Thermochimica Acta, 171 (1990) 153–167
Elsevier Science Publishers B.V., Amsterdam

PREDICTION OF EXCESS FUNCTIONS OF SOME TERNARY ORGANIC MIXTURES CONTAINING ETHANOL WITH A GROUP CONTRIBUTION MODEL

J.A. GONZALEZ, J.C. COBOS, I. GARCIA and C. CASANOVA

Departamento de Fisica Aplicada II, Universidad de Valladolid, 47071 Valladolid (Spain)

(Received 26 March 1990)

ABSTRACT

A study has been made of the performance of the Kehiaian–Guggenheim–Barker group contribution model in the characterization of the excess molar functions of ternary organic mixtures. The present work reports the predictions of the model for the concentration dependence of one set of G^E ternary data and eight sets of H^E ternary data. The nine mixtures, of ethanol, as first component, with *n*-alkanes, cyclohexane 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 H^E or excess molar Gibbs functions G^E and the maximum values of those excess functions are less than 0.11 for all the systems. Previously obtained parameters for alcohol–aliphatic, alcohol–aromatic and alcohol–cyclic interactions were tested with the binary excess functions H^E, G^E and the 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 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. Toop's or Coolinet's equations) 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 models in areas such as are considered in the present work is therefore very important. We are particularly interested in the behaviour of the DISQUAC model [3,4].

The ternary systems investigated contained four different types of group: aliphatic (CH_3–, –CH_2–), aromatic (C_6H_6, C_6H_5–), cyclic (C_6H_{12}) and hydroxyl (–OH) groups.

0040-6031/90/$03.50

As there are no reports of a system containing an *n*-alcohol having been treated in the framework of the DISQUAC model, it was necessary, as a first step, to obtain parameters corresponding to alcohol–aliphatic, alcohol–aromatic and alcohol–cyclic interactions. Interactions between aliphatic, aromatic and cyclic groups were supposed to be as previously reported [5].

Although the dipolar moments of *n*-alcohols are very similar, regardless of the number of carbon atoms in the *n*-alcohol, their dielectric constants are very different: in dimensionless units and at 298.15 K, 33, 25, 20, 18, 14, 13 and 10, for methanol, ethanol, propanol, butanol, pentanol, hexanol and octanol, respectively. This suggests that it must be necessary, when investigating systems containing an *n*-alcohol, to specify whether this alcohol is methanol, ethanol, or one of higher chain. (We consider this classification to be more suitable than that for the UNIFAC model, where the only distinction made is between methanol and the other alcohols.) For this reason, the present study is limited to systems containing ethanol.

TERNARY SYSTEMS CONSIDERED

Table 1 lists all the ternary systems and binary mixtures considered. Also indicated are the number of data points N, the temperature at which data were taken T, the minimum (F^E_{min}) and maximum (F^E_{max}) experimental values (in J mol^{-1}) of the excess functions, 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 encountered elsewhere [3,4]. All the geometrical parameters, except those for ethanol, are available from the literature [5]. For ethanol, the volume r is 1.86566, the total surface q 1.7, the fraction of aliphatic surface on an ethanol molecule 0.70385 and that of a hydroxyl 0.29615, all values calculated by Bondi's method. The systems used in the fitting to obtain the interchange parameters are reported in Tables 2–4 (Type a): the H^E and G^E data for ethanol + *n*-hexane of O'Shea and Stokes [12], the G^E data of Hwang and Robinson [30] and H^E data of Stokes and Adamsom [7] for ethanol + cyclohexane, and the G^E data of Smith and Robinson [31] and H^E data of Mrazek and van Ness [10] and van Ness and Abbott [11] for ethanol + benzene.

Experimental G^E and H^E data show that interactions between hydroxyl and aliphatic and cyclic groups are similar. At equimolar composition and 298.15 K, G^E is 1330 for the ethanol + *n*-hexane system and 1395 for ethanol + cyclohexane, and the corresponding H^E values are 580 ($x =$

TABLE 1

Ternary systems and binary mixtures considered in the present work

No.	System	N	T (K)	F^E_{max} (J mol^{-1})	F^E_{min} (J mol^{-1})	Source of data
1	Ethanol + cyclohexane + n-heptane [a]	11	293.15	699	472	Grosse-Wortmann et al. (1966) [6]
2	Ethanol + cyclohexane + n-heptane [a]	7	298.15	698	595	Grosse-Wortmann et al. (1966) [6]
3	Ethanol + cyclohexane + n-heptane [a]	7	303.15	796	672	Grosse-Wortmann et al. (1966) [6]
4	Ethanol + cyclohexane + n-heptane [a]	7	313.15	926	774	Grosse-Wortmann et al. (1966) [6]
5	Ethanol + cyclohexane + n-heptane [a]	7	333.15	1375	1092	Grosse-Wortmann et al. (1966) [6]
	Ethanol + cyclohexane [a]		298.15	638		Stokes and Adamsom (1977) [7]
	Ethanol + n-heptane [a]		298.15	641		Estimated value
	n-Heptane + cyclohexane [a]		298.15	246		Grolier (1974) [8]
6	Ethanol + benzene + n-hexane [a]	36	298.15	1173	343	Jones and Lu (1966) [9]
	Ethanol + benzene [a]		298.15	869		Mrazek and van Ness (1961) [10] Van Ness and Abbott (1976) [11]
	Ethanol + n-hexane [a]		298.15	580		O'Shea and Stokes (1986) [12]
	n-Hexane + benzene [a]		298.15	897		Paz Andrade (1973) [13]
7	Ethanol + benzene + $n$heptane [a]	26	298.15	1227	232	Lu and Jones (1966) [14]
	n-Heptane + benzene [a]		298.15	937		Müncsch (1978) [15]
8	Ethanol + cyclohexane + toluene [a]	18	298.15	1106	223	Schainable et al. (1957) [16]
	Ethanol + toluene [a]		298.15	820		Mrazek and van Ness (1961) [10] Van Ness and Abbott (1976) [11]
	Cyclohexane + toluene [a]		298.15	628		Hsu and Clever (1975) [17]
9	n-Hexane + ethanol + benzene [b]	35	328.15	1536	576	Yuan et al. (1963) [18]
	Ethanol + n-hexane [b]		328.15	1414		Yuan et al. (1963) [18]
	Ethanol + benzene [b]		328.15	1130		Yuan et al. (1963) [18]
	n-Hexane + benzene [b]		328.15	358		Yuan et al. (1963) [18]

[a] Excess function: H^E.

[b] Excess function: G^E.

TABLE 2

Molar excess enthalpies H^E and molar excess Gibbs energies G^E for ethanol + 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 5

n-Alkane	Data	T (K)	x_1	Exp. (J mol^{-1})	Calc. (J mol^{-1})	Source of data
n-C_6	G^E	283.15 [a]	0.5	1330	1337	O'Shea and Stokes (1986) [12]
		298.15 [a]	0.5	1374	1381	O'Shea and Stokes (1986) [12]
		313.15	0.5	1424	1418	Janaszewski et al., (1982) [19]
		318.15 [a]	0.4684	1425	1431	O'Shea and Stokes (1986) [12]
n-C_7	G^E	303.15	0.5	1454	1436	Van Ness and Abbott (1977) [20]
		313.15	0.5	1463	1459	Janaszewski et al. (1982) [19]
		323.15	0.5	1482	1476	Van Ness and Abbott (1977) [20]
		343.17	0.5288	1498	1484	Berro et al. (1982) [21]
n-C_8	G^E	313.15	0.5	1494	1488	Janaszewski et al. (1982) [19]
n-C_9	G^E	343.21	0.5076	1559	1531	Berro et al. (1982) [21]
n-C_5	H^E	298.15	0.4282	534	535	Collins et al. (1980) [22]
n-C_6	H^E	283.15 [a]	0.3871	441	453	O'Shea and Stokes (1986) [12]
		298.15 [a]	0.3669	580	592	O'Shea and Stokes (1986) [12]
		318.15 [a]	0.3398	855	879	O'Shea and Stokes (1986) [12]
n-C_7	H^E	303.15	0.4145	666	705	Shatas et al. (1975) [23]
		323.15	0.3741	986	1060	Shatas et al. (1975) [23]
n-C_8	H^E	293.15	0.4589	587	622	Ragaini et al. (1968) [24]
		298.15	0.4699	644	679	Ragaini et al. (1968) [24]
		308.15	0.4388	708	831	Ragaini et al. (1968) [24]
n-C_9	H^E	298.15	0.3829	700	730	Christensen et al. (1979) [25]
		303.15	0.5	730	875	Savini et al. (1965) [26]
		318.15	0.5	955	1053	Savini et al. (1965) [26]
n-C_{11}	H^E	298.15	0.379	713	809	Pfestorf et al. (1983) [27]
		308.15	0.37	911	993	Pfestorf et al. (1983) [27]
n-C_{14}	H^E	308.15	0.4327	948	1134	Ramalho and Ruel (1969) [28]
		313.15	0.4184	1048	1260	Ramalho and Ruel (1969) [28]
n-C_{16}	H^E	325.25	0.3752	1461	1735	French et al. (1979) [29]

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

0.3669) and 638 ($x_1 = 0.4194$), all values being given in J mol^{-1}. We may therefore suppose that the differences between these kinds of systems are due mainly to dispersive forces, i.e. the differences will be associated with different dispersive coefficients, as is also the case in binary mixtures containing chloroalkanes and n-alkanes or cyclohexane [32]. On the other hand, if c_i, $c_i^\star$ are determined separately, the following values are obtained: $c_1^\star = 1.775$, $c_2^\star = 0.526$, $c_3^\star = -10.12$, $c_1 = 12.41$, $c_2 = 13.60$, $c_3 = 70.87$ for the hydroxyl–aliphatic interaction; and $c_1^\star = 2.156$; $c_2^\star = 0.7286$, $c_3^\star = -9.864$, $c_1 = 11.86$, $c_2 = 11.07$, $c_3 = 71.28$ for the cyclic–hydroxyl interaction. Here we can see that the quasi-chemical coefficients are very similar.

TABLE 3

Molar excess enthalpies H^E and molar excess Gibbs energies G^E for ethanol + cyclohexane 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 5

Data [a]	T (K)	x_1	Exp. (J mol^{-1})	Calc. (J mol^{-1})	Source of data
G^E	298.15	0.5	1387	1397	Hwang and Robinson (1977) [30]
H^E	283.15	0.4721	533	552	Stokes and Adamsom (1977) [7]
	288.15	0.4661	562	581	Stokes and Adamsom (1977) [7]
	293.15	0.42	593	617	Stokes and Adamsom (1977) [7]
	298.15	0.4194	638	658	Stokes and Adamsom (1977) [7]
	308.15	0.4202	738	759	Stokes and Adamsom (1977) [7]
	318.15	0.3824	870	892	Stokes and Adamsom (1977) [7]

[a] All systems used in determination of interchange energy coefficients of alcohol–cyclic interaction.

As a result, to reduce the set of parameters we chose as common parameters $c_1 = 12.2$, $c_2 = 12.2$, $c_3 = 71.1$. The dispersive coefficients were calculated separately. Final results are given in Table 5.

TABLE 4

Molar excess enthalpies H^E and molar excess Gibbs energies G^E for ethanol + benzene or toluene mixtures at various temperatures T and equimolar composition or $x_1 = 0.3$ (where H^E is maximum): Comparison of direct experimental results with values calculated using coefficients from Table 5

Component 2	Data	T (K)	x_1	Exp. (J mol^{-1})	Calc. (J mol^{-1})	Source of data
Benzene	G^E [a]	298.15	0.5	1076	1070	Smith and Robinson (1970) [31]
Toluene	G^E	303.15	0.5	1179	1112	Van Ness and Abbott (1977) [20]
	G^E	333.15	0.5	1203	1127	Van Ness and Abbott (1977) [20]
Benzene	H^E [a]	298.15	0.3	869	875	Mrazek and van Ness (1961) [10]
			0.5	761	750	Van Ness and Abbott (1976) [11]
	H^E [a]	308.15	0.3	1020	1027	Van Ness and Abbott (1976) [11]
			0.5	909	897	Van Ness and Abbott (1976) [11]
	H^E [a]	318.15	0.3	1154	1190	Van Ness and Abbott (1976) [11]
			0.5	1079	1057	Van Ness and Abbott (1976) [11]
Toluene	H^E	298.15	0.3	820	776	Van Ness and Abbott (1976) [11]
			0.5	721	644	Van Ness and Abbott (1976) [11]
	H^E	308.15	0.3	986	935	Van Ness and Abbott (1976) [11]
			0.5	880	794	Van Ness and Abbott (1976) [11]
	H^E	318.15	0.3	1157	1109	Van Ness and Abbott (1976) [11]
			0.5	1043	964	Van Ness and Abbott (1976) [11]

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

TABLE 5

Interchange energy coefficients, dispersive $c_i^\star$ and quasichemical c_i, used in the present work, for an alcohol group in ethanol

Interaction	$c_1^\star$	$c_2^\star$	$c_3^\star$	c_1	c_2	c_3	Source of data
Alcohol–aliphatic	1.84	0.81	−9.07	12.2	12.2	71.1	Present work
Alcohol–cyclic	2.15	0.88	−9.05	12.2	12.2	71.1	Present work
Alcohol–aromatic	1.67	−2.54	−11.2	8.934	16.7	21.21	Present work
Aliphatic–cyclic	0.05123	0.1533	0	0	0	0	Kehiaian et al. (1978) [5]
Aliphatic–aromatic	0.2598	0.5623	0	0	0	0	Kehiaian et al. (1978) [5]
Cyclic–aromatic	0.2455	0.5619	0	0	0	0	Kehiaian et al. (1978) [5]

A test to show whether our argument was correct was carried out as follows. Consider the ethanol + cyclohexane system. From the H^E and G^E experimental data we subtracted the contribution due to hydroxyl–aliphatic

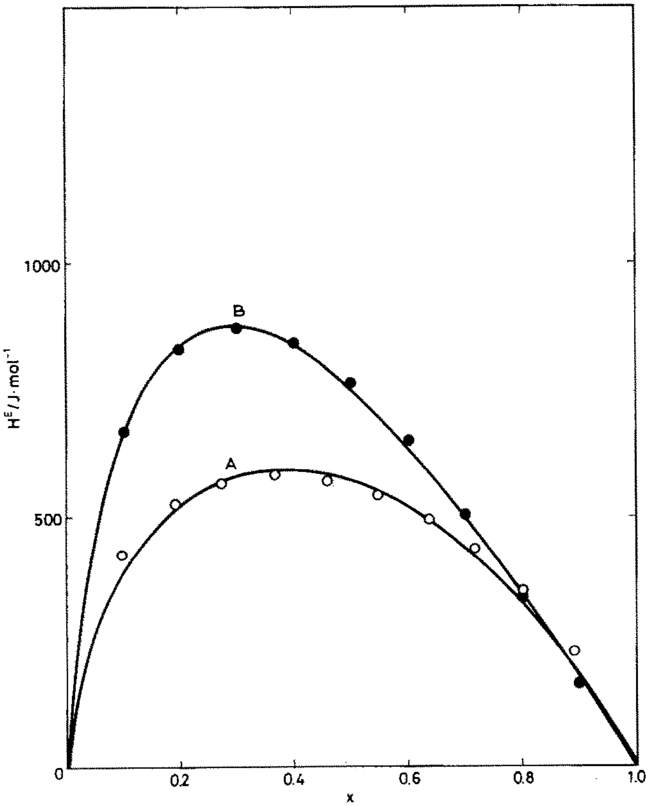

Fig. 1. Comparison of theoretical with experimental values of molar excess enthalpy H^E at 298.15 K for the mixtures ethanol(1) + *n*-hexane(2) (curve A) and ethanol(1) + benzene(2) (curve B) vs. x_1. Solid lines, predicted values; symbols, experimental values: ○ *n*-hexane (O'Shea and Stokes [12]), ● benzene (van Ness and Abbott [11]).

interaction calculated with our final parameters. The dispersive coefficients relating to the aliphatic–cyclic interaction were then calculated, and the values obtained ($c_1^\star = 0.075$, $c_2^\star = 0.1633$) were very similar to those reported in ref. 5. Naturally, to obtain a correct value for $c_1^\star$ it is necessary to take into account the size effect related to the combinatorial term of G^E (at equimolar composition and 298.15 K, $G^E_{\text{comb}} = -5$ J mol^{-1} for *n*-hexane + cyclohexane and -123 J mol^{-1} for ethanol + cyclohexane). Unfortunately, it is not possible to proceed in a similar fashion for systems containing benzene, owing to the more polarizable nature of this molecule. This is very clear from the H^E values for the *n*-hexane + cyclohexane and benzene + *n*-hexane systems: 200 and 900 J mol^{-1}, respectively, at equimolar composition and 298.15 K.

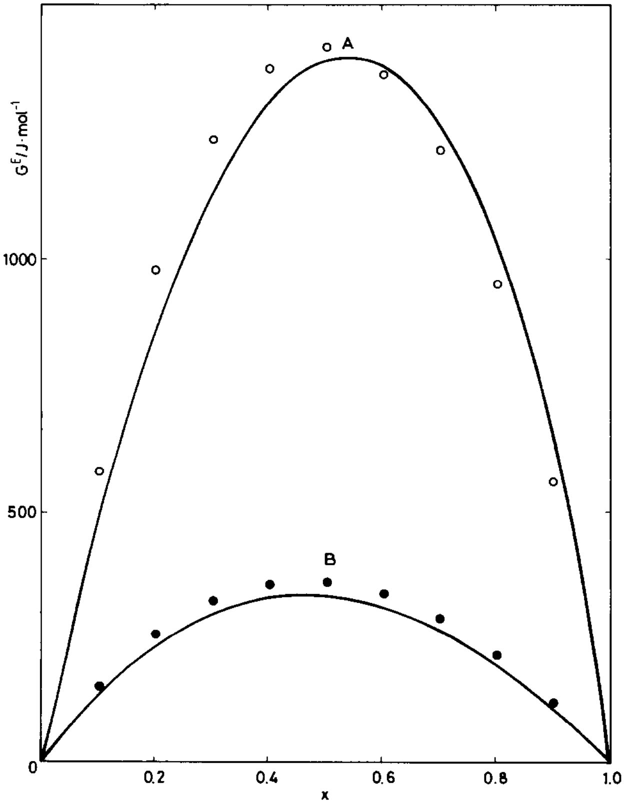

Fig. 2. Comparison of theoretical with experimental values of molar excess Gibbs energy G^E at 328.15 K for the mixtures *n*-hexane(1) + ethanol(2) (curve A) and *n*-hexane(1) + benzene(2) (curve B) vs. x_1. Solid lines, predicted values; symbols, values obtained using eqn. (6) from Yuan et al. [18]: ○ ethanol, ● benzene.

RESULTS AND DISCUSSION

Comparison of the experimental values of H^E and G^E and those predicted by the DISQUAC model (Tables 2–4) shows fairly good agreement between them. The greatest differences encountered are for ethanol + *n*-alkane systems when the *n*-alkane is one of long chain (*n*-tetradecane or *n*-hexadecane). For this reason, critical temperatures calculated for systems such as ethanol + *n*-tetradecane (55 °C) or ethanol + *n*-hexadecane (67.75 °C) are higher than the experimental values (35 [28] and 52.2 °C [29], respectively). The predicted critical compositions are more suitable: 0.797

TABLE 6

Logarithms of activity coefficients at infinite dilution $\ln \gamma_i^\infty$ in mixtures containing ethanol and *n*-alkane (*n*-hexane, *n*-heptane) or benzene or toluene: Comparison of experimental results with values calculated using coefficients from Table 5

Component 2	T (K)	$\ln \gamma_1^\infty$		$\ln \gamma_2^\infty$		Source of data
		Exp.	Calc.	Exp.	Calc.	
n-Hexane	283.15	4.514	4.534	2.42	2.00	O'Shea and Stokes (1986) [12]
	298.15	4.02	4.27	2.37	2.30	O'Shea and Stokes (1986) [12]
	318.15	3.44	3.88	2.29	2.12	O'Shea and Stokes (1986) [12]
n-Heptane	303.15	4.72	4.09	2.65	2.47	Ronc and Ratcliff (1976) [33]
		4.05		2.60		Van Ness and Abbott (1977) [20]
	323.15	3.43	3.64	2.45	2.41	Van Ness and Abbott (1977) [20]
Benzene [a]	298.15	2.53	3.00	1.502	1.54	Smith and Robinson (1970) [31]
Toluene	303.15	2.95	2.99	1.87	1.66	Van Ness and Abbott (1977) [20]
	318.15	2.53	2.66	1.72	1.62	Van Ness et al. (1967) [34]
	333.15	2.30	2.35	1.62	1.58	Van Ness et al. (1967) [34]

[a] Values estimated from Redlich–Kister equation with four coefficients.

TABLE 7

Comparison of direct experimental results with values obtained in the present work using coefficients from Table 5

System	F^E_{max} (J mol^{-1})		F^E_{min} (J mol^{-1})		σ
	Exp.	Calc.	Exp.	Calc.	
1	699	733	472	460	22
2	698	779	595	645	75
3	796	844	672	687	41
4	926	985	774	792	55
5	1375	1381	1092	1101	89
6	1173	1304	343	391	12
7	1227	1386	232	200	103
8	1106	1023	223	167	99
9	1536	1399	576	527	80

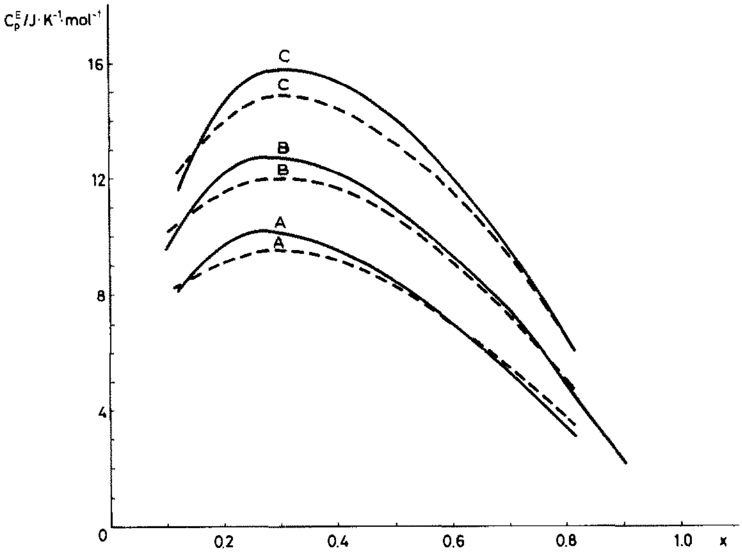

Fig. 3. Comparison of theoretical with experimental values of molar excess heat capacity C_p^E vs. x_1 at temperatures 288.15 K (curves A), 298.15 K (curves B) and 308.15 K (curves C) for the mixture ethanol(1) + *n*-heptane(2). Solid lines, predicted values; dashed lines, experimental results from Brown and Ziegler [35].

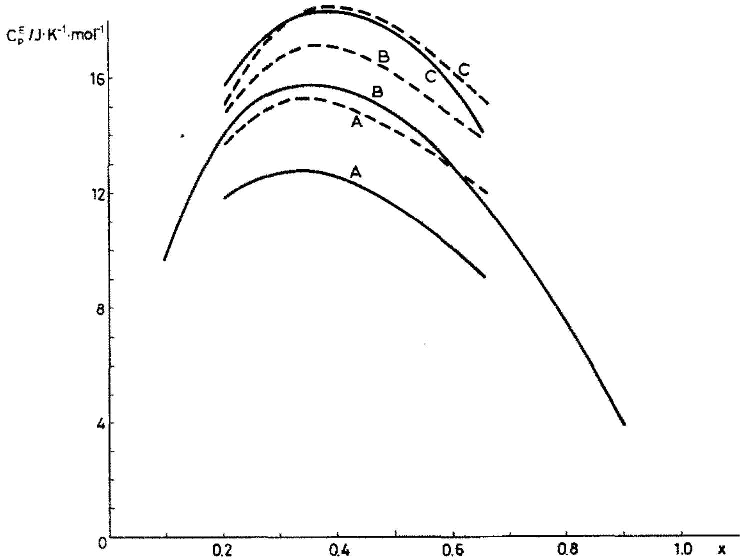

Fig. 4. Comparison of theoretical with experimental values of molar excess heat capacity C_p^E vs. x_1 at temperatures 288.15 K (curves A), 303.15 K (curves B) and 318.15 K (curves C) for the mixture ethanol(1) + toluene(2). Solid lines, predicted values; dashed lines, experimental results from Brown and Ziegler [35].

for the former mixture (experimental value, 0.77) and 0.817 for the latter (experimental value, 0.8197).

The shapes of the excess curves, i.e. H^E, G^E dependence on concentration, are also correct (see Figs. 1 and 2). With the coordination number used ($z = 4$), we obtain H^E curves shifted towards the low concentration region in ethanol, and fairly symmetrical G^E curves. Again, the curves for the higher *n*-alkanes are slightly less symmetrical, as a result of differences between experimental and calculated critical compositions in systems with miscibility gaps.

Table 6 lists values of $\ln \gamma_i^\infty$, with differences $\Delta \ln \gamma_i^\infty = \ln \gamma_i^\infty$ (experimental) $- \ln \gamma_i^\infty$ (predicted) being negative when $i = 1$ and positive when $i = 2$. (The ethanol + benzene system must not be considered, as the $\ln \gamma_i^\infty$ values were obtained not experimentally, but rather from a Redlich–Kister equation with four coefficients.)

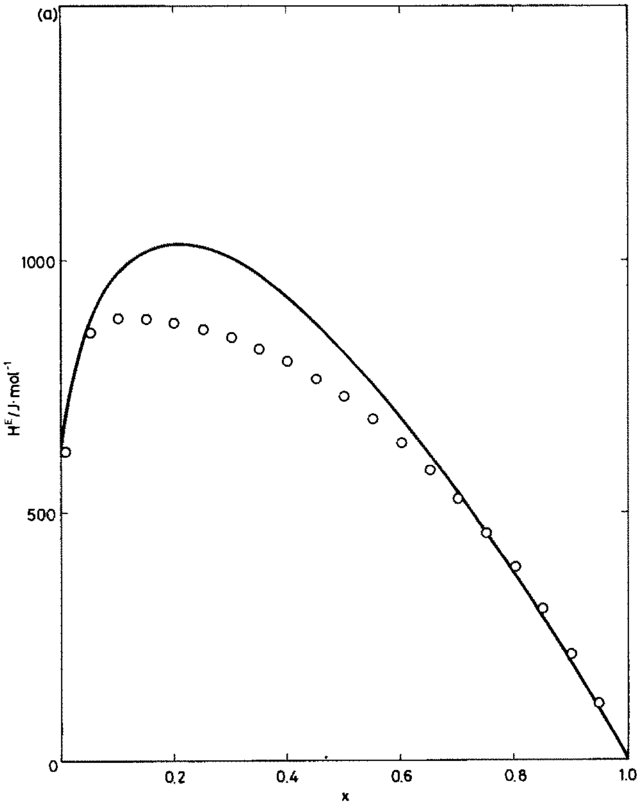

Fig. 5a. Comparison of theoretical with experimental values of molar excess enthalpy H^E for the mixture ethanol(1) + benzene(2) + *n*-hexane(3) vs. x_1 at 298.15 K and $x_2/x_3 = 0.3333$. Solid lines, predicted values; o, values obtained using a van Ness correlation equation with ten coefficients fitted using ternary data from Jones and Lu [9].

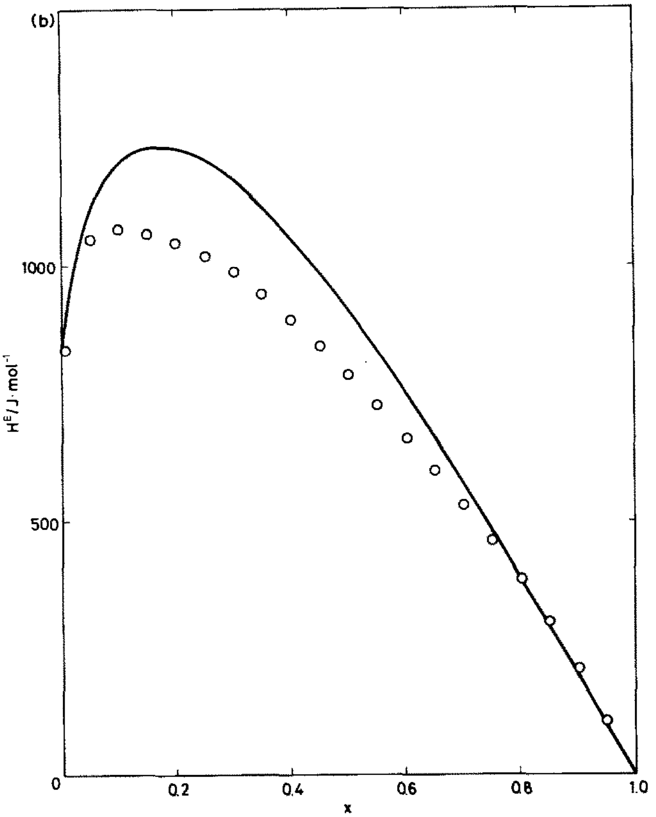

Fig. 5b. Comparison of theoretical with experimental values of molar excess enthalpy H^E for the mixture ethanol(1)+benzene(2)+ *n*-hexane(3) vs. x_1 at 298.15 K and $x_2/x_3 = 0.6666$. Solid lines, predicted values; ○, values obtained using a van Ness correlation equation with ten coefficients fitted using ternary data from Jones and Lu [9].

In the case of the ethanol + toluene mixtures, the curves of G^E (experimental) vs. x_1 are shifted slightly to the right in comparison with the curves predicted by the DISQUAC model. In the case of the ethanol + *n*-alkane systems, we think the $\Delta \ln \gamma_i^\infty$ values are related to the Flory–Huggins equation, which is known to overestimate the combinatorial entropy. In effect, while there is good agreement between the shapes and sizes of the TS^E vs. x_1 curves for the ethanol + benzene system (at 298.15 K), the same is not the case for the ethanol + *n*-hexane system (at the same temperature). The DISQUAC model predicts a change in sign (at the same temperature, and with $x = 0.01$) of the excess entropy, with $TS^E \approx 2$ J mol^{-1}, but experimentally, although TS^E does change in sign at a similar concentration, its value is greater (44 J mol^{-1}).

It is very important that the DISQUAC model gives fairly good predictions of the variation of C_p^E with temperature and concentration [35,36,37] (see Figs. 3 and 4). C_p^E always increases with temperature in the case of the ethanol + n-heptane mixture, but decreases, from a certain temperature, in the case of the ethanol + toluene system. We think this is a success of the DISQUAC model, and a justification of our parameters, particularly of the third interchange coefficients.

The results of our comparison of experimental and predicted values, maximum and minimum, (all in J mol^{-1}) for the ternary systems considered are given in Table 7. The standard deviations σ, defined as

$$\sigma = \left[\frac{\left(F_{\text{calc}}^{\text{E}} - F_{\text{exp}}^{\text{E}} \right)^2}{N} \right]^{1/2} \qquad (1)$$

are also listed. Table 1 lists the binary mixtures involved in these ternary systems. These have greater excess functions than the former. In the 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,

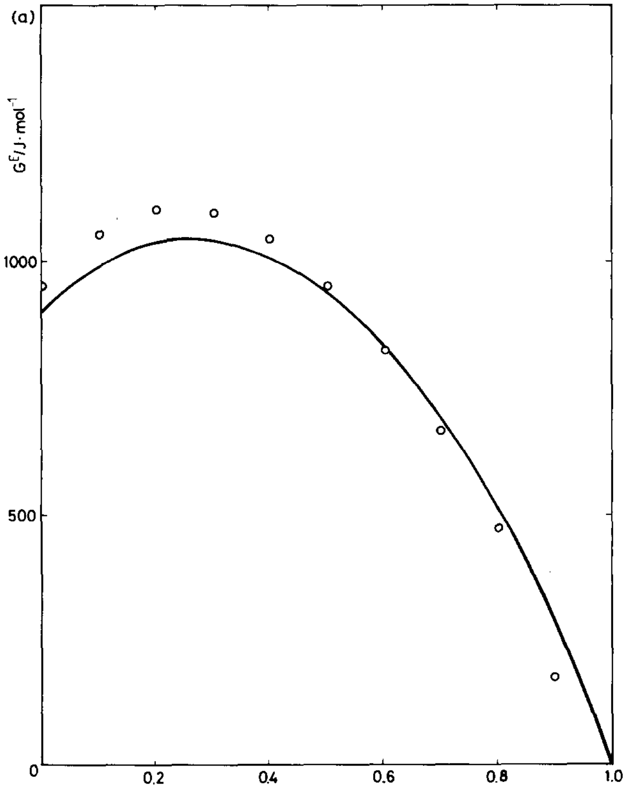

Fig. 6a. Comparison of theoretical with experimental values of molar excess Gibbs energy G^{E} for the mixture n-hexane(1) + ethanol(2) + benzene(3) vs. x_1 at 328.15 K and $x_2/x_3 = 0.3333$. Solid lines, predicted values; o, values obtained using eqn. (6) from Yuan et al. [18].

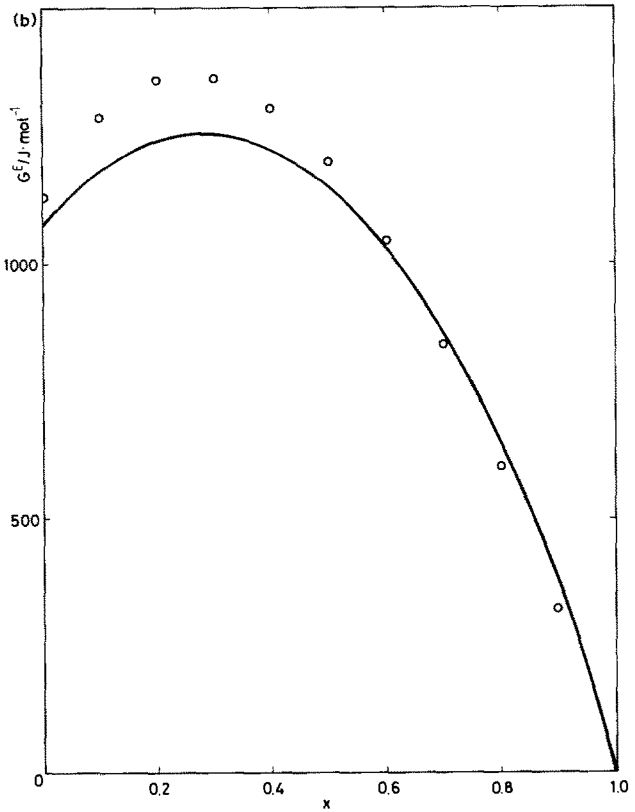

Fig. 6b. Comparison of theoretical with experimental values of molar excess Gibbs energy G^E for the mixture n-hexane(1) + ethanol(2) + benzene(3) vs. x_1 at 328.15 K and $x_2/x_3 = 0.6666$. Solid lines, predicted values; ○, values obtained using eqn. (6) from Yuan et al. [18].

with an alcohol in the mixture, each component makes a different contribution to the breaking of the hydrogen bond.

Values for the ternary mixtures ethanol + benzene + n-hexane (H^E at 298.15 K) and n-hexane + ethanol + benzene (G^E at 328.15 K) are plotted in Figs. 5 and 6, respectively, for two different concentration ratios, $x_2/x_3 = 0.3333$ and 0.6666. We can see that predictions are good for these ternary systems.

The calculated values are greater than the experimental data, except in two cases. In the ethanol + cyclohexane + toluene mixture, with six different interactions, this is related to the H^E prediction for the ethanol + toluene system. Table 4 shows that the theoretical values are smaller than the experimental ones, which means that the interchange coefficients do not compensate sufficiently for the decrease of aromatic surface. Thus, at the maximum for this ternary system, the dispersive contribution of the alcohol–aromatic interaction is about −260 J mol^{-1}, which is too negative when compared with the other contributions (see Table 8).

TABLE 8

Contributions to H^E of different interactions in the ethanol + cyclohexane + toluene system

Interaction	Dispersive ($J\ mol^{-1}$)		Quasi-chemical ($J\ mol^{-1}$)		Total ($J\ mol^{-1}$)	
	Max.	Min.	Max.	Min.	Max.	Min.
Alcohol–aliphatic	−89	−67	−53	−63	−142	−130
Alcohol–cyclic	64	47	171	68	235	115
Alcohol–aromatic	−260	−197	760	291	500	94
Aliphatic–cyclic	68	20	0	0	68	20
Aliphatic–aromatic	−30	59	0	0	−30	59
Cyclic–aromatic	391	8	0	0	391	8

In the case of the ethanol + benzene + *n*-hexane system, the differences $[G^E(\text{calculated}) - G^E\ (\text{experimental})]$ are negative, while the corresponding H^E differences are positive. This may be due to the special form of the ln γ_i expression. The ethanol + benzene mixture has the same number of groups as the actual ternary system; but in this ternary system the presence of *n*-hexane results in an extra negative term $(zq_i \ln(X_{\text{aliphatic}}/\alpha_{\text{aliphatic}})$. Only when the *n*-hexane concentration is high (0.7, 0.8) do the G^E differences become positive, owing to the greater weight of the dispersive contribution to G^E. Naturally, this behaviour needs to be studied in systems where the third component has more than one group.

REFERENCES

1 C. Pando, J.A.R. Renuncio, J.A.G. Calzon, J.J. Christensen and R.M., Izatt, J. Solution Chem., 16 (1987) 503.
2 W.E. Acree, Jr., Thermodynamic Properties of Non-Electrolyte Solutions, Academic Press, London, 1984, Chap. 4.
3 K.V. Kehiaian and B. Marongiu, Fluid Phase Equilibria, 21 (1985) 197.
4 J. Muñoz Embid, O. Santos, I. Velasco, C. Gutiérrez Losa and H.V. Kehiaian, Fluid Phase Equilibria, 38 (1987) 1.
5 H.V. Kehiaian, J.-P. Grolier and G.C. Benson, J. Chim. Phys., 75 (1978) 1031.
6 H. Grosse-Wortmann, W. Jost and H.G. Wagner, Z. Phys. Chem., 70 (1966) 602.
7 R.H. Stokes and M. Adamsom, J. Chem. Soc., Faraday Trans. 1, (1977) 1232.
8 J.P. Grolier, Int. Data Ser. Sel. Data Mixtures, Ser. A, N3 (1974) 217.
9 H.K.DeQ. Jones and B.C.-Y. Lu, J. Chem. Eng. Data, 11 (1966) 488.
10 P.V. Mrazek and H.C. van Ness, AIChE J., 7 (1961) 190.
11 H.C. van Ness and M.M. Abbott, Int. Data Ser. Sel. Data Mixtures, Ser. A, N1 (1976) 20, 28.
12 S.J. O'Shea and R.H. Stokes, J. Chem. Thermodyn., 18 (1986) 691.
13 M.I. Paz Andrade, Int. Data Ser. Sel. Data Mixtures, Ser. A, N2 (1973) 96.
14 B.C.-Y. Lu and H.K.DeQ. Jones, Can. J. Chem. Eng., 44 (1966) 251.
15 E. Müncsch, Thermochim. Acta, 22 (1978) 237.
16 H.W. Schainable, H.C. van Ness and J.M. Smith, AIChE J., 3 (1957) 147.

17 K.-Y. Hsu and H.L. Clever, J. Chem. Thermodyn., 7 (1975) 435.

18 K.S. Yuan, J.C.K. Ho, A.K. Keshpande and B.C.-Y. Lu, J. Chem. Eng. Data, 8 (1963) 549.

19 B. Janaszewski, P. Oracz, M. Goral and S. Warycha, Fluid Phase Equilibria, 9 (1982) 295.

20 H.C. van Ness and M.M. Abbott, Int. Data Ser. Sel. Data Mixtures, Ser. A, 1 (1977) 1.

21 C. Berro, M. Rogalski and A. Peneloux, Fluid Phase Equilibria, 8 (1982) 55.

22 S.G. Collins, J.J. Christensen, R.M. Izatt and R.W. Hanks, J. Chem. Thermodyn., 12 (1980) 609.

23 J.P. Shatas, M.M. Abbott and H.C. van Ness, J. Chem. Eng. Data, 20 (1975) 406.

24 V. Ragaini, R. Santi and S. Carra, Lincei-Rend. Sci. Fis. Mat. e Nat., 45 (1968) 540.

25 J.J. Christensen, R.M. Izatt, B.D. Stitt, R.W. Hanks and K.D. Williamson, J. Chem. Thermodyn., 11 (1979) 1029.

26 C.G. Savini, D.R. Winterhalter and H.C. van Ness, J. Chem. Eng. Data, 10 (1965) 168.

27 R. Pfestorf, J. Schumelzer, M. Krug, B. Zeiger, U. Stych, and K. Quitzsch, Fluid Phase Equilibria, 12 (1983) 283.

28 R.S. Ramalho and M. Ruel, J. Chem. Eng. Data, 14 (1969) 20.

29 H.T. French, A. Richards and R.H. Stokes, J. Chem. Thermodyn., 11 (1979) 671.

30 S.C. Hwang and R.L. Robinson, J. Chem. Eng. Data, 22 (1977) 319.

31 V.C. Smith and R.L. Robinson, J. Chem. Eng. Data, 15 (1970) 391.

32 H.V. Kehiaian and B. Marongiu, Fluid Phase Equilibria, 40 (1988) 23.

33 M. Ronc and C.R. Ratcliff, Can. J. Chem. Eng., 54 (1976) 326.

34 H.C. van Ness, C.A. Socek, G.L. Peloquin and R.L. Machado, J. Chem. Eng. Data, 12 (1967) 217.

35 N.G. Brown, Jr. and W.T. Ziegler, J. Chem. Eng. Data, 24 (1979) 319.

36 M.J. Pedersen, W.B. Kay and H. Hershey, J. Chem. Thermodyn., 7 (1975) 1107.

37 S.C.P. Hwa and W.T. Ziegler, J. Phys. Chem., 70 (1966) 2572.