Comparative study of the formalism of Flory–Huggins as generalized by Pouchly and the formalism of Flory–Prigogine–Patterson in ternary polymer systems, n-alkane–butanone–poly(dimethylsiloxane)

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There are two formalisms to describe the sorption equilibrium in a polymer-mixed solvent system (TPS). In the Flory–Huggins (FH) thermodynamic model, empirical ternary interaction parameters, g_T and χ_T, are necessary to evaluate the preferential adsorption coefficient (λ) and total sorption potential (Y). These ternary parameters have already been defined as a function of the three binary interaction parameters, g_{i3}^0 ($i=1, 2$) and g_{12}. In the Flory–Prigogine–Patterson (FPP) formalism, thermodynamic quantities depend on the molecular characteristics (s, α and α'), and exchange interactions of all three components simultaneously being ternary *per se*. A comparative analysis between both formalisms in ten TPS has allowed us, for the first time, to define s, α and α' as functions of $g_{13}^0$and g_{23}^0. A similar study extended to four TPS in which g_{i3}^0 values have been previously fitted to λ and A_2 (directly related to Y) experimental results, yields s, α and α' values adjusted as well as to these experimental results. This new methodology has been applied to n-alkane–butanone–poly(dimethylsiloxane) (PDMS) systems. This was shown that, as for other systems with PDMS as polymer, other contributions different from dissimilarities in free volume should be introduced in the simplified model of FPP.

(Keywords: Flory–Huggins thermodynamic model; Flory–Prigogine–Patterson formalism; thermodynamic model)

INTRODUCTION

In ternary systems formed by a polymer as solute dissolved in a binary solvent mixture, a sorption equilibrium is established, which can be fully described by total (Y) and preferential (λ) sorption coefficients. These coefficients have been defined through two different formalisms: Flory–Huggins[1,2,3] (FH) and Flory–Prigogine–Patterson[4,5] (FPP).

The FH formalism as generalized by Pouchly[6,7] defines λ and Y for a solvent(1)–solvent(2)–polymer(3) system as a function of binary interaction parameters at polymer infinite dilution g_{13}^0, g_{23}^0, χ_{13}^0 and χ_{23}^0, interaction parameter between solvents, $g_{12}(\phi_{10})$ (those parameters can be evaluated from independent experiments) and ternary interaction parameters at polymer infinite dilution $g_T^0(u_1)$, $(\delta g_T/\delta u_1)_{\phi_3\to 0}$ and $(\delta g_T/\delta \phi_3)_{\phi_3\to 0}$ (which cannot be experimentally obtained).

Pouchly and Patterson[8] first, and afterward Pouchly and Zivny (through the analysis of results of λ (ref. 9) and Y calculated from intrinsic viscosity[10] for several systems) verified the proportionality between $g_T^0(u_1)$ and $g_{12}(\phi_{10})$ and between $\chi_T^0(u_1)(\chi_T^0(u_1)=g_T^0(u_1)-(1/2)(\delta g_T/\delta\phi_3)_{\phi_3\to 0}$ and $g_{12}(\phi_{10})$ by means of the constants a_g and a_χ, respectively. Therefore, the ternary parameters were substituted by these constants, though, a_g and a_χ remained as adjustable parameters to experimental results of λ and Y.

In previous papers[11,12] it was empirically assumed that ternary interactions can be regarded as a function of three simultaneous binary interactions. These assumptions provided two different expressions both for $g_T^0(u_1)$ and $\chi_T^0(u_1)$ solely as functions of binary interaction parameters g_{i3}^0, χ_{i3} ($i=1, 2$) and $g_{12}(\phi_{10})$. Therefore, the equilibrium properties of ternary polymer systems (TPS) can be predicted through FHP formalism exclusively from interaction parameters of the respective binary systems. Nevertheless, from a practical point of view, often it is more useful to evaluate g_{13}^0 and g_{23}^0 as adjustable parameters to λ and second virial coefficient (A_2 directly related to Y) experimental values, which is relatively easy[11–14] and the results so obtained fit well, as was tested in a large number of TPS, with those independently calculated from the functions of $\chi_{i3}(\phi_3)$[12,15] for the respective binary systems. However, in spite of this agreement between adjusted and calculated g_{i3}^0 values, and due to the mathematical form of λ and Y expressions sometimes, especially for the TPS with large g_{12} values, numerical difficulties on λ and Y prediction can appear.

On the other hand, Horta[16] recently obtained expressions for λ and Y similar in their form to the FHP equations using the FPP formalism based on molecular parameters. However, as both formalisms have different

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initial statements the corresponding terms to ternary parameters (g_T^0 or χ_T^0) in the latter are substituted in the former by terms in which the effects of dissimilarities in free volume (α) and in molecular surface to volume ratio (s) between polymer and solvents are taken into account. Usually, λ and Y predicted values from FPP equations show either qualitative or quantitative discrepancies with respect to experimental ones, it being necessary to use an adjustable parameter, as happened in the FHP formalism. Heretofore, s has been exclusively used to adjust experimental and calculated λ and Y values, although with irregular results[17,18].

Apparently, and apart from the possible inherent mathematical difficulties, the simultaneous comparative analysis among all the different constants in both formalisms ($s, \alpha, g_{13}^0, g_{23}^0$ etc.) may exhibit a relevant importance: it could be a new way to learn about the molecular characteristics of ternary interactions, and to predict λ and Y experimental results from values close to those obtained for characteristic magnitudes of pure substances (for s, α etc.) and for those calculated through $\chi_{i3}(\phi_3)$ function in the respective binary systems (for g_{13}^0 and g_{23}^0).

In this work the equations for λ and Y from both formalisms are compared, and the terms corresponding to ternary interactions (FHP), as a function of g_{i3}^0 ($i=1,2$), have been equalized to the representative terms of dissimilarities in free volume (α) and in molecular surface to volume ratio (s) between polymer and solvents (FPP formalism). From these comparisons, the identification of terms has allowed to obtain expressions from which the values of different constants in FPP can be calculated exclusively as a function of g_{i3}^0 ($i=1,2$). These equations have been verified in ten TPS, for which bibliographic values of g_{i3}^0, χ_{i3}^0 ($i=1,2$) and characteristic magnitudes of pure components (from which s, α etc. can be obtained) were available. Likewise, in four TPS the equations obtained through comparison of both formalisms have been verified using values of s and α from the literature and g_{i3}^0 ($i=1,2$) values adjusted to λ and Y experimental results, which can be an indirect way to simultaneously adjust α and s to λ and Y values.

Finally, through the above equations the values of different constants in FPP formalism (α and s) have been evaluated using recent λ and Y experimental results and compared with those obtained for characteristic magnitudes of pure substances for several n-alkane-butanone (MEK)-poly(dimethylsiloxane) (PDMS) systems[19–25].

THEORY

Total (Y) and preferential (λ) sorption coefficients defining sorption equilibrium for a ternary polymer system are given by[9,10]

$$Y=(V_1/(2RT))(M_{33}-(M_{13}^2/M_{11})) \tag{1}$$

$$\lambda=-\bar{v}_3(M_{13}/M_{11}) \tag{2}$$

where the M_{ij} values are the limits at polymer infinite dilution of the second derivatives of the Gibbs energy of mixing, and $\bar{v}_3$ is the partial specific volume of polymer. The M_{ij} values corresponding expressions have been defined in the extended FH formalism[9,10].

From a phenomenological point of view, λ is a magnitude directly accessible from experiment. Therefore, it is possible to compare experimental and theoretical values of λ. Y is not a magnitude directly accessible from experiment, but it can be related to the experimental second virial coefficient A_2:

$$Y=[V_1A_2/(\bar{v}_3)^2][1/F(x)] \tag{3}$$

where $F(x)$ gives the excluded volume dependence and usually $F(x)\equiv 1$ (refs 26, 27). Thus, experimental and theoretical values of Y may be compared. In equations (1) and (2) binary interaction parameters g_{12}, g_{13}^0, g_{23}^0, χ_{13}^0 and χ_{23}^0 appear after substitution M_{ij} values functions[9,10]. These parameters can be evaluated experimentally. Nevertheless, the ternary parameters g_T^0, $(\delta g_T/\delta u_1)_{\phi_3\to 0}$ and $(\delta g_T/\delta\phi_3)_{\phi_3\to 0}$ also appear and being unknown, they do not permit the use of expressions in the extended Flory–Huggins theory.

A ternary parameter and its derivatives can be substituted by a_g and a_χ constants[9,10], but they remain as adjustable constants to experimental data. In previous papers[11,13] we have found equations for a_g and a_χ solely as functions of binary parameters through empirical correlations.

Substituting these values into M_{13} and M_{33} these magnitudes can be expressed by:

$$\begin{aligned}N_{13}&=[M_{13}V_1]/(RT)=r-1+g_{13}^0-rg_{23}^0\\&\quad-(1-(g_{13}^0g_{23}^0)/(1-D))d(\phi_{10}\phi_{20}g_{12})/d\phi_{10}\end{aligned} \tag{4}$$

$$\begin{aligned}N_{33}&=[M_{33}V_1]/(2RT)=1/2(\phi_{10}+r\phi_{20})-\chi_{13}^0\phi_{10}\\&\quad-r\chi_{23}^0\phi_{20}+(1-(2g_{13}^0g_{23}^0-D)\\&\quad\div(1-D)g_{12}\phi_{10}\phi_{20}\end{aligned} \tag{5}$$

being $D=g_{13}^0(g_{23}^0-\chi_{23}^0)+g_{23}^0(g_{13}^0-\chi_{13}^0)$.

For these systems for which g_{i3}^0, χ_{i3}^0 and g_{12} are known, λ and A_2 values calculated through equations (1), (2), (4) and (5) were compared with experimental data and a good agreement has been found[11,13]. Latterly[12,14], we have proposed new equations for g_T^0 and $(\delta g_T/\delta\phi_3)_{\phi_3\to 0}$ as a function of binary interaction parameters g_{i3}^0 and χ_{i3}^0 ($i=1,2$) which allow us to write N_{13} and N_{33} as:

$$\begin{aligned}N_{13}&=[M_{13}V_1]/(RT)=r-1+g_{13}^0-rg_{23}^0\\&\quad-(1-(g_{13}^0g_{23}^0))/(1-D')d(\phi_{10}\phi_{20}g_{12})/d\phi_{10}\end{aligned} \tag{6}$$

$$\begin{aligned}N_{33}&=[M_{33}V_1]/(2RT)=1/2(\phi_{10}+s\phi_{20})-\chi_{13}^0\phi_{10}\\&\quad-r\chi_{23}^0\phi_{20}+(1-(2g_{13}^0g_{23}^0-g_{13}^0g_{23}^0D'))\\&\quad\div(1-D')g_{12}\phi_{10}\phi_{20}\end{aligned} \tag{7}$$

being $D'=D/(2g_{13}^0g_{23}^0)$.

λ and A_2 results evaluated through equations (6) and (7) fit well with experimental data[12,14].

Equations (4) and (5) (set A of approximations) and equations (6) and (7) (set B of approximations) are based on the Flory–Huggins theory as generalized by Pouchly (FHP)[6,7,9,10].

Horta[16] through the Flory–Prigogine–Patterson theory (FPP) gives expressions for M_{13} and M_{33} similar in their form to equations (4) and (5) or (6) and (7). Those expressions (set C of approximations) take into account the dissimilarities in free volume (α) and in surface to volume ratio (s) between polymer and solvents but the differences between solvents are neglected, as Pouchly and Patterson did in their theory[4]. Horta expresses M_{13} and M_{33} by

$$\begin{aligned}N_{13}&=[M_{13}V_1]/(RT)=r-1+g_{13}^0-rg_{23}^0\\&\quad-(\bar{V}_{12}/\bar{V}_3)(s-\alpha)d(\phi_{10}\phi_{20}g_{12})/d\phi_{10}\end{aligned} \tag{8}$$

$$N_{33}=[M_{33}V_1]/(RT)=1/2(\phi_{10}+r\phi_{20})-\chi^0_{13}\phi_{10}$$
$$-r\chi^0_{23}\phi_{20}+(\bar{V}_{12}/\bar{V}_3)^2(s^2-s\alpha-\alpha')g_{12}\phi_{10}\phi_{20} \quad (9)$$

$\bar{V}_i$ is the reduced volume of component i:$s=s_3/s_{12}$, where s_i is the molecular surface to volume ratio; $\alpha=\alpha_{12}T(P^*_3/P^*_{12})(1-T^*_{12}/T^*_3)$ and $\alpha'=\alpha P^*_3/P^*_{12}$, where P^*_i and T^*_i are characteristic reduced values for pressure and temperature[28] respectively, and α_i is the thermal expansion coefficient. (The subscript '12' stands for a liquid mixture considered as a single solvent with average properties[18,29].) Equations (4) and (5), (6) and (7) and (8) and (9) are similar in their form. The constants $[1-(g^0_{13}g^0_{23})/(1-D)]$, $[1-(2g^0_{13}g^0_{23}-D)/(1-D)]$, $[1-(g^0_{13}g^0_{23})/(1-D')$ and $[1-(2g^0_{13}g^0_{23}-g^0_{13}g^0_{23}D')/(1-D')]$ in equations (4)–(7) consider ternary interactions[11,12].

As above, in equations (8) and (9) the constants $(\bar{V}_{12}/\bar{V}_3)(s-\alpha)$ and $(\bar{V}_{12}/\bar{V}_3)^2(s^2-s\alpha-\alpha')$ will take into account ternary interaction analysed as the dissimilarities in α and s between polymer and solvents.

The main difference among FPP constants and FHP constants is that the former accounts for the dissimilarities effects (non specific effects) such as polar or specific interactions present in the system[16] through s, α and α' separately while FHP constants appear after the introduction of a term which assumes all the effects in the polymer system in a global manner.

RESULTS AND DISCUSSION

As it was mentioned in the Introduction, the scope of this paper is to analyse the predictive capacity of FPP formalism for magnitudes describing sorption equilibrium in TPS (λ and A_2), specially for a series of n-alkane(1)-butanone(2)-poly(dimethylsiloxane) (PDMS)(3) recently studied[19–25]. From a simple inspection of sets of equations (4), (5), (6), (7) and (8), (9) it is relatively easy to understand the difficulties, because of the necessary large amount of information, to properly apply the expressions of M_{13} and M_{33} for the theoretical prediction of A_2 and λ through equations (1), (2) and (3). The deviations in those values with respect to ideal ones arising in TPS may be attributed to the terms in which g_{12} functions appear. On the other hand, it is also evident that small variations in the values of the factors multiplying those terms can introduce significant differences between experimental and predicted results, these differences being more pronounced the larger are the g_{12} values. In cosolvent ternary polymeric systems, as for example n-alkane-MEK-PDMS, g_{12} values are always large and positive[24]. Obviously, it seems to be convenient to study those factors. In equations (4), (5) and (6), (7) it is relatively simple to find that g^0_{13} and g^0_{23} are the two adjustable parameters (χ^0_{13} and χ^0_{23} can be obtained from A_2 values in the binary system, respectively) in M_{13} and M_{33} expressions to compare theoretical and experimental values of λ and A_2. For instance, from the combination of equations (2) and (4) the following relation can be obtained:

$$-N_{11}\lambda/v_3=r-1+g^0_{13}-rg^0_{23}-(1-(g^0_{13}g^0_{23}))$$
$$\div(1-D)d(\phi_{10}\phi_{20}g_{12})/d\phi_{10} \quad (10)$$

being $N_{11}=[M_{11}V_1]/(RT)$.

From the intercept and slope of the plot $-N_{11}\lambda/v_3$ *versus* $d(\phi_{10}\phi_{20}g_{12})/d\phi_{10}$, g^0_{13} and g^0_{23} can be calculated. When the values of g^0_{13} and g^0_{23} so evaluated are introduced in equation (5) values are obtained of M_{33} and consequently A_2 (if the single liquid approximation is applied, $M_{13}=0$ in equation (1) which fits very well with experimental results). The validity of this method and other similar has been extensively verified in the series n-alkane-MEK-PDMS and in a large number of other TPS[11–14,23,30]. Normally, g^0_{13} and g^0_{23} values obtained with the above method are in good agreement[11–14] to those independently calculated through values of $\chi_{i3}(\phi_3)$, which can be evaluated from chemical potential of the solvent in the corresponding binary system polymer–solvent[12,15].

The methods already used to adjust g^0_{13} and g^0_{23} values in equations (4), (5) and (6), (7) to experimental results are not valid in the case of equations (8) and (9), because in these equations there are five different adjustable parameters g^0_{13}, g^0_{23}, $(\bar{V}_{12}/\bar{V}_3)s$, $(\bar{V}_{12}/\bar{V}_3)\alpha$ and $(\bar{V}_{12}/\bar{V}_3)^2\alpha'$.

A valid procedure of fitting among the factors $1-((g^0_{13}g^0_{23})/(1-D))$, $1-((g^0_{13}g^0_{23})/(1-D'))$ and $(\bar{V}_{12}/\bar{V}_3)(s-\alpha)$ could be the identification of terms among them, since not only have they similar physical significance in equations (4), (6) and (8), but they also have equivalent algebraic form. Similar comments can be made with respect to the identification of terms among the factors $1-((2g^0_{13}g^0_{23}-D)/(1-D))$, $1-((2g^0_{13}g^0_{23}-g^0_{13}g^0_{23}D')/(1-D'))$ and $(\bar{V}_{12}/\bar{V}_3)^2(s^2-s\alpha-\alpha')$ in equations (5), (7) and (9).

The advantage of this procedure is evident: once the values of g^0_{13} and g^0_{23} have been adjusted to experimental results of λ and A_2 by using equations (4), (5) and (6), (7) through the methods already mentioned and verified[11–14,23,21], the identification among the terms of the factors depending exclusively on g^0_{13} and g^0_{23} with those depending solely on $(\bar{V}_{12}/\bar{V}_3)s$, $(\bar{V}_{12}/\bar{V}_3)\alpha$ and $(\bar{V}_{12}/\bar{V}_3)^2\alpha'$ would automatically adjust these magnitudes to λ and A_2 experimental values.

A detailed numerical analysis in a large number of TPS (as we will show later) of hypothetical double equivalence among the factors multiplying g_{12} functions in equations (4) and (8), and (5) and (9) (set A and C of approximations):

$$1-((g^0_{13}g^0_{23})/(1-D))=(\bar{V}_{12}/\bar{V}_3)(s-\alpha) \quad (11)$$

$$1-((2g^0_{13}g^0_{23}-D)/(1-D))=(\bar{V}_{12}/\bar{V}_3)^2(s^2-s\alpha-\alpha') \quad (12)$$

allows the identification of the terms:

$$(\bar{V}_{12}/\bar{V}_3)s=1-((g^0_{13}g^0_{23}-(D/2))/(1-D))\equiv G^1 \quad (13)$$

$$(\bar{V}_{12}/\bar{V}_3)\alpha=(D/2)/(1-D)\equiv H^1 \quad (14)$$

$$(\bar{V}_{12}/\bar{V}_3)^2\alpha'=k/(1-D)^2$$
$$=((g^0_{13}g^0_{23})^2-(D/2)(1-D+g^0_{13}g^0_{23}))$$
$$\div(1-D)^2\equiv J^1 \quad (15)$$

On the other hand, similar identification but in equations (6) and (8), (7) and (9) (set B and C of approximations):

$$1-((g^0_{13}g^0_{23})/(1-D'))=(\bar{V}_{12}/\bar{V}_3)(s-\alpha) \quad (16)$$

$$1-((2g^0_{13}g^0_{23}-g^0_{13}g^0_{23}D')/(1-D'))$$
$$=(\bar{V}_{12}/\bar{V}_3)^2(s^2-s\alpha-\alpha') \quad (17)$$

yields the following relations:

$$(\bar{V}_{12}/\bar{V}_3)s=1-(g^0_{13}g^0_{23}-(D'/2))/(1-D')\equiv G^2 \quad (18)$$

$$(\bar{V}_{12}/\bar{V}_3)\alpha=(D'/2)/(1-D')\equiv H^2 \quad (19)$$

$$(\bar{V}_{12}/\bar{V}_3)^2\alpha' = k'/(1-D')^2 = ((g^0_{13}g^0_{23})^2 - (D'/2)(D'-1+3g^0_{13}g^0_{23}-2g^0_{13}g^0_{23}D')) \div (1-D')^2 \equiv J^2 \qquad (20)$$

To verify the equivalences expressed in equations (13)–(15) and (18)–(20), the results of $(\bar{V}_{12}/\bar{V}_3)s$, $(\bar{V}_{12}/\bar{V}_3)\alpha$ and $(\bar{V}_{12}/\bar{V}_3)^2\alpha'$ calculated from characteristic magnitudes of pure substances (from references given as footnotes in *Table 1*) are shown in *Table 1*. Also, in *Table 1*, the values of $1-((g^0_{13}g^0_{23}-(D/2))/(1-D))$ and $1-((g^0_{13}g^0_{23}-(D'/2))/(1-D'))$ (considering equations (13) and (18)), $(D/2)/(1-D)$ and $(D'/2)/(1-D')$ (taking into account equations (14) and (19) and $k/(1-D)^2$ and $k'/(1-D')^2$ (using equations (15) and (20)) are immediately shown after the values of $(\bar{V}_{12}/\bar{V}_3)s$, $(\bar{V}_{12}/\bar{V}_3)\alpha$ and $(\bar{V}_{12}/\bar{V}_3)^2\alpha'$. respectively.

The values presented in *Table 1* for each one of the above magnitudes for the ten first systems include the full set of results obtained from all the information existing in literature for $g^0_{13}, g^0_{23}, \chi^0_{13}$ and χ^0_{23} parameters from binary systems. Also for those systems, in an independent column are shown the average values of the results corresponding to the diverse functions of g^0_{i3} and χ^0_{i3}, respectively. For the last four systems in *Table 1*, besides the values of $(\bar{V}_{12}/\bar{V}_3)s$, $(\bar{V}_{12}/\bar{V}_3)\alpha$ and $(\bar{V}_{12}/\bar{V}_3)^2\alpha'$ obtained through characteristic magnitudes of corresponding pure substances, the values of magnitudes depending on g^0_{13} and g^0_{23} are included, calculated from the fitting of those parameters to λ and A_2 experimental results of TPS.

Owing to the necessary approximations to ease the practical application of the FPP expressions for λ and $Y^{11-14,16}$, all the magnitudes referring to solvent mixture (subscript '12') for the calculation of s, α, α' and $\bar{V}_{12}$ are considered as the average of the corresponding values for the pure solvents. This consideration has been taken into account in all equivalent equations (11)–(20) originated by the comparison among equations (4), (5) and (6), (7) with relations (8), (9) (set of approximations A, B and C).

Furthermore, the values of g^0_{i3} $(i=1,2)$ have been calculated through the integration of the function of $\chi_{i3}(\phi_3)$ $(i=1,2)$ in the whole range of polymer concentration, $\phi_3=0-1$. Although, and due to the lack of $\chi_{i3}(\phi_3)$ values at several polymer concentrations sometimes it is necessary to use the extrapolation method to evaluate $g^0_{i3}(\phi_3)^{12}$. Similar reasons can explain the occasional

Table 1 Numeric comparison among equations (13)–(15) and (18)–(20) in several ternary polymer systems. Abbreviations: $G^1=(1-g^0_{13}g^0_{23}-(D/2))/(1-D)$; $G^2=(1-g^0_{13}g^0_{23}-D'/2))/(1-D')$; $H^1=(D/2)/(1-D)$; $H^2=(D'/2)/(1-D')$; $J^1=K/(1-D)^2$; $J^2=K'/(1-D')^2$; Bz = benzene; Ch = cyclohexane; PDMS = poly(dimethylsiloxane); HEX = n-hexane; MEK = butanone; HEP = n-heptane; NON = nonane; PIB = polyisobutylene; Oct = n-octane; Pent = pentane; Act = acetone; PS = polystyrene; EtBz = ethylbenzene; AcN = acetonitrile; CIBu = chlorobutane; PMMA = poly(methylmethacrylate); Met = methanol; Cl_4C = carbontetrachloride; Av* = average value

System	$V_{12}s/V_3$	G^1	G^2	Av*	$V_{12}\alpha/V_3$	H^1	H^2	Av*	$(V_{12}/V_3)^2\alpha'$	J^1	J^2	Av*
Bz/Ch/PDMS	0.834^a	0.695^a	0.714^a	0.714	0.029^a	0.078^a	0.128^a	0.093	0.018^a	0.038^a	0.163^a	0.095
(25°C)		0.715^a	0.733^a			0.061^a	0.106^a			0.038^a	0.141^a	
HEX/MEK/PDMS	0.662^e	0.749b	0.768^b	0.742	0.052^e	0.043^b	0.085^b	0.065	0.038^e	0.038^b	0.112^b	0.078
(20°C)	0.677^e	0.719^b	0.734^b			0.048^b	0.086^b			0.044^b	0.127^b	
HEP/MEK/PDMS	0.674^e	0.712^b	0.726^b			0.049^b	0.086^b			0.047^b	0.127^b	
(20°)		0.689^b	0.702^b	0.702	0.043^e	0.053^b	0.086^b	0.078	0.029^b	0.059^b	0.144^b	0.097
		0.685^c	0.700^c			0.070^c	0.127^c			0.046^c	0.164^c	
NON/MEK/PDMS	0.700^e	0.712^b	0.726^j			0.049^b	0.085^b			0.047^b	0.127^b	
(20°C)	0.677^e	0.698^b	0.710^k	0.705	0.032^e	0.052^b	0.085^b	0.077	0.022^e	0.055^b	0.139^b	0.096
		0.686^c	0.700^c			0.075^c	0.118^c			0.048^c	0.164^c	
Bz/Ch/PIB	0.674^a	0.674^a	0.687^a	0.708	0.104^a	0.081^a	0.124^a	0.071	0.090^a	0.051^a	0.174^a	0.095
(25°C)		0.732^a	0.742^a			0.027^a	0.051^a			0.051^a	0.102^a	
Bz/Oct/PIB	0.650^a	0.632^a	0,.642^a	0.662	0.108^a	0.123^a	0.166^a	0.119	0.102^a	0.058^a	0.224^a	0.124
(25°C)		0.681^a	0.694^a			0.077^a	0.120^a			0.049^a	0.167^a	
Bz/Pent/PIB	0.632^a	0.525^a	0.526^a	0.564	0.156^a	0.190^a	0.200^a	0.166	0.158^a	0.126^a	0.287^a	0.185
(25°C)		0.599^a	0.604^a			0.123^a	0.153^a			0.087^a	0.241^a	
Act/Ch/PS	0.494^a	0.401^d	0.412^d	0.407	0.158^a	0.211^d	0.178^d	0.195	0.163^a	0.264^d	0.427^d	0.345
(25°C)												
MEK/Ch/PS	0.552^a	0.549^d	0.550^d	0.550	0.156^a	0.177^d	0.196^d	0.186	0.175^a	0.106^a	0.304^d	0.205
(25°C)												
EtBz/MEK/PS	0.558^a	0.689^a	0.710^a	0.699	0.128^a	0.110^a	0.177^a	0.143	0.137^a	0.021^a	0.189^a	0.105
(25°C)												
ACN/CIBu/PMMA	0.579^f	0.557^g	0.558^h	0.558	0.177^f	0.130^g	0.146^h	0.138	0.210^f	0.124^g	0.273^h	0.199
(25°C)												
Bz/Met/PMMA	0.598^a	0.629^a	0.638^c	0.633	0.116^a	0.113^c	0.15^c	0.132	0.105^a	0.066^c	0.218^c	0.142
(25°C)												
Bz/Met/PS	0.531^a	0.567^i	0.568^i	0.568	0.141^a	0.081^i	0.094^i	0.088	0.153^a	0.141^i	0.237^i	0.189
(25°C)												
ACN/Cl_4C/PMMA	0.565^j	0.619^g	0.673^c	0.604	0.125^j	0.085^g	0.063^c	0.111	0.106^j	0.092^g	0.146^k	0.153
(25°C)			0.521^k				0.184^k				0.223^k	

[a] Calculated from reference 15

[b] Calculated from references 12 and 15

[c] Calculated from reference 12

[d] Calculated from reference 9

[e] Calculated from characteristic magnitudes of the pure substances in *Table 2* of this paper

[f] Calculated from reference 16

[g] Calculated from references 11 and 13

[h] Calculated from references 12 and 14

[i] Calculated from references 9 and 10

[j] Calculated from references 17 and 32

[k] Calculated from reference 14

uncertainty in χ_{i3}^0 values used[15]. Finally, the values of g_{13}^0 and g_{23}^0 are usually obtained for different molecular weight of polymer samples[12,15].

In spite of the large amount of approximations utilized, it is possible to observe in *Table 1* that for the systems Bz–Ch–PIB, Bz–Oct–PIB, Bz–Pent–PIB, MEK–Ch–Ps and Et–Bz–PS (in all of these systems solely the characteristic magnitudes of pure components or values of g_{i3}^0 and χ_{i3}^0 obtained from binary systems have been used), the assumed equalities in equations (13)–(15) and (18), (20) are quite well fulfilled. In fact, the substitution of the average values (included in *Table 1*) of factors depending on g_{13}^0 and g_{23}^0, instead of real values of $(\bar{V}_{12}/\bar{V}_3)s$, $(\bar{V}_{12}/\bar{V}_3)\alpha$ and $(\bar{V}_{12}/\bar{V}_3)^2\alpha'$, will provide practically the same values for λ and A_2. Therefore, for those systems completely different approximations in FH and FPP formalisms allow to obtain similar results for λ and A_2, although the experimental values of equilibrium sorption for those systems are not known. The four first systems in *Table 1* have the same kind of polymer, PDMS, and the information used for the calculation of different parameters has been identical to that for above systems. In all the cases the values of $(\bar{V}_{12}/\bar{V}_3)s$ calculated from equations (13) and (18) using average values of factors depending on g_{i3}^0 and χ_{i3}^0 are in good accordance with the real ones (with the exception of the system Bz–Ch–PDMS). However, the mean values calculated for $(\bar{V}_{12}/\bar{V}_3)\alpha$ and $(\bar{V}_{12}/\bar{V}_3)^2\alpha'$ show systematically quite large deviations with respect to real ones (evaluated from magnitudes of pure components). These discrepancies among the factors considering the ternary interactions in FH formalism ($D/(1-D)$, $D'/(1-D')$, $k/(1-D)^2$ and $k'/(1-D')^2$) and its equivalents in FPP formalism taking into account dissimilarities in free volume between polymer and solvents ($(V_{12}/V_3)\alpha$ and $(V_{12}/V_3)^2\alpha'$), can be explained by two different ways. Firstly, the dissimilarities in free volume in those TPS cannot be directly described by the corresponding values of pure components, or secondly that other contributions different to $(\bar{V}_{12}/\bar{V}_3)\alpha$ and $(\bar{V}_{12}/\bar{V}_3)^2\alpha'$ are not considered in the expression for N_{13} and N_{33} in FPP formalism (set C of approximations; equations (8) and (9)), at least in TPS with PDMS as polymer.

As it was already mentioned, there are some systems for which the values of g_{i3}^0 and χ_{i3}^0 are obtained through the fitting to λ and A_2 experimental results. Before starting with a comparative analysis, similar to that for ten first systems of *Table 1*, by using λ and A_2 experimental values for the systems n-alkane–MEK–PDMS[19–25] it is convenient to verify the equivalences expressed in equations (13)–(15) and (18)–(20) for those TPS with experimental bibliographic values. This is the case for the last four systems included in *Table 1*. The whole set of experimental values needed to adjust g_{i3}^0 and χ_{i3}^0 to λ and A_2 for each one of the above systems are indicated in the footnote to *Table 1*. Obviously, the substitution of the values of the factors depending on g_{i3}^0 and χ_{i3}^0 or its average values in equations (4), (5) or (6), (7) can reproduce the experimental results of λ and A_2. Likewise, in all the systems the values of those factors agree quite well with the corresponding ones of $(\bar{V}_{12}/\bar{V}_3)s$, $(\bar{V}_{12}/\bar{V}_3)\alpha$ and $(\bar{V}_{12}/\bar{V}_3)^2\alpha'$ (calculated exclusively from values of pure substances). Therefore, the assumptions in equations (13)–(15) and (17)–(19) (or similar in equations (11), (12) and (16), (17)) will be fulfilled. Then, from equations (8) and (9) (set C of approximations) the prediction of λ and A_2 experimental values will be possible. Finally, it must be pointed out that in these last four systems included in *Table 1*, the ternary interactions predicted through FH formalism (set A and B of approximations) are numerically coincident with the dissimilarities in surface to volume ratio and in free volume between polymer and solvents, predicted from FPP formalism (set A of approximations).

The exhaustive study in the 14 TPS of assumptions made in equations (13)–(15) and (18)–(20) allows us to use these relations in the ternary systems n-alkane–MEK–PDMS. In *Table 3* data are gathered in the same way as in *Table 1*, all the values corresponding to those systems whose experimental results have been recently published[19–25]. From *Table 3* it is easy to observe that solely the equivalence expressed in equation (18) is relatively fulfilled. In other words, only the values of $(\bar{V}_{12}/\bar{V}_3)s$ (set C of approximations) can be predicted from the results of $1-(g_{13}^0g_{23}^0-(D'/2))/(1-D')$ (set B of approximations). In general, it can be also seen that the values of $D/(1-D)$ or $k/(1-D)^2$ (set A of approximations) and $D'/(1-D')$ or $k'/(1-D')^2$ (set B of approximations) are notably higher than the corresponding ones for $(\bar{V}_{12}/\bar{V}_3)\alpha$ and $(\bar{V}_{12}/\bar{V}_3)^2\alpha'$ (from set C of approximations). In fact, the deviations observed in *Table 1* for the systems containing PDMS as polymer, are emphasized when the factors depending on g_{i3}^0 and χ_{i3}^0 adjusted to experimental values of λ and A_2 are used.

Therefore, the fact that in the case of n-alkane–MEK–PDMS systems, and in other similar systems, only the equivalence proposed in equation (18) is fulfilled, could indicate the need for introducing in the set B and C of approximations a new method of adjusting to experimental results. Certainly, other methods based on the use of s as adjusting parameter to λ and A_2 experimental values (through equations (8), (9), (2), (1) and (3); set C of approximations) have been proposed, but with dissimilar results[17,18].

The similarity observed between the values of s calculated (from characteristic magnitudes) and adjusted (from equations (28), (33)) seems to indicate that the parameters to adjust should be α and α' (or $(\bar{V}_{12}/\bar{V}_3)\alpha$ and $(\bar{V}_{12}/\bar{V}_3)^2\alpha'$). This implies a modification in the procedure of fitting previously introduced, hence s must be known from the values of characteristic magnitudes of pure components. Likewise, through the new methodology the possible numerical influence of the small differences between s values (adjusted and calculated) in the values of α and α' can be also researched.

Let us consider the application of the new method to a system, for example HEP–MEK–PDMS. The fitting among the experimental results of λ and $(\bar{V}_{12}/\bar{V}_3)\alpha$ gives for this system a value for $(\bar{V}_{12}/\bar{V}_3)\alpha=0.206$. Thus, this value together with $(\bar{V}_{12}/\bar{V}_3)s=0.674$ will be automatically adjusted to λ. Assuming that a good approximation is $(\bar{V}_{12}/\bar{V}_3)\alpha\approx(\bar{V}_{12}/\bar{V}_3)\alpha'$, then $(\bar{V}_{12}/\bar{V}_3)^2\alpha'=0.218$ ($\bar{V}_{12}/\bar{V}_3=1.058$ from *Table 2*). Subsequently, the value of the adjusted factor in equation (24) will be: $(\bar{V}_{12}/\bar{V}_3)^2(s-s\alpha-\alpha')=0.097$. When the experimental values of Y are used to fit that factor, its value is 0.072 (from the results for HEP–MEK–PDMS included in column E in *Table 3* and the values of A_2 from reference 12). As both values are quite similar, it is inferable that the results obtained for $(\bar{V}_{12}/\bar{V}_3)s$ (0.674), $(\bar{V}_{12}/\bar{V}_3)\alpha$ (0.206) and $(\bar{V}_{12}/\bar{V}_3)^2\alpha'$ (0.218) can be considered as simultaneously adjusted to experimental values of λ and A_2. On the other hand, and similarly to observed in *Table 1* for the systems with PDMS as polymer, the adjusted values of $(\tilde{V}_{12}/\tilde{V}_3)\alpha$ and $(\tilde{V}_{12}/\tilde{V}_3)^2\alpha'$ are larger than those obtained from the characteristic magnitudes of pure substances (see *Table 3*).

Following a similar procedure of calculation, the values of the different parameters of FPP formalism as adjusted to λ and A_2 experimental results for the ternary systems n-alkane–MEK–PDMS included in *Table 3* are shown in

Table 2 Characteristic molecular magnitudes of n-alkane/butanone/poly(dimethylsiloxane) (PDMS) system substances at 20°C

Substance	V (cm^3 g^{-1})	V^* (cm^3 mol^{-1})	V	P^* (J cm^{-3})	T^* (°K)	s (Å^{-1})	$\alpha \times 10^3$ (°K^{-1})	S_3/S_i
n-hexane	1.1540^{a,b}	80.97^{a,b}	1.3142^{a,b}	426^{a,b}	4425^{a,b}	1.02^{b}	1.36^{a,b}	0.62^{b}
		99.48^{c}	1.3129^{c}	420.8^{c}	4420^{c}		1.38^{c}	
n-heptane	1.1343^{c}	114.63^{d}	1.2886^{c}	429.2^{c}	4670^{c}	1.01^{d}	1.252^{d}	
		113.65^{c}						
n-nonane	1.1047^{b}	142.0^{c}	1.2587^{c}	443^{b}	4966^{b}	0.98^{d}	1.090^{d}	0.67^{b}
	1.1072^{b}			437.5^{c}	5000^{c}		1.065^{b}	
n-decane	1.0972^{c}	155.76^{e}	1.2485^{c}	435^{e}	5130^{c}	0.965^{h}	1.041^{e}	
		156.10^{c}					1.020^{c}	
n-undecane	1.0895^{c}	170.3^{c}	1.2402^{c}	441.7^{c}	5240^{c}	0.952^{b}	0.980^{c}	
n-dodecane	1.0820^{c}	184.3^{c}	1.2336^{c}	445.8^{c}	5350^{c}	0.94^{d}	0.95^{c}	
n-hexadecane	1.0668^{c}	241.1^{c}	1.2144^{c}	445.8^{c}	5680^{c}	0.90^{d}	0.855^{c}	
Butanone	0.9552^{a}	68.87^{a}	1.3004^{a}	587^{a}	4547^{a}	0.87^{f}	1.291^{a}	0.69^{a}
PDMS	0.8381^{a,g}	0.843^{d}	1.2248^{a,g}	343^{a,g}	5494^{a,g}	0.60^{d}	0.9054^{a,g}	

[a] Reference 33
[b] Reference 34
[c] Reference 35
[d] Reference 36
[e] Reference 37
[f] Reference 33 and $s_3 = 0.60$ Å^{-1}
[g] Reference 38
[h] Interpolated values among n-alkanes through representation of *s versus* number of carbon atoms

Table 3 Numerical comparison among members of equations (13)–(15) and (18)–(20) in n-alkane/butanone/PDMS systems at 20°C

System		(A)		(B)	(C)	(D)		(E)	(F)
HEX/MEK/PDMS	$(V_{12}/V_3)s$	0.662, 0.677	G^1			0.530^{a}	G^2		
	$(V_{12}/V_3)\alpha$	0.052	H^1			0.217^{a}	H^2		
	$(V_{12}/V_3)^2\alpha'$	0.038	J^1			0.106^{a}	J^2		
HEP/MEK/PDMS	$(V_{12}/V_3)s$	0.674	G^1	0.585^{b}	0.553^{c}	0.552^{d}	G^2	0.640^{e}	0.645^{f}
	$(V_{12}/V_3)\alpha$	0.043	H^1	0.169^{b}	0.201^{c}	0.211	H^2	0.172^{e}	0.153^{f}
	$(V_{12}/V_3)^2\alpha'$	0.029	J^1	0.074^{b}	0.088^{c}	0.089^{d}	J^2	0.228^{e}	0.215^{f}
NON/MEK/PDMS	$(V_{12}/V_3)s$	0.700, 0.677	G^1			0.569^{g}	G^2	0.647^{h}	0.681^{i}
	$(V_{12}/V_3)\alpha$	0.032	H^1			0.184^{g}	H^2	0.162^{b}	0.124^{i}
	$(V_{12}/V_3)^2\alpha'$	0.022	J^1			0.081^{g}	J^2	0.218^{h}	0.177^{i}
DEC/MEK/PDMS	$(V_{12}/V_3)s$	0.681	G^1			0.562^{j}	G^2	0.643^{k}	0.663^{l}
	$(V_{12}/V_3)\alpha$	0.028	H^1			0.174^{j}	H^2	0.147^{k}	0.122^{l}
	$(V_{12}/V_3)^2\alpha'$	0.020	J^1			0.063^{j}	J^2	0.213^{k}	0.187^{l}
UND/MEK/PDMS	$(V_{12}/V_3)s$	0.683	G^1	0.592^{m}		0.587^{n}	G^2	0.654^{o}	
	$(V_{12}/V_3)\alpha$	0.025	H^1	0.136^{m}		0.137^{n}	H^2	0.121^{o}	
	$(V_{12}/V_3)^2\alpha'$	0.017	J^1	0.086^{m}		0.090^{n}	J^2	0.191^{o}	
DOD/MEK/PDMS	$(V_{12}/V_3)s$	0.686	G^1			0.573^{p}	G^2		
	$(V_{12}/V_3)\alpha$	0.022	H^1			0.144^{p}	H^2		
	$(V_{12}/V_3)^2\alpha'$	0.015	J^1			0.100^{p}	J^2		
HED/MEK/PDMS	$(V_{12}/V_3)s$	0.696	G^1			0.614^{g}	G^2		
	$(V_{12}/V_3)\alpha$	0.015	H^1			0.043^{q}	H^2		
	$(V_{12}/V_3)^2\alpha'$	0.010	J^1			0.122^{q}	J^2		

G^i, H^i and J^i see *Table 1*
(A) Calculated values from magnitudes characteristic of the pure substances in *Table 2*
(B) Values of g^0_{i3} and χ^0_{i3} from reference 11 with set A of approximations
(C) Values of g^0_{i3} and χ^0_{i3} from reference 13 with set A of approximations
(D) Values of g^0_{i3} and χ^0_{i3} from reference 31 with set A of approximations
(E) Values of $g^0_{i3}$and χ^0_{i3} from reference 12 with set B of approximations
(F) Values of g^0_{i3} and χ^0_{i3} from reference 14 with set B of approximations
[a] $g^0_{13} = 0.522$, $g^0_{23} = 0.918$, $\chi^0_{13} = 0.43$, $\chi^0_{23} = 0.5$ ($M_w = 150\,000$)
[b] $g^0_{13} = 0.520$, $g^0_{23} = 0.840$, $\chi^0_{13} = 0.43$, $\chi^0_{23} = 0.5$ ($\mathrm{M}_w = 150\,000$)
[c] $g^0_{13} = 0.542$, $g^0_{23} = 0.853$, $\chi^0_{13} = 0.43$, $\chi^0_{23} = 0.5$ (mixed M_w)
[d] $g^0_{13} = 0.530$, $g^0_{23} = 0.890$, $\chi^0_{13} = 0.428$, $\chi^0_{23} = 0.5$ ($M_w = 125\,000$)
[e] $g^0_{13} = 0.506$, $g^0_{23} = 0.784$, $\chi^0_{13} = 0.43$, $\chi^0_{23} = 0.5$ ($M_w = 150\,000$)
[f] $g^0_{13} = 0.451$, $g^0_{23} = 0.864$, $\chi^0_{13} = 0.43$, $\chi^0_{23} = 0.5$ ($M_w = 150\,000$)
[g] $g^0_{13} = 0.524$, $g^0_{23} = 0.858$, $\chi^0_{13} = 0.429$, $\chi^0_{23} = 0.5$ ($M_w = 125\,000$)
[h] $g^0_{13} = 0.488$, $g^0_{23} = 0.798$, $\chi^0_{13} = 0.431$, $\chi^0_{23} = 0.5$ ($M_w = 150\,000$)
[i] $g^0_{13} = 0.438$, $g^0_{23} = 0.810$, $\chi^0_{13} = 0.431$, $\chi^0_{23} = 0.5$ ($M_w = 150\,000$)
[j] $g^0_{13} = 0.532$, $g^0_{23} = 0.853$, $\chi^0_{13} = 0.449$, $\chi^0_{23} = 0.5$ ($M_w = 125\,000$)
[k] $g^0_{13} = 0.495$, $g^0_{23} = 0.787$, $\chi^0_{13} = 0.45$, $\chi^0_{23} = 0.5$ ($M_w = 150\,000$)
[l] $g^0_{13} = 0.452$, $g^0_{23} = 0.817$, $\chi^0_{13} = 0.45$, $\chi^0_{23} = 0.5$ ($M_w = 150\,000$)
[m] $g^0_{13} = 0.537$, $g^0_{23} = 0.797$, $\chi^0_{13} = 0.468$, $\chi^0_{23} = 0.5$ ($M_w = 125\,000$)
[n] $g^0_{13} = 0.521$, $g^0_{23} = 0.828$, $\chi^0_{13} = 0.468$, $\chi^0_{23} = 0.5$ ($M_w = 125\,000$)
[o] $g^0_{13} = 0.485$, $g^0_{23} = 0.776$, $\chi^0_{13} = 0.469$, $\chi^0_{23} = 0.5$ ($M_w = 150\,000$)
[p] $g^0_{13} = 0.528$, $g^0_{23} = 0.840$, $\chi^0_{13} = 0.475$, $\chi^0_{23} = 0.5$ ($M_w = 125\,000$)
[q] $g^0_{13} = 0.508$, $g^0_{23} = 0.778$, $\chi^0_{13} = 0.587$, $\chi^0_{23} = 0.5$ ($M_w = 150\,000$)

Table 4 Values of $(V_{12}/V_3)s$, $(V_{12}/V_3)\alpha$ and $(V_{12}/V_3)^2\alpha'$ that adjust to experimental results of λ and A_2 taking $(V_{12}/V_3)s$ the one calculated from charcteristics magnitudes of pure substances, in n-alkane-butanone-PDMS systems at 20°C

Ternary systems		(A)	(B)	(A)	(B)
HEP/MEK/PDMS	$(V_{12}/V_3)s$	0.640^e	0.674	0.645^f	0.674
	$(V_{12}/V_3)\alpha$	0.172^e	0.206	0.153^f	0.182
	$(V_{12}/V_3)^2\alpha'$	0.228^e	0.218	0.215^f	0.192
	$(V_{12}/V_3)^2(s^2-s\alpha-\alpha')$	0.072	0.097	0.103	0.139
NON/MEK/PDMS	$(V_{12}/V_3)s$	0.647^h	0.700	0.681^i	0.700
	$(V_{12}/V_3)\alpha$	0.162^h	0.215	0.124^i	0.143
	$(V_{12}/V_3)^2\alpha'$	0.218^h	0.225	0.177^i	0.150
	$(V_{12}/V_3)^2(s^2-s\alpha-\alpha')$	0.096	0.115	0.202^i	0.240
DEC/MEK/PDMS	$(V_{12}/V_3)s$	0.643^k	0.681	0.663^l	0.681
	$(V_{12}/V_3)\alpha$	0.147^k	0.185	0.122^l	0.140
	$(V_{12}/V_3)^2\alpha'$	0.213^k	0.193	0.187^l	0.146
	$(V_{12}/V_3)^2(s^2-s\alpha-\alpha')$	0.106	0.145	0.172	0.222
UND/MEK/PDMS	$(V_{12}/V_3)s$	0.654^o	0.683		
	$(V_{12}/V_3)\alpha$	0.121^o	0.150		
	$(V_{12}/V_3)^2\alpha'$	0.191^o	0.156		
	$(V_{12}/V_3)^2(s^2-s\alpha-\alpha')$	0.158	0.208		

(A): Values of $(V_{12}/V_3)s$, $(V_{12}/V_3)\alpha$ and $(V_{12}/V_3)^2\alpha'$ that adjust to experimental results of λ and A_2 through equations (8), (9), (1), (2) and (3). The references in this table are the same as those in *Table 3*.

(B): Values of $(V_{12}/V_3)s$, $(V_{12}/V_3)\alpha$ and $(V_{12}/V_3)^2\alpha'$ considering $(V_{12}/V_3)s$ from characteristic magnitudes of pure substances and adjusting $(V_{12}/V_3)\alpha$ and $(V_{12}/V_3)^2\alpha'$ to experimental results of λ and A_2 (with the results of column A) as explained in the text

See *Table 3* for explanation of superscripts

Table 4. So, in the column A of that table we show the values of $(\bar{V}_{12}/\bar{V}_3)s$, $(\bar{V}_{12}/\bar{V}_3)\alpha$ and $(\bar{V}_{12}/\bar{V}_3)^2\alpha'$ that together with a determined set of values of g^0_{i3} and χ^0_{i3} (see the corresponding calls in column A) yield values of $(\bar{V}_{12}/\bar{V}_3)(s-\alpha)$ and $(\bar{V}_{12}/\bar{V}_3)^2(s^2-s\alpha-\alpha')$, which are absolutely adjusted to λ and A_2 experimental results through equations (8), (9), (1), (2) and (3). In the column B we include similar values which allow us to obtain results for $(\bar{V}_{12}/\bar{V}_3)(s-\alpha)$—perfectly fitted to experimental magnitudes of λ—and $(\bar{V}_{12}/\bar{V}_3)^2(s^2-s\alpha-\alpha')$ similar to the corresponding ones in column A. In consequence, through the equations mentioned before those values will give A_2 results practically coincident with the experimental ones. In any case, the values of $(V_{12}/V_3)^2(s^2-s\alpha-\alpha')$ calculated in column B for every system and for each set of g^0_{i3} and χ^0_{i3} agree quite well with the values of $1-2a_\chi$ published elsewhere[22,23]. From these results of $1-2a_\chi$, A_2 values are obtained which fit completely with the experimental ones, as can be seen in the figures of that reference.

CONCLUSIONS

In conclusion, it can be pointed out that the magnitudes $(\bar{V}_{12}/\bar{V}_3)s$, $(\bar{V}_{12}/\bar{V}_3)\alpha$ and $(\bar{V}_{12}/\bar{V}_3)^2\alpha'$ for the systems n-alkane–MEK–PDMS collected in *Table 4* and obtained by using assumptions of equations (18)–(20) are adjusted to λ and A_2 experimental results Although, in these systems, as in others with PDMS as polymer (*Tables 1* and *2*), the values of $(\bar{V}_{12}/\bar{V}_3)\alpha$ and $(\bar{V}_{12}/\bar{V}_3)^2\alpha'$ are always higher than the ones calculated from characteristic magnitudes of pure substances. That is to say, in these systems, according to the FPP formalism, the contributions from the contact energies between polymer segments and solvent molecules as taken place on the molecular surface (represented by $(\bar{V}_{12}/\bar{V}_3)s$) is more likely to be calculated from FPP or FH formalisms. However, another contribution from the free volume dissimilarity between polymer chains and simple liquids (represented by $(\bar{V}_{12}/\bar{V}_3)\alpha$ or $(\bar{V}_{12}/\bar{V}_3)^2\alpha'$) is lower from FPP formalism (characteristic magnitudes of pure substances) than from the FH formalism as modified by Pouchly. It seems, then, that in the systems n-alkane–MEK–PDMS other contributions to ternary parameters, besides those represented by $(\bar{V}_{12}/\bar{V}_3)s$ and $(\bar{V}_{12}/\bar{V}_3)\alpha$ (or $(\bar{V}_{12}/\bar{V}_3)^2\alpha'$), may be present. The numerical coincidence between the two formalisms would imply that the sign both of $(\bar{V}_{12}/\bar{V}_3)\alpha$ or $(\bar{V}_{12}/\bar{V}_3)^2\alpha'$ and these new contributions in the factor $(\bar{V}_{12}/\bar{V}_3)(s-\alpha)$ and $(\bar{V}_{12}/\bar{V}_3)^2(s^2-s\alpha-\alpha')$ must be the same. The possible existence of contributions different to $(\bar{V}_{12}/\bar{V}_3)s$, $(\bar{V}_{12}/\bar{V}_3)\alpha$ or $(\bar{V}_{12}/\bar{V}_3)^2\alpha'$ to ternary parameters have been already accepted[15]. Contributions related to the simplifications are introduced to obtain equations (8) and (9). Among these simplifications, for instance, are no considerations of the exchange interaction entropy term, introduced by Flory[31] or the assumption of random mixing of segments.

Therefore, in this work a new methodology to compare FPP and FHP formalism is introduced, which allows for the first time by TPS, evaluation of s, α and α' (FPP parameters) from g^0_{i3} and χ^0_{i3} (FHP parameters), and vice versa as well as simultaneous adjustment of λ and A_2 experimental values to s, α and α' parameters.

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