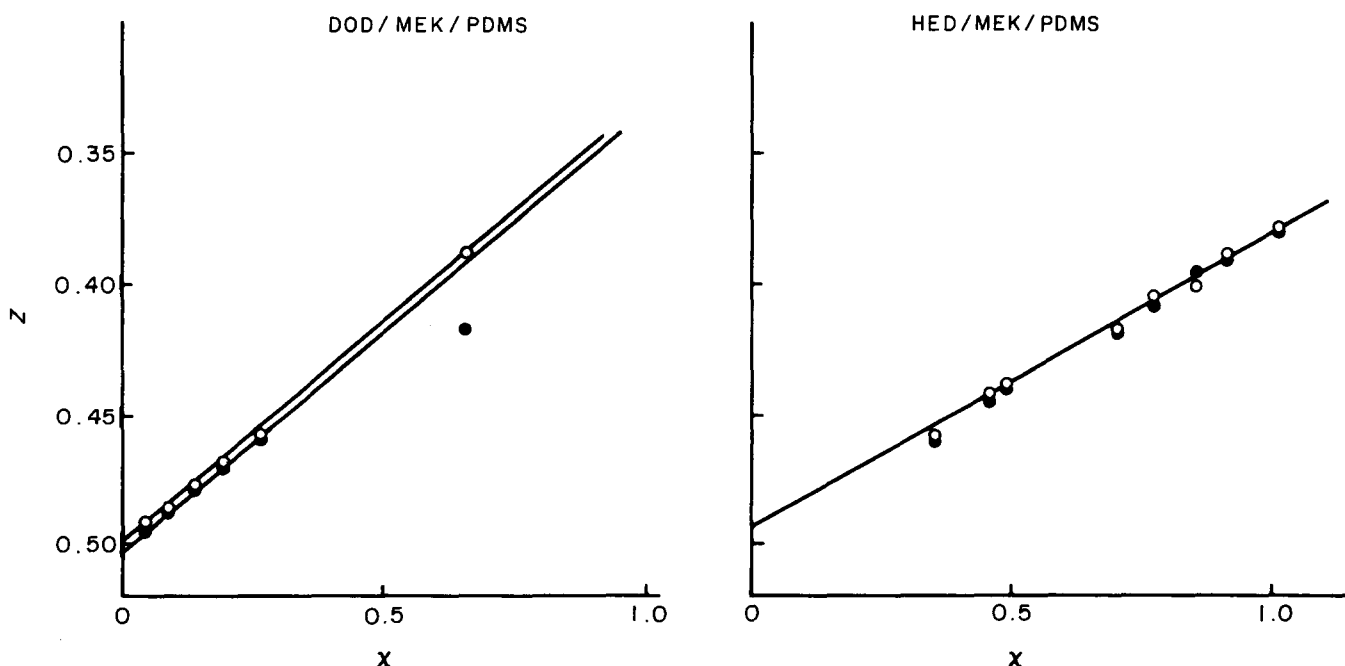
$$(1 - 2a_\chi) = \frac{\frac{1}{2}(s - 1) + \chi_{13}^0 - s\chi_{23}^0}{\phi_{10}^i \phi_{20}^i \frac{dg_{12}(\phi_{10}^i)}{d\phi_{10}} + (\phi_{20}^i - \phi_{10}^i)g_{12}(\phi_{10}^i)} \quad (12)$$

Once  $a_\chi$  is known, its substitution in equations (8) or (9) allows us to evaluate  $A_2$  in terms of  $\lambda$  values through:

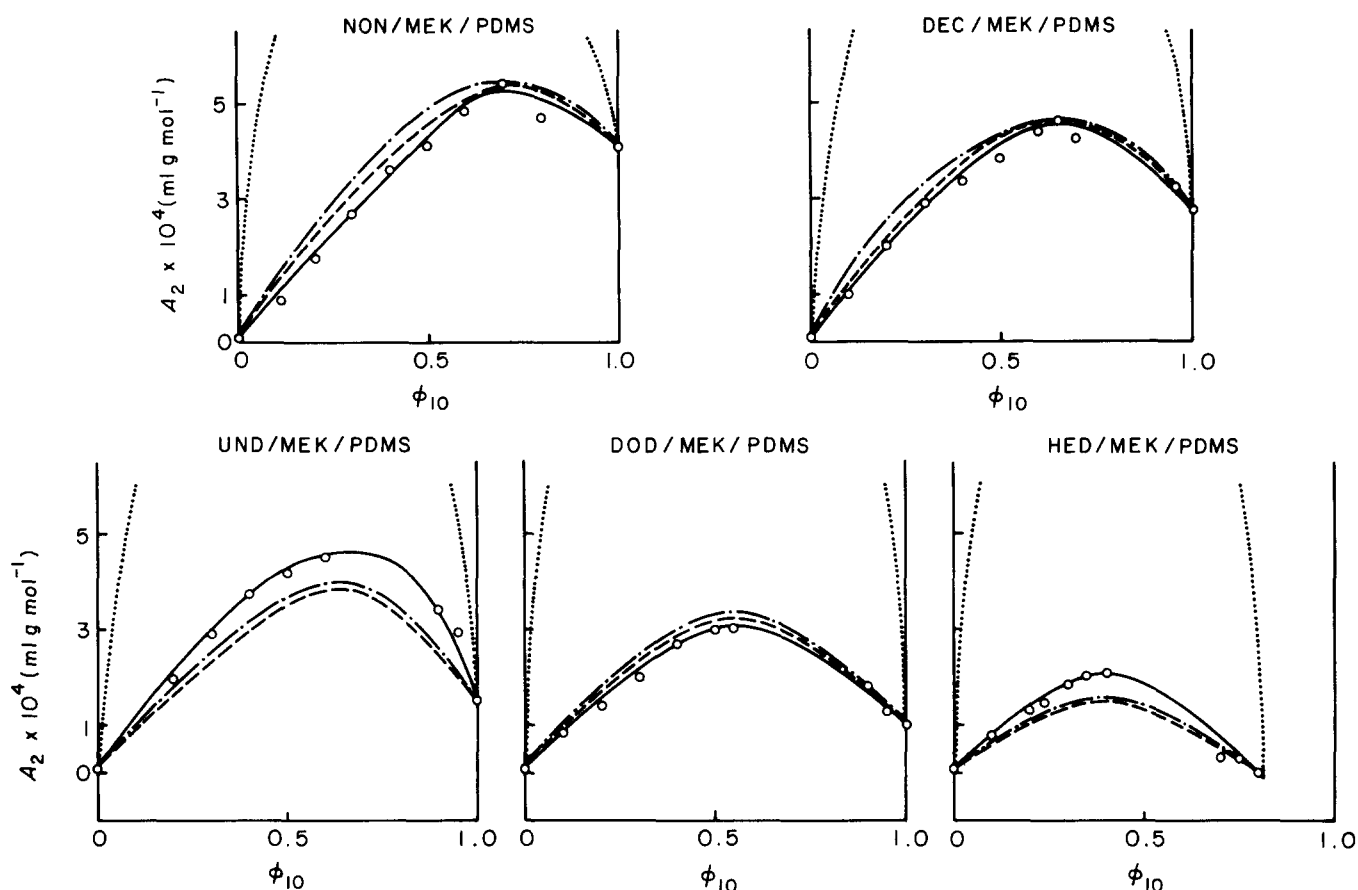
$$A_2 = \frac{\bar{v}_3^2}{2V_1} \left( \phi_{10} + s\phi_{20} - 2\chi_{13}^0\phi_{10} - 2s\chi_{23}^0\phi_{20} + 2(1 - 2a_\chi)g_{12}\phi_{10}\phi_{20} - \gamma \frac{\lambda^2 N_{11}}{\bar{v}_3^2} \right) \quad (13)$$

Application of equation (13) to predict  $A_2$  values from measured  $\lambda$  values thus demands, besides binary interaction parameters, a known  $a_\chi$  value, which can of course be evaluated from equation (12), once the inversion point is determined from  $\lambda$  measurements. It is this previous knowledge of the inversion point that prevents the inverse application of equation (13) to predict  $\lambda$  values from experimental  $A_2$  values, since, if no measurements on  $\lambda$  have been realized, neither the inversion point nor  $a_\chi$  are known. An alternative way, however, as shown later, will allow that inverse application.

Application of equation (13) to NON, DEC, UND, DOD and HED systems, over the whole composition range of solvent mixtures, is illustrated in Figure 2, where  $A_2$  values, as deduced from equation (13), are compared to experimental ones. All the functions and parameters necessary for application of equation (13) are gathered in Table 5. With respect to the  $\lambda(\phi_{10})$  function, no clear dependence of  $\lambda$  on molecular weight in all these studied systems was experimentally observed<sup>6-9</sup>, at least over the measured range of molecular weights. Because of that, in  $A_2$  evaluation through equation (13), single smooth  $\lambda$  curves through the diverse experimental data have been used, as Munk *et al.*<sup>4,5</sup> and Pouchlý *et al.*<sup>2</sup> have done before. Here  $\chi_{13}^0$  and  $\chi_{23}^0$  were those for a PDMS sample



**Figure 1** Linearized plot of equation (9): (○) when  $\gamma = 0$  and (●) when  $\gamma = 1$ , for DOD and HED systems



**Figure 2** Variations with system composition of second virial coefficients ( $A_2$ ) for a PDMS sample ( $M_3 = 150\,000$ ) at  $20.0^\circ\text{C}$  for NON, DEC, UND, DOD and HED systems: (○), experimental values; (—), smoothed curve to match experimental points; (⋯), calculated through FH formalism; (---), calculated from equation (13) when  $\gamma = 0$ ; (-·-·-), calculated from equation (13) when  $\gamma = 1$

**Table 5** Parameter values needed for  $A_2$  and  $\lambda$  evaluation, from equations (13) and (15), respectively

System	$g_{12}(\phi_{10})^{a-c}$	$\chi_{13}^d$	$\chi_{23}^d$	$(1-2a_\chi)$			
				$\phi_{10}$		$(1-2a_\chi)$	
				From $\lambda = 0$	From $A_2^{\max}$	From $\lambda = 0$ through (13)	From $A_2^{\max}$ through (15)
NON	$1.229 + 0.446\phi_{10} - 0.666\phi_{10}^2 + 1.114\phi_{10}^3$ <sup>a</sup>	0.431 <sup>d</sup>	0.499	0.73	0.70	0.133	0.128
DEC	$1.240 - 0.496\phi_{10} + 4.652\phi_{10}^2 - 8.448\phi_{10}^3 + 5.554\phi_{10}^4$ <sup>a</sup>	0.450 <sup>d</sup>	0.499	0.67	0.65	0.134	0.149
UND	$1.137 - 0.828\phi_{10} + 1.912\phi_{10}^2$ <sup>b</sup>	0.470 <sup>d</sup>	0.499	0.64	0.60	0.200	0.220
DOD	$1.143 - 0.909\phi_{10} + 6.441\phi_{10}^2 - 11.37\phi_{10}^3 + 7.010\phi_{10}^4$ <sup>c</sup>	0.471 <sup>e</sup>	0.499	0.59	0.55	0.173	0.158
HED	$1.236 - 2.116\phi_{10} + 11.40\phi_{10}^2 - 19.07\phi_{10}^3 + 11.31\phi_{10}^4$ <sup>c</sup>	0.587-0.604 <sup>f</sup>	0.499	0.40	0.40	0.220	0.295

<sup>a</sup>From ref. 9

<sup>b</sup>From ref. 8

<sup>c</sup>As evaluated from light scattering measurements<sup>27-30</sup>

<sup>d</sup>From refs. 6 and 7

<sup>e</sup>As evaluated from  $A_2$  (ref. 4)

<sup>f</sup>From intercept of equation (9), when  $\gamma = 1$  and when  $\gamma = 0$  respectively. These values are higher than 0.50 because n-hexadecane is a nonsolvent for PDMS

with  $M_w = 150\,000$ . Of course,  $\lambda$  values for that polymer sample are very close to the smoothed curves.

As Figure 2 shows, predicted  $A_2$  values for all the systems fit the experimental ones fairly well, both when the single liquid approach ( $\gamma = 0$ ) is followed and when preferential sorption effects are accounted for in total sorption ( $\gamma = 1$ ). Also, in Figure 2,  $A_2$  values calculated through the usual FH equation have been depicted. As widely discussed<sup>18-26</sup>, neglect of the ternary interactions results in large discrepancies between calculated and experimental values.

Regarding the alternative way followed to predict  $\lambda$  values from experimental  $A_2$  values, the application of the

condition of maximum to the second virial coefficient, recalling that at that solvent composition  $\lambda = 0$ , yields

$$1 - 2a_\chi = \frac{1}{2g_{12}(\phi_{10}^i)\phi_{10}^i\phi_{20}^i} \left( A_2^i \frac{2V_1}{v_3^2} - (\phi_{10} + s\phi_{20}) + 2\chi_{13}^o\phi_{10}^i + 2s\chi_{23}^o\phi_{20}^i \right) \quad (14)$$

which allows  $a_\chi$  to be evaluated from the maximum  $A_2$  value, and from binary interaction parameters. Of course once  $a_\chi$  is thus evaluated, equation (13) (with  $\gamma = 1$ ) can now be applied to predict  $\lambda$  from experimental  $A_2$  data,

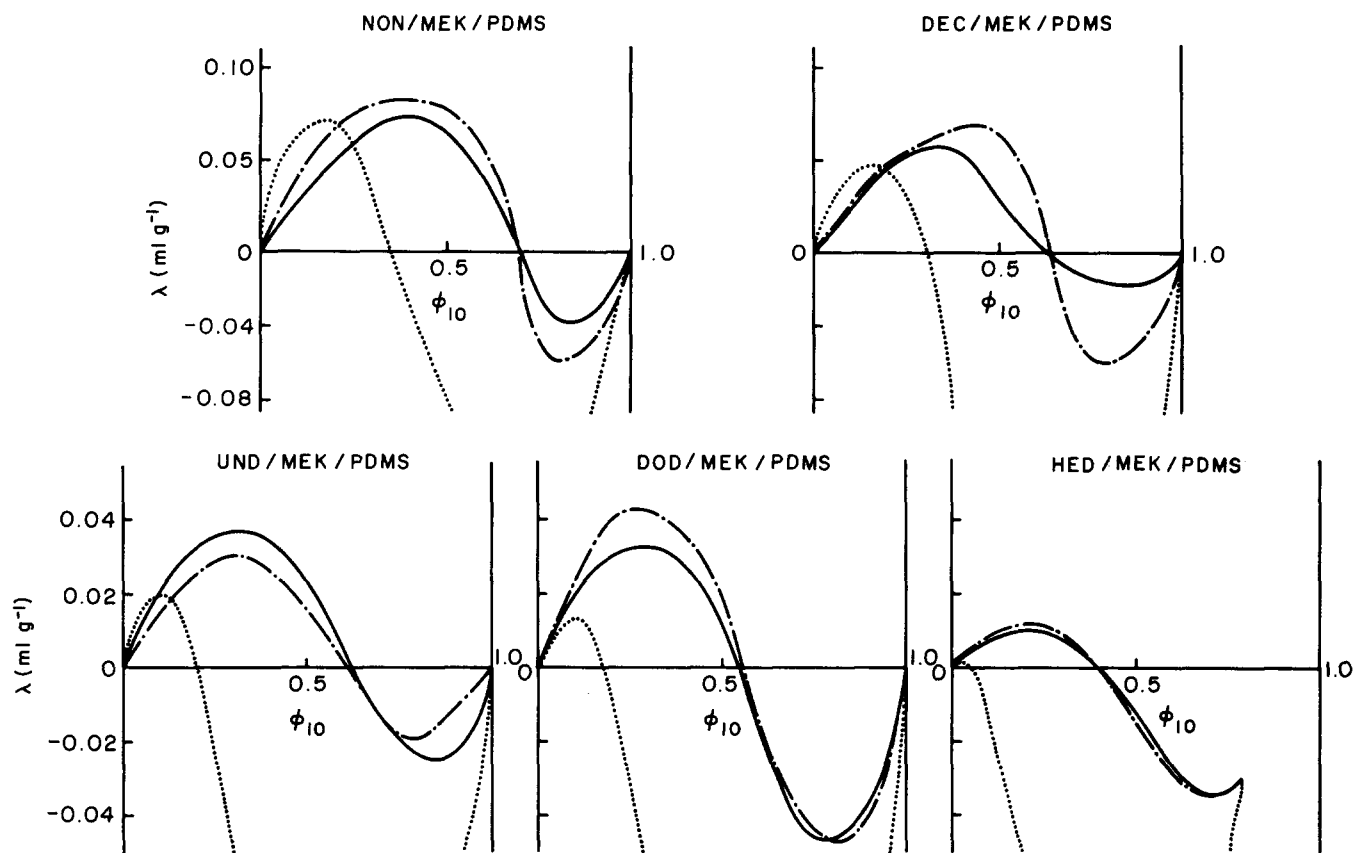


Figure 3 Variations with system composition of preferential solvation coefficients ( $\lambda$ ) at 20.0°C for NON, DEC, UND, DOD and HED systems: (—), smoothed curve to match experimental points; (····), calculated through Read's expression; (-·-·-), calculated from equation (15)

explicitly by

$$\lambda = \frac{\bar{v}_3}{N_{11}^{1/2}} \left( -A_2 \frac{2V_1}{\bar{v}_3^2} + (\phi_{10} + s\phi_{20}) - 2\chi_{13}^0\phi_{10} - 2s\chi_{23}^0\phi_{10} + 2(1 - 2a_x)g_{12}\phi_{10}\phi_{20} \right)^{1/2} \quad (15)$$

As in the case of equation (13), all the functions and parameters needed for equation (15) are also collected in Table 5. As Table 5 shows, small deviations appear between both  $\phi_{10}^i$  sets of values. It must be remembered that the first set of  $\phi_{10}^i$  values proceeds from the smooth  $\lambda$  curves through the experimental values obtained for diverse molecular weight samples, whereas the second set proceeds from the depicted  $A_2$  curve through 8–10 experimental values for the  $M_3 = 150\,000$  PDMS sample. Those small deviations in the experimental uncertainty are also reflected in both sets of  $a_x$  values.

In Figure 3,  $\lambda$  values predicted from experimental  $A_2$  data, as evaluated through (15), are compared to smoothed experimental  $\lambda$  curves, and, as shown, fair agreement between predicted and experimental values is observed in all systems. Also, in Figure 3,  $\lambda$  values calculated through the widely used Read expression<sup>19</sup> have been depicted. Once more, serious discrepancies arise, in all the systems, between these last calculated  $\lambda$  values and the respective experimental values, as also happens in  $A_2$  evaluation from  $\lambda$  data, because of the neglect of ternary interactions.

As a conclusion, in spite of its use being restricted to those systems in which the maximum in  $A_2$  coincides with the inversion point in  $\lambda$ , it seems that the above treatment is one step further in the applicability of FH formalism as

generalized by Pouchlý<sup>1</sup> to predict equilibrium properties of ternary systems.

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