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# Prediction of excess enthalpies of some ternary systems involving a binary mixture with a miscibility gap using a group contribution model

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## Abstract

A new study has been made of the performance of the Kehiaian–Guggenheim–Barker group contribution model in the characterization of the excess molar enthalpies ($H^E$) of ternary organic mixtures. The present work reports the predictions of the model for seven sets of $H^E$ ternary data. The seven mixtures of methanol, as first component, with *n*-alkanes and aromatic hydrocarbons were treated in the framework of the DISQUAC model. The ratios of the standard deviations between experimental and predicted excess molar enthalpies and the maximum value of this excess function are less than 0.38 for all the systems. Previously obtained parameters for alcohol–aliphatic and alcohol–aromatic interactions were tested with the binary excess functions $H^E$, $G^E$ and excess heat capacity $C_p^E$, liquid–liquid equilibria, and activity coefficients at infinite dilution.

## INTRODUCTION

The many empirical equations for the prediction of excess functions of ternary systems can be regarded as different geometrical methods for establishing the contribution to the excess function of each of the three binary mixtures involved [1,2]. Symmetric equations (e.g. Colinet's equation) assign the same weight to each of the three binary contributions, while asymmetric equations (e.g. Hillert's equation) give more weight to the binary contributions 1–2 and 1–3, the role of the component designated as component 1 being very important.

Application of any group contribution model to ternary systems requires much time and effort but can yield a large quantity of information. Testing the model in areas such as those considered in the present work is therefore very important. We are interested in the behaviour of the DISQUAC model [3,4]. So, in previous papers, we have treated multicomponent organic mixtures of hydrocarbons and ternary organic mixtures containing ethanol

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using this group contribution model [5,6]. In all cases a fairly good representation was obtained.

Owing to the high polarity of methanol and to its miscibility gaps with *n*-alkanes at room temperature, systems containing methanol are at the limit of applicability of any group contribution model. For this reason, the present work shows how useful the DISQUAC model is, not only in prediction of excess functions of ternary systems, but also in the treatment of binary mixtures containing a very polar component.

The ternary systems investigated contained three different types of groups: aliphatic, type a ($CH_3^-$, $-CH_2-$), aromatic, type b ($C_6H_6$, $C_6H_5-$) and hydroxyl, type h ($-OH$) groups.

Although the dipole moments of *n*-alcohols are very similar, their dielectric constants are very different [6], which suggests that it may be necessary, when investigating systems containing an *n*-alcohol, to specify whether this alcohol is methanol, ethanol or one of higher chain length. So, as a first step, we obtained parameters corresponding to alcohol–aliphatic and alcohol–aromatic interactions (the alcohol group being in a methanol molecule). Interactions between aliphatic and aromatic groups we assumed to be as previously reported [7].

## TERNARY SYSTEMS CONSIDERED

Table 1 lists all the ternary systems considered and binary mixtures involved. Also indicated are the number of data points *N*, the temperature

TABLE 1

Ternary systems, and binary mixtures involved, considered in the present work

| No. | System | *N* | *T* (K) | $H^E_{max}$ (J mol$^{-1}$) | $H^E_{min}$ (J mol$^{-1}$) | Ref. |
|---|---|---|---|---|---|---|
| 1 | Methanol + benzene + *n*-hexane | 36 | 298.15 | 1313 | 230 | 8 |
| | Methanol + benzene | | 298.15 | 718 | | 9 |
| | Methanol + *n*-hexane | | 298.15 | 516 [a] | | 9 |
| | Benzene + *n*-hexane | | 298.15 | 897 | | 10 |
| 2 | Methanol + benzene + *n*-heptane | 13 | 293.15 | 842 | 166 | 11 |
| 3 | Methanol + benzene + *n*-heptane | 13 | 298.15 | 922 | 149 | 11 |
| 4 | Methanol + benzene + *n*-heptane | 38 | 298.15 | 1460 | 440 | 12 |
| 5 | Methanol + benzene + *n*-heptane | 13 | 303.15 | 986 | 168 | 11 |
| 6 | Methanol + benzene + *n*-heptane | 13 | 308.15 | 1053 | 172 | 11 |
| | Methanol + *n*-heptane | | 303.15 | 546 [b] | | 9 |
| | Benzene + *n*-heptane | | 298.15 | 959 | | 11 |
| 7 | Methanol + toluene + *n*-hexane | 92 | 298.15 | 1040 | 361 | 13 |
| | Methanol + toluene | | 298.15 | 703 | | 9 |
| | Toluene + heptane | | 298.15 | 532 | | 14 |

[a] Immiscible system at $x_1 = 0.3$; value at $x_1 = 0.25$.

[b] Immiscible system at $x_1 = 0.3$; value at $x_1 = 0.2$.

TABLE 2

Molar excess enthalpies $H^E$ and molar excess Gibbs energies $G^E$ for methanol + *n*-alkane mixtures at various temperatures *T*, and compositions $x_1$ at which the excess function is maximum. Comparison of direct experimental results with values calculated using coefficients from Table 4

| Data | $T$ (K) | $x_1$ | Exp. (J mol$^{-1}$) | Calc. (J mol$^{-1}$) | Ref. |
|---|---|---|---|---|---|
| n-*Hexane* | | | | | |
| $G^E$ | 298.15 [a] | 0.2 [b] | 1126 | 1084 | 15 |
| $G^E$ | 308.15 | 0.5 | 1628 | 1566 | 16 |
| $G^E$ | 323.15 | 0.5 | 1676 | 1605 | 16 |
| $G^E$ | 333.15 | 0.5 | 1703 | 1626 | 16 |
| $G^E$ | 348.15 | 0.5 | 1740 | 1649 | 16 |
| $H^E$ | 298.15 [a] | 0.25 [b] | 516 | 536 | 9 |
| $H^E$ | 298.15 | 0.2 [b] | 484 | 484 | 15 |
| $H^E$ | 303.15 | 0.3 [b] | 583 | 618 | 9 |
| $H^E$ | 306.85 | 0.4 | 640 | 697 | 9 |
| $H^E$ | 313.15 [a] | 0.4 | 718 | 754 | 9 |
| $H^E$ | 318.15 [a] | 0.4 | 782 | 808 | 9 |
| $H^E$ | 323.15 [a] | 0.4 | 850 | 869 | 9 |
| n-*Heptane* | | | | | |
| $H^E$ | 303.15 | 0.2 [b] | 546 | 510 | 9 |
| $H^E$ | 318.15 | 0.3 [b] | 798 | 829 | 9 |
| $H^E$ | 333.15 | 0.4 | 1059 | 1105 | 9 |

[a] System used in the determination of interchange energy coefficients of alcohol–aliphatic interaction.

[b] Partially miscible system.

at which data were taken *T*, the minimum ($H^E_{\min}$) and the maximum ($H^E_{\max}$) experimental values (in J mol$^{-1}$) of the excess enthalpies and the sources of the data. All data are valid at atmospheric pressure.

## ESTIMATION OF INTERACTION PARAMETERS

The theoretical equations of the DISQUAC model may be found elsewhere [3,4]. All the geometrical parameters except those for methanol are available from the literature [7]. For methanol, the volume $r$ is 1.26811, the total surface $q$, 1.23448, the fraction of aliphatic surface on a methanol molecule, 0.59218, and that of a hydroxyl 0.40782, all values calculated by Bondi's method.

The systems used in the fitting to obtain the interchange parameters are reported in Tables 2 and 3 (type a): $H^E$ data of Van Ness and Abbott [9] and $G^E$ data of Hwang and Robinson [15] for the methanol + *n*-hexane system, $H^E$ data of Van Ness and Abbott [9] and $G^E$ data of Brown et al. [17] for the methanol + benzene mixture.

TABLE 3

Molar excess enthalpies $H^E$ and molar excess Gibbs energies $G^E$ for methanol + benzene or + toluene or + ethylbenzene mixtures at various temperatures $T$ and equimolar composition or $x_1 = 0.3$ (when $H^E$ is maximum). Comparison of direct experimental results with values calculated using coefficients from Table 4

| Component 2 | Data | $T$ (K) | $x_1$ | Exp. (J mol$^{-1}$) | Calc. (J mol$^{-1}$) | Ref. |
|---|---|---|---|---|---|---|
| Benzene | $G^E$ | 298.15 [a] | 0.5 | 1260 | 1266 | 17 |
| | $G^E$ | 298.15 | 0.5 | 1240 | | 15 |
| | $G^E$ | 308.15 | 0.5 | 1280 | 1286 | 17 |
| | $G^E$ | 318.15 | 0.5 | 1300 | 1302 | 17 |
| Toluene | $G^E$ | 318.15 | 0.5 | 1372 | 1333 | 18 |
| Benzene | $H^E$ | 293.15 | 0.3 | 664 | 669 | 19 |
| | $H^E$ | 293.15 | 0.3 | 653 | | 11 |
| | $H^E$ | 293.15 | 0.5 | 628 | 577 | 19 |
| | $H^E$ | 293.15 | 0.5 | 537 | | 11 |
| | $H^E$ | 298.15 | 0.3 | 722 | 723 | 11 |
| | $H^E$ | 298.15 [a] | 0.3 | 718 | | 9 |
| | $H^E$ | 298.15 | 0.3 | 720 | | 20 |
| | $H^E$ | 298.15 | 0.5 | 589 | 624 | 11 |
| | $H^E$ | 298.15 [a] | 0.5 | 622 | | 9 |
| | $H^E$ | 298.15 | 0.5 | 624 | | 20 |
| | $H^E$ | 303.15 | 0.3 | 776 | 780 | 11 |
| | $H^E$ | 303.15 | 0.5 | 620 | 676 | 11 |
| | $H^E$ | 308.15 | 0.3 | 838 | 842 | 11 |
| | $H^E$ | 308.15 [a] | 0.3 | 841 | | 9 |
| | $H^E$ | 308.15 | 0.3 | 820 | | 17 |
| | $H^E$ | 308.15 | 0.5 | 665 | 733 | 11 |
| | $H^E$ | 308.15 [a] | 0.5 | 732 | | 9 |
| | $H^E$ | 308.15 | 0.5 | 720 | | 17 |
| | $H^E$ | 318.15 [a] | 0.3 | 967 | 978 | 9 |
| | $H^E$ | 318.15 | 0.3 | 972 | | 20 |
| | $H^E$ | 318.15 | 0.3 | 940 | | 17 |
| | $H^E$ | 318.15 [a] | 0.5 | 852 | 860 | 9 |
| | $H^E$ | 318.15 | 0.5 | 869 | | 20 |
| | $H^E$ | 318.15 | 0.5 | 840 | | 17 |
| Toluene | $H^E$ | 298.15 | 0.3 | 697 | 669 | |
| | | | 0.5 | 622 | 582 | 9 |
| | $H^E$ | 308.15 | 0.3 | 854 | 789 | |
| | | | 0.5 | 761 | 688 | 9 |
| | $H^E$ | 318.15 | 0.3 | 993 | 928 | |
| | | | 0.5 | 891 | 814 | 9 |
| Ethylbenzene | $H^E$ | 298.15 | 0.3 | 742 | 695 | |
| | | | 0.5 | 678 | 621 | 9 |
| | $H^E$ | 308.15 | 0.3 | 893 | 821 | |
| | | | 0.5 | 818 | 732 | 9 |
| | $H^E$ | 318.15 | 0.3 | 1035 | 969 | |
| | | | 0.5 | 950 | 867 | 9 |

[a] Systems used in the determination of interchange energy coefficients of alcohol–aromatic interaction.

TABLE 4

Interchange energy coefficients, dispersive $C_{st,l}^{dis}$ and quasichemical $C_{st,l}^{quac}$ (s, t = a, b, h; type a aliphatic group, type b aromatic group, type h hydroxyl group; l = 1, 2, 3) used in the present work

| (s,t) | $C_{st,1}^{dis}$ | $C_{st,2}^{dis}$ | $C_{st,3}^{dis}$ | $C_{st,1}^{quac}$ | $C_{st,2}^{quac}$ | $C_{st,3}^{quac}$ | Ref. |
|---|---|---|---|---|---|---|---|
| (a,h) | 1.35 | 1.60 | −12.50 | 12.20 | 8.10 | 71.10 | This work |
| (a,h) [a] | 1.84 | 0.81 | −9.07 | 12.20 | 12.20 | 71.10 | 6 |
| (b,h) | 1.14 | −1.13 | −12.33 | 10.30 | 16.70 | 21.21 | This work |
| (b,h) [a] | 1.67 | −2.54 | −11.23 | 8.93 | 16.70 | 21.21 | 6 |
| (a,b) | 0.2598 | 0.5623 | 0 | 0 | 0 | 0 | 7 |

[a] Hydroxyl group in ethanol.

### *Methanol* + n*-alkanes*

These mixtures are characterized by a single type of contact (a, h).

Owing to the miscibility gaps of methanol + *n*-alkanes at room temperature, the fitting of the interchange coefficients becomes rather complicated. For this reason, it is useful to take into account the tendency of the parameters for the whole set of *n*-alcohols. In this way, it seems that the first and third quasichemical interchange coefficients can be held constant with values equal to 12.2 and 71.1 respectively. The first dispersive coefficient was adjusted to represent the homogeneous region of $G^E$ at 298.15 K. The value is fairly small because we have tried to reproduce as well as possible the critical temperatures and compositions of methanol + *n*-hexane or + *n*-heptane mixtures. Similarly, the second quasichemical and dispersive coefficients, $C_{ah,2}^{quac}$ and $C_{ah,2}^{dis}$, were fitted using the $H^E$ data of the homogeneous region at room temperature, and the third dispersive parameter, $C_{ah,3}^{dis}$, was obtained to reproduce the dependence on temperature of $H^E$.

### *Methanol + aromatic compounds*

These systems are characterized by three types of contact: (a,h), (a,b), and (b,h). The entirely dispersive (a,b) parameters of *n*-alkanes + aromatic compounds are well known [7], $C_{ab,1}^{dis} = 0.2598$, $C_{ab,2}^{dis} = 0.5623$. The (a,h) parameters were estimated as shown above. As $G^E$ and $H^E$ were available for the methanol + benzene system at 298.15 K, the fitting of (b,h) parameters was straightforward. Second and third quasichemical coefficients were held constant for the whole set of *n*-alcohols.

Final parameters are listed in Table 4.

## RESULTS AND DISCUSSION

Comparison of the experimental values of $H^E$ and $G^E$ and those predicted by the DISQUAC model (Tables 2 and 3) shows fairly good agreement between them.

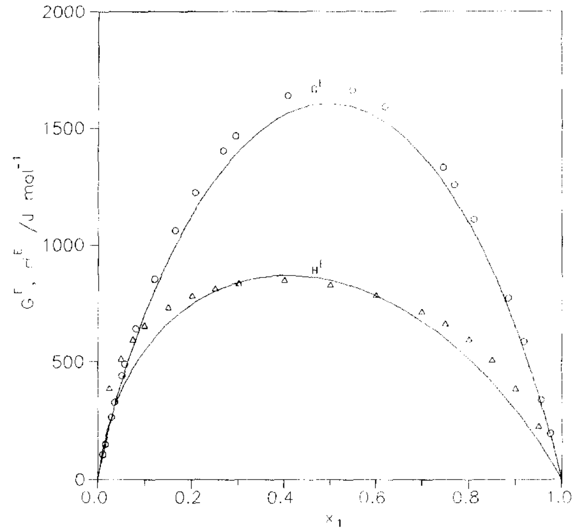

Fig. 1. Comparison of theoretical with experimental values ot molar excess enthalpy $H^E$ and molar excess Gibbs energy $G^E$ at 323.15 K for the methanol(1) + *n*-hexane(2) mixture vs. $x_1$. Solid lines, predicted values, symbols, experimental values: (△) $H^E$ [9], (○) $G^E$ [16].

In the case of methanol + *n*-alkane mixtures with the coordination number used ($z = 4$), we obtain fairly symmetrical $G^E$ curves, the predicted dependence on concentration being correct (Fig. 1). At low concentration this behaviour is retained, as Table 5 shows: in this way, calculated ln $\gamma_i^\infty$ are near experimental values. However, it is known that values of critical temperatures are very sensitive to those of the first interchange coefficients. Because the critical temperatures of methanol + *n*-hexane, or + *n*-heptane,

TABLE 5

Logarithm of activity coefficients at infinite dilution ln $\gamma_i^\infty$ in mixtures containing methanol and an *n*-alkane (*n*-hexane or *n*-hexadecane). Comparison of experimental results with values calculated using coefficients from Table 4

| $T$ (K) | ln $\gamma_1^\infty$ | | ln $\gamma_2^\infty$ | | Ref. |
|---|---|---|---|---|---|
| | Exp. | Calc. | Exp. | Calc. | |
| n-*Hexane* | | | | | |
| 308.15 | 4.293 | 4.246 | 3.206 | 2.932 | 16 |
| 323.15 | 3.839 | 3.978 | 2.991 | 2.872 | 16 |
| 333.15 | 3.569 | 3.779 | 2.995 | 2.833 | 16 |
| 348.15 | 3.219 | 3.455 | 2.868 | 2.773 | 16 |
| n-*Hexadecane* | | | | | |
| 303.15 | 3.674 | 3.600 | – | 4.693 | 21 |
| 313.15 | 3.569 | 3.434 | – | 4.591 | 21 |
| 323.15 | 3.371 | 3.254 | – | 4.496 | 21 |

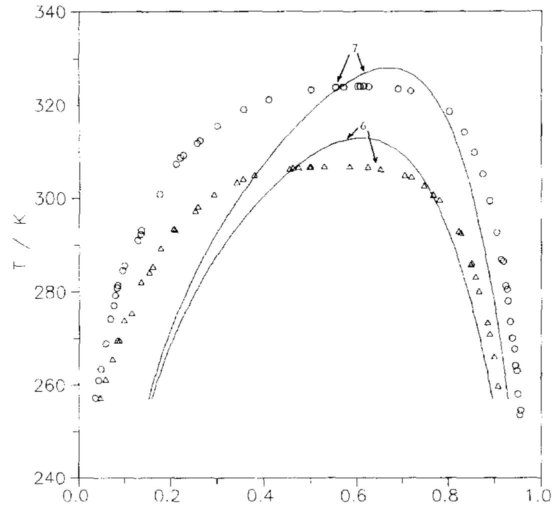

Fig. 2. Comparison of theory with experiment for the liquid–liquid equilibrium temperature $T$ vs. $x_1$ in methanol + $n$-alkane mixtures. Solid lines, predicted values; symbols, experimental results [22]: (△) methanol + $n$-hexane, (○) methanol + $n$-heptane.

systems obtained using the DISQUAC model, 312.8 and 328.0 K respectively, are near to the experimental values (306.75 and 324.06 K [22]), it may be said that our first interchange parameters are reasonably correct.

Owing to the proximity of the critical point, the shapes of $H^E$ curves of mixtures containing methanol and $n$-hexane or $n$-heptane are extremely flat. This dependence on concentration is roughly reproduced by the DISQUAC model (Fig. 1). For this reason, the critical compositions are poorly represented (calculated values: 0.611 for methanol + $n$-hexane and 0.672 for methanol + $n$-heptane; experimental values 0.546 and 0.610 respectively [22]) and the shape of the predicted liquid–liquid equilibria curve is very different from that of the experimental one (Fig. 2).

Comparison of second interchange parameters for alcohol–aliphatic interaction in mixtures containing methanol or ethanol (Table 4) shows that the quasichemical coefficient is in the first case somewhat small, 8.1, and in the second case is 12.2. A higher value would be desirable to keep the excess partial molar enthalpy at infinite dilution of the alcohol more or less constant. Unfortunately, proceeding in this way, $H^E$ curves markedly shifted to the low concentration region in alcohol would be obtained.

Figure 3 shows the dependence on concentration of the $C_p^E$ curve for the methanol + $n$-heptane system at 298.15 K (in the homogeneous region). The experimental $C_p^E$ is positive over the whole range of concentration [23]. The calculated $C_p^E$ shows the same behaviour at higher temperatures. At 298.15 K and in the region rich in alcohol, $C_p^E$ becomes negative, probably because of fitting the third dispersive coefficient using only $H^E$ data at temperatures

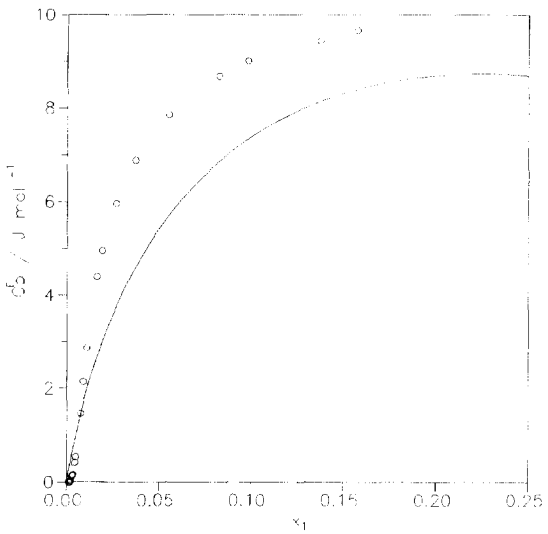

Fig. 3. Comparison of theoretical with experimental values of molar excess heat capacity $C_p^E$ at 298.15 K for the methanol + $n$-heptane mixture vs. $x_1$. Solid line, predicted values; symbols, experimental values [23].

at which the methanol + $n$-hexane system is homogeneous over the whole range of concentration.

In the case of the methanol + benzene system (Fig. 4) the shapes of $H^E$ and $G^E$ are very well represented. Although the shapes of the curves of those systems containing toluene or ethylbenzene are also correct, experimental

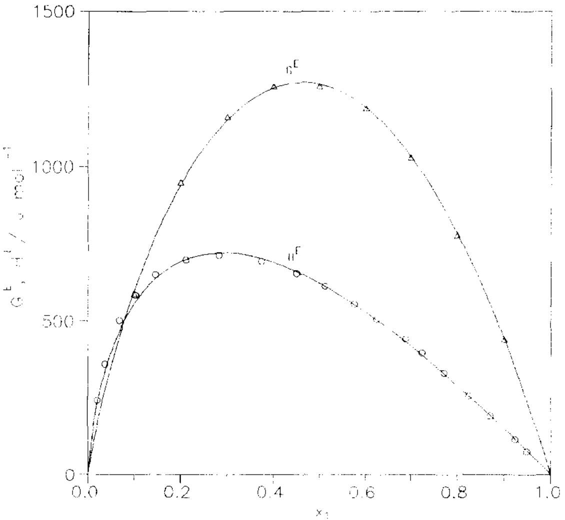

Fig. 4. Comparison of theoretical with experimental values of molar excess enthalpy $H^E$ and molar excess Gibbs energy $G^E$ at 298.15 K for the methanol(1) + $n$-benzene (2) mixture vs. $x_1$. Solid lines, predicted values; symbols, experimental values: (○) $H^E$ [9], (△) $G^E$ [17].

values are higher than predicted ones, which means that the interchange coefficients do not compensate sufficiently for the decrease of aromatic surface. Owing to the more active nature of the toluene or ethylbenzene molecules, these kinds of mixtures could be treated adequately using pure dispersive coefficients.

As is known, if the alcohol complexes are considered as molecules, the dissociation resulting from mixing increases the number of molecules in solution. If the total number of atoms is the same, the total number of degrees of freedom is unchanged. However, the number of translational and rotational degrees of freedom is increased at the expense of the vibrational degrees of freedom. If the latter are largely unexcited at the temperature considered, the mixing process results in an increase in the number of active degrees of freedom, in an increase in $C_p^E$ and in positive values of $C_p^E$. Thus $C_p^E$ increases with temperature for alcohol–aromatic systems. But since the amount of association of alcohols decreases and the degree of excitation of vibrational degrees of freedom increases with increasing temperature, one would not expect the heats of mixing to increase with temperature indefinitely. This behaviour was observed using the DISQUAC model in the ethanol + toluene system [6], and it is also observed for the methanol + benzene mixture. We think this is a success of the DISQUAC model and a justification of our parameters, particularly of the third interchange coefficients, not only of those related to alcohol–aromatic interaction but also of the alcohol–aliphatic ones.

The results of our comparison between experimental and predicted values, maximum and minimum (all in J mol$^{-1}$), for the ternary systems considered are given in Table 6. The standard deviations $\sigma$ defined as

$$\sigma = \left[\Sigma\left(\mathrm{H}_{\mathrm{cal}}^{\mathrm{E}} - H_{\mathrm{exp}}^{\mathrm{E}}\right)^2/N\right]^{1/2} \tag{1}$$

are also listed. Table 1 lists the binary mixtures involved in these ternary

TABLE 6

Comparison of direct experimental results with values obtained in the present work using coefficients from Table 4

| System | $H_{\mathrm{max}}^{\mathrm{E}}$ (J mol$^{-1}$) | | $H_{\mathrm{min}}^{\mathrm{E}}$ (J mol$^{-1}$) | | $\sigma$ |
|---|---|---|---|---|---|
| | Exp. | Calc. | Exp. | Calc. | |
| 1 | 1313 | 1445 | 230 | 250 | 208 |
| 2 | 842 | 1276 | 166 | 237 | 322 |
| 3 | 922 | 1387 | 149 | 260 | 286 |
| 4 | 1460 | 1313 | 440 | 449 | 173 |
| 5 | 986 | 986 | 168 | 284 | 266 |
| 6 | 1053 | 1452 | 172 | 311 | 257 |
| 7 | 1040 | 1189 | 361 | 451 | 231 |

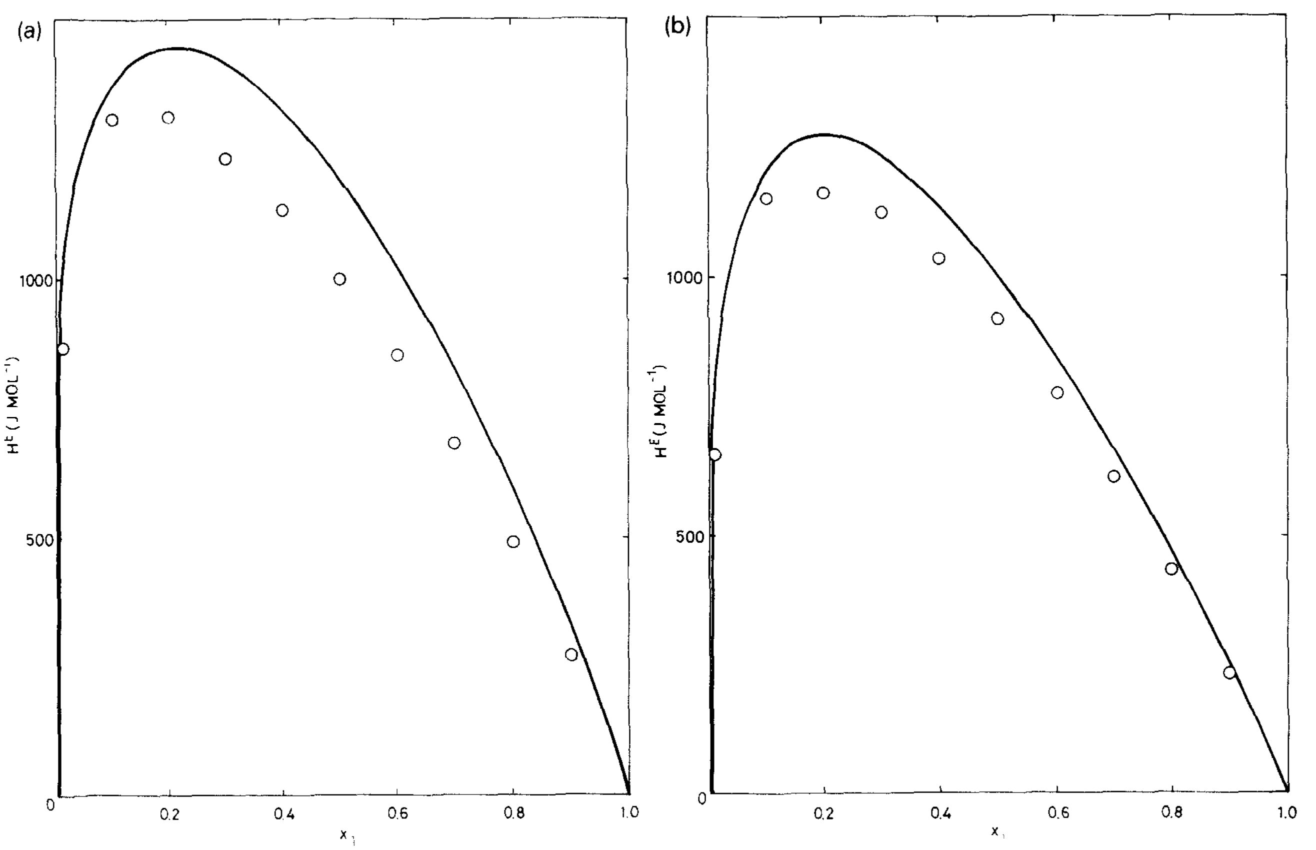

Fig. 5. (a) Comparison of theoretical with experimental values of molar excess enthalpy $H^E$ for the mixture methanol(1) + benzene(2) + *n*-hexane(3) vs. $x_1$ at 298.15 K and $x_2/x_3 = 1.500$. Solid lines, predicted values; symbols, experimental values [8]. (b) Comparison of theoretical with experimental values of molar excess enthalpy $H^E$ for the mixture methanol(1) + benzene(2) + *n*-hexane(3) vs. $x_1$ at 298.15 K and $x_2/x_3 = 4.000$. Solid lines, predicted values; symbols, experimental values [8].

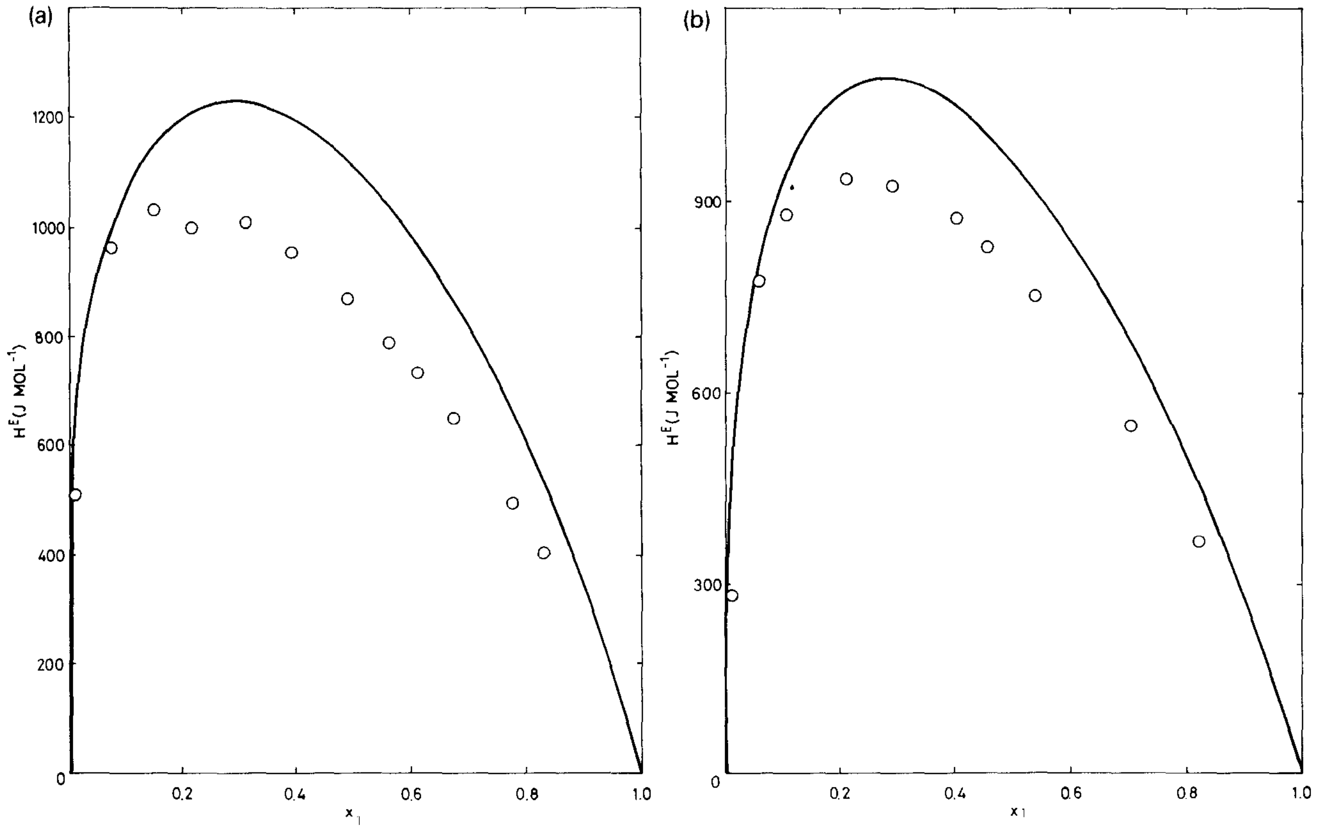

Fig. 6. (a). Comparison of theoretical with experimental values of molar excess enthalpy $H^E$ for the mixture methanol(1) + toluene(2) + *n*-heptane(3) vs. $x_1$ at 298.15 K and $x_2/x_3 = 1.8520$. Solid lines, predicted values; symbols, experimental values [13]. (b) Comparison of theoretical with experimental values of molar excess enthalpy $H^E$ for the mixture methanol(1) + toluene(2) + *n*-heptane(3) vs. $x_1$ at 298.15 K and $x_2/x_3 = 4.7118$. Solid lines, predicted values; symbols, experimental values [13].

systems which have greater excess enthalpies than binary systems. In ternary mixtures containing only $n$-alkane, aromatic or cyclic compounds this is not the case, owing to the presence of dispersive forces only. In the present case, with an alcohol in the mixture, each component makes a different contribution to the breaking of the hydrogen bond.

Values for the ternary mixtures methanol + benzene + $n$-hexane and methanol + toluene + $n$-heptane at 298.15 K are plotted in Figs. 5 and 6 respectively for different concentration ratios $x_2/x_3$.

In our previous work [6], we found that calculated values are usually greater than experimental ones, the differences between them being more important at high dilution of one of the components. Obviously, this behaviour is retained in ternary mixtures containing methanol but, as Table 6 shows, the standard deviations are in some cases too large, particularly in systems 2, 3, 5 and 6. Naturally, in the mixtures under study one would expect to obtain standard deviations greater than in other ternary systems [5,6] mainly because the process of mixing is here very complex: at 303.15 K the methanol + $n$-heptane system, with a miscibility gap, becomes miscible when a third component (benzene or toluene) is added. The DISQUAC model overestimates the excess enthalpy of the immiscible binary mixture: the calculated value at $x_1 = 0.5$ is 727 J mol$^{-1}$, while the experimental one is 491 J mol$^{-1}$ (at 303.15 K the standard deviation for $H^E$ of the methanol + $n$-heptane system in the heterogeneous region is 197 J mol$^{-1}$ and decreases to 129 if the whole range of concentration is considered). For this reason, only when the molar fraction of methanol is low will predicted values be near the experimental ones, as Figs. 5 and 6 show. Differences between standard deviations of systems 3 and 4 are due to the much higher values of Sergeeva's data: at $x_1 = 0.199$ and $x_2 = 0.65$ $H^E$ is 1460 J mol$^{-1}$, while using the prediction equation in [11] a value of 1009 J mol$^{-1}$ is obtained. New experimental data at temperatures at which none of the binaries present a miscibility gap would be desirable to achieve a more complete test of the model.

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