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DISQUAC analysis of binary liquid organic mixtures containing cyclic or linear alkanols and cycloalkanes or *n*-alkanes

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Abstract

Literature data for cycloalkanol + cycloalkane or *n*-alkane mixtures are critically reviewed and characterized in terms of the DISQUAC model incorporating intramolecular effects related to the inclusion of a functional group, OH, in an aliphatic ring.

Although the interaction parameters follow similar rules to those encountered for other heterocycles (amines, ethers, ketones), some differences are found, e.g., the quasichemical coefficients are independent not only (as usual) of the alkane, but also of the cycloalkanol.

It is shown that for such systems steric effects are less important than ring strain.

A treatment of 1-alkanols + cycloalkanes (except C_6H_{12}) mixtures using the interaction parameters determined previously for cyclohexane is included.

Keywords: DISQUAC model; Ring strain; Quasichemical coefficients

1. Introduction

In previous papers, we have examined, in terms of the DISQUAC model, an extended quasi-chemical group contribution model [1, 2], thermodynamic properties, namely vapor–liquid equilibria, liquid–liquid and solid–liquid equilibria, molar excess functions, Gibbs energy (G^E), enthalpy (H^E), and heat capacity (C_p^E), and partial molar excess quantities at infinite dilution of binary mixtures containing 1-alkanols and organic solvents (*n*-alkanes, 1-alkanols, cyclohexane, benzene or toluene, or tetrachloromethane) [3–11]. The model usually provides a fairly good representation of these types of

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mixtures, as well as related ternary systems, which are described on the basis of binary interactions only [3,4,6,12–13].

The basic purpose of this work is to study special intramolecular effects, namely, the inclusion of the functional group OH in an aliphatic cycle. In the present paper we treat binary mixtures containing a cycloalkanol as the heterocyclic molecule and an organic solvent, which contains only aliphatic hydrocarbon groups, namely methyl (CH_3), methylene in a linear chain (CH_2), and methylene in a ring (c-CH_2), i.e., *n*-alkanes or cycloalkanes.

Previously, other cyclic molecules ((c-CH_2)$_{m-1}$–X, where X represents the functional group under consideration) have been studied in terms of DISQUAC, e.g., X is NH, O, or CO [14–16]. These studies have shown that the inclusion of a polar functional group X in an aliphatic ring may change considerably the group interaction parameters. This change was ascribed to: (a) a smaller steric effect exerted by cyclomethylene groups adjacent to X in cyclic molecules, compared to *n*-alkyl groups; and (b) electron delocalization (ring strain). Both effects strengthen the interaction between cyclic molecules compared to linear molecules. The steric effect increases the quasichemical interchange parameters, while the ring strain increases the dispersive parameters to the X/alkane contacts [16].

As already mentioned, binary mixtures of 1-alkanols and cyclohexane have been widely investigated in the framework of DISQUAC [3,4,8]. In order to complete this study the effect of changing the cycloalkane is now examined.

2. Theory

Alkanol + alkane systems are regarded as possessing three types of surfaces: (i) type a (CH_3 and CH_2 groups in *n*-alkanes or 1-alkanols), (ii) type c (c-CH_2 and c-CH groups in cycloalkanes and cyclic alkanols, and (iii) type h (OH in alkanols).

The equations used to calculate G^E and H^E are the same as in other applications [17].

The temperature dependence of the interaction parameters has been expressed in terms of the dispersive and quasichemical interchange coefficients $C^{DIS}_{sh,l}$ and $C^{QUAC}_{sh,l}$, where s = a or c, and $l = 1$ (Gibbs energy) $l = 2$ (enthalpy), or $l = 3$ (heat capacity).

Table 1
Relative group increments for molecular volumes, $r_G = V_G/V_{CH_4}$ and areas $q_G = A_G/A_{CH_4}$; c–CH_2 and c–CH are, respectively, a methylene or a methine group in an *m*-atom ring ($V_{CH_4} = 17.12 \times 10^{-6}$ m^3 mol^{-1}; $A_{CH_4} = 2.90 \times 10^{-5}$ m^2 mol^{-1})

Group	r_G	q_G	
CH_3^a	0.79848	0.73103	
CH_2^a	0.59755	0.46552	
c–CH_2^b	0.58645	0.66377–0.0385m	$4 \leq m \leq 8$
c–CH^b	0.38493	0.39480–0.0385m	$4 \leq m \leq 8$
OH^c	0.46963	0.50345	

[a] Ref. [19]. [b] Ref. [15]. [c] Ref. [5].

3. Assessment of geometrical parameters

The relative molecular volumes, r_i, the surfaces, q_i, and the surface fractions, α_{si}, of all the non-cyclic molecular species have been calculated on the basis of the group volumes and surfaces recommended by Bondi (1968) [18], arbitrarily taking the volume and surface of methane as unity [19]. The geometrical parameters of the cyclic aliphatic groups have been estimated previously [15]. Table 1 lists the geometrical parameters of the groups referred to in this work.

4. Estimation of the interaction parameters

4.1. *Cycloalkanols + cycloalkanes*

These systems were characterized by a single type of contact (c, h), i.e., no distinction was made between the c-CH_2 groups in cyclic alkanols and cycloalkanes, or between c-CH_2 and c-CH groups, which are assumed to exert the same force field.

We note that:

(a) The quasichemical coefficients $C^{\mathrm{QUAC}}_{\mathrm{ch},l}$ are independent of the cycloalkanol and of the cycloalkane.

(b) For a given cyclic alcohol, the dispersive coefficient $C^{\mathrm{DIS}}_{\mathrm{ch},1}$ changes with the cycloalkane as the maximum of the G^E for the mixtures and is constant from cycloheptane (see below). The $C^{\mathrm{DIS}}_{\mathrm{ch},l}$ ($l = 2,3$) coefficients are independent of the cycloalkane, except in the case of cyclopentane, with an enthalpic parameter which is smaller than for other cycloalkanes (Table 2).

Table 2

Interchange coefficients, dispersive $C^{\mathrm{DIS}}_{\mathrm{ch},l}$ and quasichemical $C^{\mathrm{QUAC}}_{\mathrm{ch},l}$ ($l = 1$, Gibbs energy; $l = 2$, enthalpy; $l = 3$, heat capacity) for contacts (c, h). (Type c, c-CH_2 or c-CH in cyclic molecules, alkanols or alkanes; type h, OH in cyclic alkanols.) The coordination number used for the QUAC part is $z = 4$. n and m indicate the number of carbon atoms in the cyclic alkanols and cycloalkanes, respectively

(n, m)	$C^{\mathrm{DIS}}_{\mathrm{ch},1}$	$C^{\mathrm{DIS}}_{\mathrm{ch},2}$	$C^{\mathrm{DIS}}_{\mathrm{ch},3}$	$C^{\mathrm{QUAC}}_{\mathrm{ch},1}$	$C^{\mathrm{QUAC}}_{\mathrm{ch},2}$	$C^{\mathrm{QUAC}}_{\mathrm{ch},3}$
(5, 5)	3.75	3.55	− 20.00	12.20	15.00	71.10
(5, 6)	3.55	3.90	− 20.00	12.20	15.00	71.10
(5, 7)	1.75	3.90	− 20.00	12.20	15.00	71.10
(5, 8)	1.75	3.90	− 20.00	12.20	15.00	71.10
(6, 5)	4.25	3.25	− 20.00	12.20	15.00	71.10
(6, 6)	4.00	3.80	− 20.00	12.20	15.00	71.10
(6, 7)	2.40[a]	3.80[a]	− 20.00	12.20	15.00	71.10
(6, 8)	2.40[a]	3.80[a]	− 20.00	12.20	15.00	71.10
(7, 5)	4.95[a]	4.75[a]	− 20.00	12.20	15.00	71.10
(7, 6)	4.75[a]	5.40[a]	− 20.00	12.20	15.00	71.10
(7, 7)	3.15	5.40	− 20.00	12.20	15.00	71.10

[a] Estimated value.

4.2. *Cycloalkanols* + n-*alkanes*

These systems are characterized by three types of contact: (a, c), (a, h) and (c, h). We proceeded in the same way as with the cyclic ethers [15] and ketones [16], neglecting the (a, c) parameters, using the (c, h) parameters of cyclic alcohols + cycloalkanes determined previously, and adjusting the (a, h) parameters. It was found that:

(a) The quasichemical coefficients $C^{QUAC}_{ah,l}$, equaled the quasichemical coefficients $C^{QUAC}_{ch,l}$ i.e. they are independent of the class of alkane (Table 3); and

(b) The dispersive coefficients $C^{DIS}_{ah,l}$ were quite close to the $C^{DIS}_{ch,l}$ parameters (Table 3).

4.3. *1-Alkanols + cycloalkanes (except cyclohexane)*

These systems are characterized by three types of contact: (a, c), (a, h) and (c, h). The intercharge coefficients for the (a, h) contact have been obtained previously on the basis

Table 3
Interchange coefficients, dispersive $C^{DIS}_{ah,l}$ and quasichemical $C^{QUAC}_{ah,l}$ ($l = 1$, Gibbs energy; $l = 2$, enthalpy; $l = 3$, heat capacity) for contacts (a, h). (Type a, CH_3 or CH_2 in *n*-alkanes or 1-alkanols; type h, OH in alkanols.) The coordination number used for the QUAC part is $z = 4$. *m* indicates the number of carbon atoms in the alkanol

m	$C^{DIS}_{ah,1}$	$C^{DIS}_{ah,2}$	$C^{DIS}_{ah,3}$	$C^{QUAC}_{ah,1}$	$C^{QUAC}_{ah,2}$	$C^{QUAC}_{ah,3}$
			Cycloalkanols + *n*-alkanes			
5	3.65[a]	3.70	−18.00	12.20	15.00	71.10
6	4.05	3.90	−18.00	12.20	15.00	71.10
7	4.85[a]	5.30[a]	−18.00	12.20	15.00	71.10
			1-Alkanols + *n*-alkanes			
5[b]	3.95	0.71	−20.0	12.20	15.00	71.10
6[b]	5.30	1.10	−21.5	12.20	14.40	71.10
7[b]	6.52	2.04	−27.5	12.20	13.75	71.10

[a] Estimated value. [b] Ref. [5].

Table 4
Interchange coefficients, dispersive $C^{DIS}_{sh,l}$ and quasichemical $C^{QUAC}_{sh,l}$ ($l = 1$, Gibbs energy; $l = 2$, enthalpy; $l = 3$, heat capacity) for contacts (s, h) (s = a, c; type a, CH_3 or CH_2 in 1-alkanols; type c, c-CH_2 in cycloalkanes; type h, OH in 1-alkanols.) The coordination number used for the QUAC part is $z = 4$; *m* indicates the number of carbon atoms in the alkanol

m	$C^{DIS}_{ah,1}$	$C^{DIS}_{ah,2}$	$C^{DIS}_{ah,3}$	$C^{DIS}_{ch,1}$	$C^{DIS}_{ch,2}$	$C^{DIS}_{ch,3}$	$C^{QUAC}_{sh,1}$	$C^{QUAC}_{sh,2}$	$C^{QUAC}_{sh,3}$
1[a]	1.35	1.60	−9.10	1.67	2.10[b]	−9.10	12.20	8.10	71.10
2[a]	1.84	0.81	−9.10	2.20	0.92	−9.10	12.20	12.20	71.10
3[a]	2.55	0.18	−15.50	2.80	0.18	−14.00	12.20	15.20	71.10

[a] Ref. [8]. [b] For cyclopentane $C^{DIS}_{ch,2} = 1$.

of data for 1-alkanol + n-alkane mixtures [5, 8]. The (a, c) interaction is represented by dispersive parameters only, given elsewhere [14]. Cycloheptane and cyclooctane can be described with the parameters of cyclohexane. Cyclopentane behaves quite differently from these, the $C^{\mathrm{DIS}}_{\mathrm{ac},1}$ coefficients being practically zero [14]. The (c, h) parameters obtained for the 1-alkanols + cyclohexane systems [8] are also valid for the mixtures studied containing another cycloalkane (Table 4), except for the methanol + cyclopentane system characterized by $C^{\mathrm{DIS}}_{\mathrm{ch},2} = 1$ (see Discussion).

5. Discussion

Tables 5–7 and Figs. 1–6 are numerical and graphical comparisons, respectively, between experimental data and DISQUAC predictions. In Table 5, for the sake of clarity,

Table 5
Molar excess functions F^{E} $(T; x_1)$, Gibbs energies, enthalpies or heat capacities for cycloalkanol or 1-alkanol + cycloalkane or + n-alkane mixtures at various temperatures (T/K) and $x_1 = 0.5$ (Gibbs energies) or $x_1 = 0.3$ (enthalpies). Comparison of experimental results (exp.) with calculated values (calc.) using the coefficients from Tables 2–4. Also listed are the standard deviations, σ (Eq. (1)), and the number of data for each system N

System	T/K	N	F^{E}		σ^1		Source of data
			Exp.	Calc.	Exp.	Calc.	
			$G^{\mathrm{E}}(T; x_1 = 0.5)$/J mol^{-1}				
c-C_5OH + c-C_5^a	298.15	14	991	981	1.7	23.5	[20]
c-C_5OH + c-C_6^a	298.15	20	1035	1033	7.3	22.5	[21]
c-C_5OH + c-C_7	298.15	14	987	946	28.3	106	[22]
c-C_5OH + c-C_8^a	298.15	14	919	940	53.5	52.2	[22]
c-C_6OH + c-C_5	298.15	19	923	905	6.0	17.4	[21]
c-C_6OH + c-C_6	298.15	23	971	973	4.2	15.4	[20]
c-C_7OH + c-C_7^a	298.15	18	913	916	12.6	21.0	[22]
c-C_6OH + n-C_7^a	303.15	9	1252	1249	4.2	16.5	[23]
	323.26	9	1244	1265	2.5	19.2	[23]
	343.32	9	1233	1254	1.2	21.4	[23]
	373.28	9	1180	1169	0.1	21.9	[23]
			$H^{\mathrm{E}}(T; x_1 = 0.3)$/J mol^{-1}				
c-C_5OH + c-C_5^a	298.15	29	587	602	2.8	16.0	[20]
c-C_5OH + c-C_6^a	298.15	25	644	656	3.5	16.0	[21]
c-C_5OH + c-C_7^a	298.15	20	670	680	2.5	17.0	[22]
c-C_5OH + c-C_8^a	298.15	35	661	692	2.0	18.0	[22]
c-C_6OH + c-C_5^a	298.15	17	567	555	1.2	18.0	[21]
c-C_6OH + c-C_6^a	298.15	32	646	615	2.5	29.0	[20]
c-C_7OH + c-C_7^a	298.15	31	670	685	1.6	21.0	[22]
c-C_5OH + n-C_6	298.15	12	661	701	1.9	51.0	[24]
c-C_5OH + n-C_7	298.15	12	738	756	1.9	59.0	[24]
		16^a	733		2.3	32.0	[25]

Table 5 (*Continued*)

System	T/K	N	F^E		σ^1		Source of data
			Exp.	Calc.	Exp.	Calc.	
$c\text{-}C_5OH + n\text{-}C_8$	298.15	12	779	808	1.8	61.0	[24]
$c\text{-}C_5OH + n\text{-}C_{10}$	298.15	14	831	903	2.4	77.0	[24]
$c\text{-}C_5OH + n\text{-}C_{12}$	298.15	11	861	987	1.6	84.0	[24]
$c\text{-}C_6OH + n\text{-}C_6$	298.15	12	661	741	2.1	110	[24]
$c\text{-}C_6OH + n\text{-}C_7$	298.15	12	745	798	1.7	76.0	[24]
$c\text{-}C_6OH + n\text{-}C_8$	298.15	11	816	851	2.1	70.0	[24]
$c\text{-}C_6OH + n\text{-}C_{10}$	298.15	11	898	948	2.4	58.0	[24]
$c\text{-}C_6OH + n\text{-}C_{12}$	298.15	11	1060	1034	2.8	59.0	[24]
$MeOH^2 + c\text{-}C_5$	298.15	13	494	556	2.8	55.0	[26]
$EtOH + c\text{-}C_5$	298.15	13	529	530	2.8	9.9	[26]
$PrOH + c\text{-}C_5$	298.15	15	525	508	2.8	19.0	[26]
$EtOH + c\text{-}C_7$	298.15	13	623	640	2.8	23.0	[26]
$PrOH + c\text{-}C_7$	298.15	12	630	643	2.8	12.0	[26]
$EtOH + c\text{-}C_8$	298.15	14	584	650	2.8	43.0	[26]
$PrOH + c\text{-}C_8$	298.15	14	629	715	2.8	66.0	[26]
			$C_p^E(T; x_1)/\mathrm{J\,mol^{-1}\,K^{-1}}$				
$c\text{-}C_6OH + c\text{-}C_6$	298.15		5.8[b]	6.7			[27]
$c\text{-}C_5OH + n\text{-}C_7$	298.15	11	12.26[c]	13.92	0.16	1.20	[28]

[a] System used in the estimation of the interchange coefficients. [b] $x_1 = 0.505$. [c] $x_1 = 0.3$.
Key: MeOH, methanol; EtOH, ethanol; PrOH, 1-propanol.

the standard deviations are defined by

$$\sigma(F^E) = \{1/N \Sigma (F^E_{cal} - F^E_{exp})^2\}^{1/2} \tag{1}$$

where N is the number of data points and F^E_{cal}, the values obtained from the DISQUAC model, are also listed and compared with those standard deviations given in the original works calculated on the basis of the fitting equations used.

For systems containing cyclic alkanols, DISQUAC predictions agree with general trends observed in other alcoholic solutions: curves of H^E vs. x_1 (mole fraction of alcohol) are skewed to low concentration of this compound (Figs. 1, 2, 4); curves for G^E are more symmetrical (Figs. 1, 2, 4); excess entropy is s-shaped, with positive values at low x_1 as a consequence of increasing the orientational disorder associated with the breaking of the hydrogen bonds between the alcohol molecules (Fig. 3); high C_p^E (unfortunately the model does not represent the negative region at very low concentration of alcohol, see Fig. 5 and Ref. [28]); G^E decreasing from sufficiently high temperatures [23] (Table 5).

We observed some large discrepancies between measured and predicted values in Table 5, which may be attributed to experimental inaccuracies, For example, the experimental $H^E(x_1)$ curves of cycloalkanols + n-alkanes mixtures reported by Kaur

Table 6
Natural logarithms of activity coefficients at infinite dilution of compound i, $\ln \gamma_i^\infty$, in cycloalkanol (1) + alkane (2) mixtures at various temperatures (T/K). Comparison of experimental results (exp.) with values calculated (calc.) using the coefficients from Tables 2-4

System	T/K	$\ln \gamma_i^\infty$ Exp.	$\ln \gamma_i^\infty$ Calc.	Source of data
		$\ln \gamma_1^\infty$		
$c\text{-}C_5OH + c\text{-}C_5$	298.15	4.108[a]	4.141	[20]
$c\text{-}C_5OH + c\text{-}C_6$	298.15	4.466[a]	4.121	[21]
$c\text{-}C_5OH + c\text{-}C_7$	298.15	1.276[a]	3.921	[22]
$c\text{-}C_5OH + c\text{-}C_8$	298.15	3.358[a]	3.885	[22]
$c\text{-}C_6OH + c\text{-}C_5$	298.15	4.086[a]	4.035	[21]
$c\text{-}C_6OH + c\text{-}C_6$	298.15	4.079[a]	4.045	[20]
$c\text{-}C_7OH + c\text{-}C_7$	298.15	3.682[a]	3.899	[22]
		$\ln \gamma_2^\infty$		
$c\text{-}C_5OH + c\text{-}C_5$	298.15	1.338[a]	1.243	[20]
$c\text{-}C_5OH + c\text{-}C_6$	298.15	1.470[a]	1.351	[21]
$c\text{-}C_5OH + c\text{-}C_7$	298.15	1.960[a]	1.219	[22]
$c\text{-}C_5OH + c\text{-}C_8$	298.15	1.215[a]	1.208	[22]
$c\text{-}C_5OH + n\text{-}C_6$	298.15	1.872[b]	1.676	[29]
$c\text{-}C_6OH + c\text{-}C_5$	298.15	1.176[a]	1.110	[21]
$c\text{-}C_6OH + c\text{-}C_6$	298.15	1.273[a]	1.234	[20]
	303.15	1.215[b]	1.222	[29]
$c\text{-}C_6OH + n\text{-}C_6$	298.15	1.815[b]	1.610	[29]
	303.15	1.734[b]	1.595	[29]
$c\text{-}C_7OH + c\text{-}C_6$	298.15	1.138[b]	1.177	[29]
$c\text{-}C_7OH + c\text{-}C_7$	298.15	1.200[a]	1.148	[22]
$c\text{-}C_7OH + n\text{-}C_6$	298.15	1.635[b]	1.587	[29]

[a] From an equation of the type: $G^E = x_1 x_2 \Sigma a_k x_2^{(k-1)/2}$. [b] From gas–liquid chromatography with no phase correction.

et al. [24] are in contradiction with the trends mentioned above. Moreover, they seem to be too symmetrical when compared with data from Hamam et al. [25] (see also Fig. 4), and not flat enough to justify the high values of the partial excess enthalpies at infinite dilution of alcohol (26.2 and 25.1 kJ mol^{-1} for cyclopentanol or cyclohexanol + n-heptane systems at 298.15 and 303.15 K, respectively [25, 30]).

The experimental inaccuracies may be due to the fact that many of the measurements were carried out at temperatures close to the melting point of one component in the mixture (cyclohexanol, 298.3 K; cyclooctane, 287.45 K [30, 31]). This also may explain the unexpected decrease in the H^E maximum in the 1-alkanol + cycloalkane series for cyclooctane (Table 5, Fig. 6), because a flow calorimeter was used in the determination of H^E.

Table 7
Partial molar excess enthalpies of alkanol (1) + alkane(2) mixtures at infinite dilution $H_i^{E,\infty}$ and at various temperatures T. Comparison of experimental results (exp.) with values calculated (calc.) using the coefficients from Tables 2-4.

System	T/K	$H_1^{E,\infty}$/kJ mol^{-1}		$H_2^{E,\infty}$/kJ mol^{-1}		Source of data
		Exp.	Calc.	Exp.	Calc.	
c-C_5OH + n-C_7	298.15	26.2	17.7		2.51	[25]
c-C_6OH + n-C_7	303.15	25.1	19.1		2.86	[30]
EtOH + c-C_5	298.15	23.3	14.7	2.08	1.81	[31]
EtOH + c-C_7	298.15	24.2	15.0	3.29	2.51	[31]

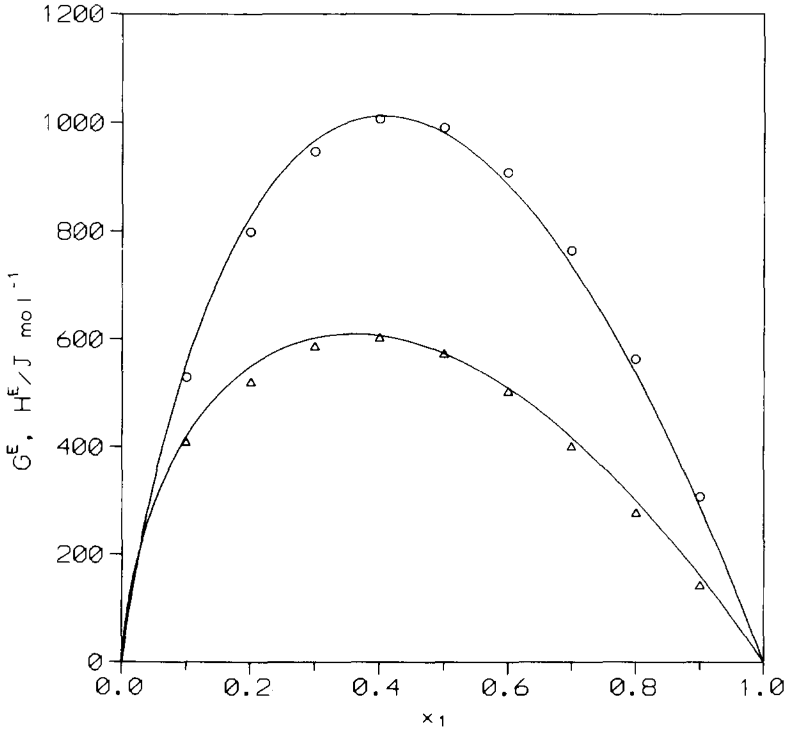

Fig. 1. Comparison of theory with experiment for the molar excess Gibbs energy G^E and excess enthalpy H^E at 298.15 K of cyclopentanol(1) + cyclopentane(2) mixture: full lines, predicted values; experimental results: ○, G^E; △, H^E [20].

As a matter of interest, it should be pointed out that the maximum of this excess function typically increases in the alcohol + alkane series with the size of the second compound. From this point of view, the significantly lower value of H^E for cyclopentane in the cycloalkanol + cycloalkane series, is noteworthy.

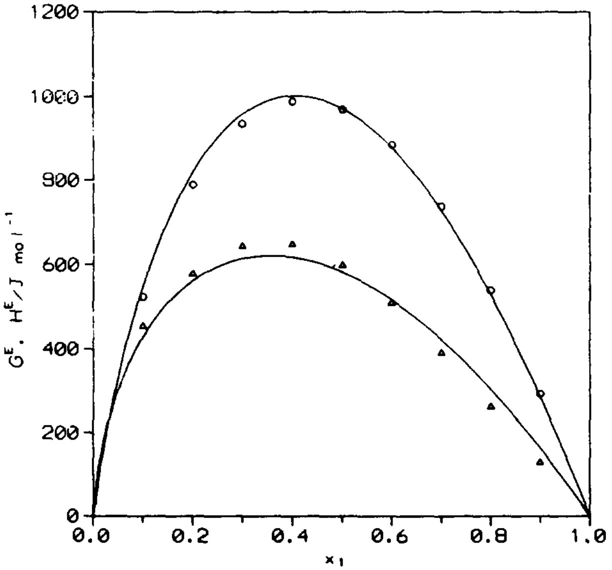

Fig. 2. Comparison of theory with experiment for the molar excess Gibbs energy G^E and excess enthalpy H^E at 298.15 K of cyclohexanol(1) + cyclohexane(2) mixture: full lines, predicted values; points experimental results: ○, G^E; Δ, H^E [20].

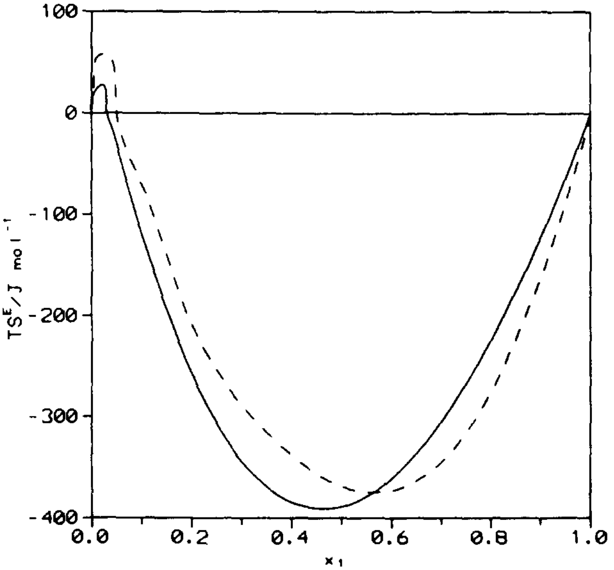

Fig. 3. Comparison of theory with experiment for TS^E (T, temperature; S^E, molar excess entropy) at 298.15 K of cyclohexanol(1) + cyclohexane(2) mixture: full line, predicted values; dashed line, experimental results [20].

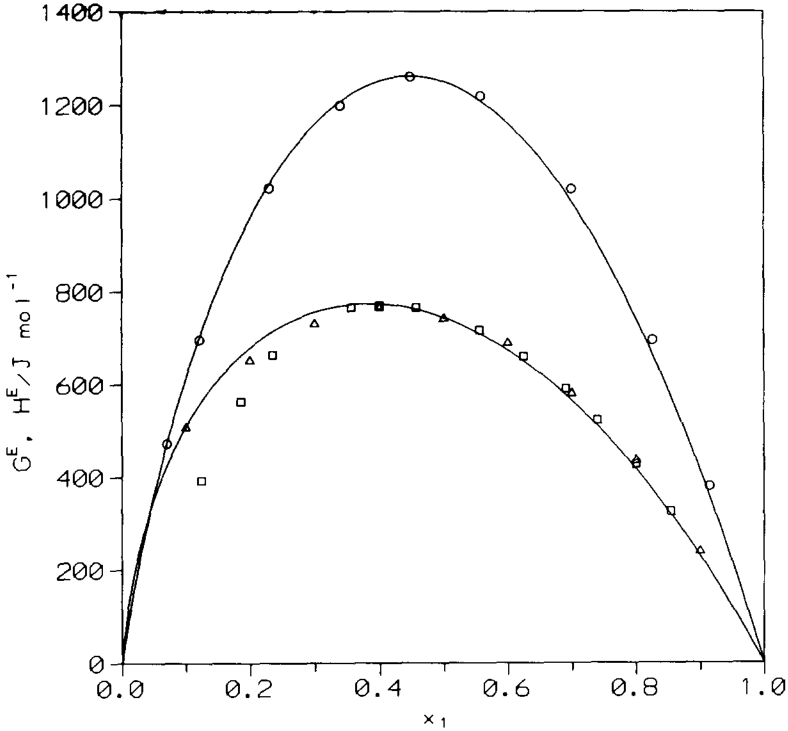

Fig. 4. Comparison of theory with experiment for the molar excess Gibbs energy G^E at 303.15 K of the cyclohexanol(1) + n-heptane(2) mixture and for excess enthalpy H^E at 298.15 K of the cyclopentanol(1) + n-heptane(2) mixture: full lines, predicted values; points experimental results: ○, G^E; [23]; Δ, [25]; □ [24], H^E.

The representation of partial molar excess quantities at infinite dilution is, as known, theoretically very difficult. For the mixtures investigated , the results (Tables 6 and 7) are similar to those encountered for other alcoholic solutions [5, 7–9], in particular the rather poor prediction of the partial molar excess enthalpies at infinite dilution which is the most important limitation of the model [8].

However, it is remarkable that the so-called rules obtained in estimating the interaction parameters are similar to those encountered previously for mixtures containing linear or cyclic amines, ethers or ketones [14–16]. Nevertheless, some differences were found.

In the case of cyclic alcohol + alkane mixtures, the increasing steric effect does not imply, as usual, a decrease in the quasichemical coefficients with the size of the alkanol (they are constant and independent of the compounds in the mixture, see Tables 2 and 3), but a decrease in the ratio between the quasichemical and dispersive contributions to H^E. This ratio increases for systems containing 1-alkanols, because their dispersive

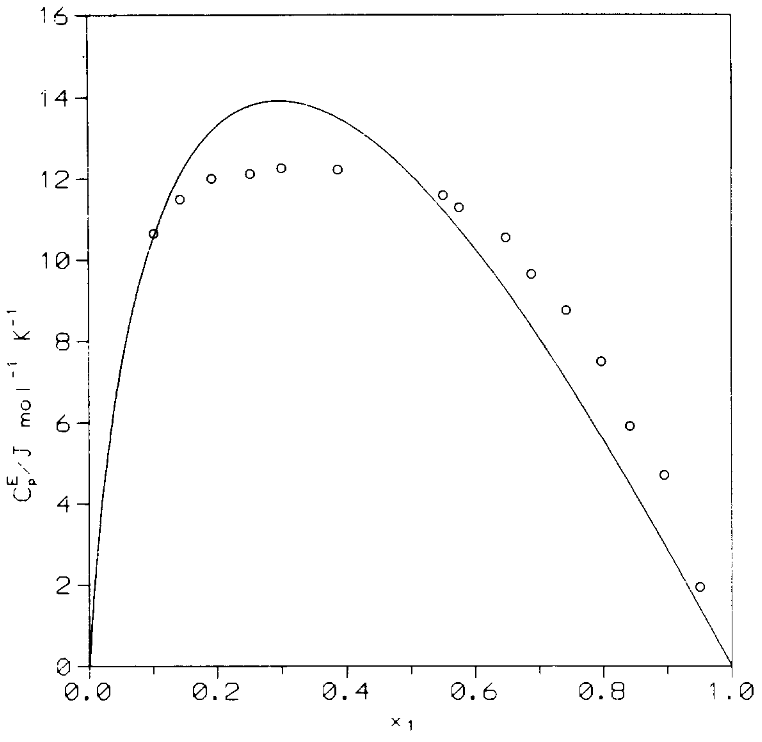

Fig. 5. Comparison of theory with experiment for the molar excess heat capacity C_p^E at 298.15 K of cyclopentanol(1) + *n*-heptane(2) mixture: full line, predicted values; points, experimental results [28].

enthalpic interaction parameters are much lower than for cycloalkanols. So, the ring strain seems to be more important than the steric effect for mixtures with cyclic alcohols. This may also be supported by the similar enthalpies of vaporization of 1-pentanol and cyclopentanol (56.94 and 57.70 kJ mol^{-1}, respectively, at 298.2 K [32]) and for 1-hexanol and cyclohexanol (61.63 and 62.01 kJ mol^{-1}, respectively, at 298.2 K [33]).

For systems containing only cyclic molecules, we observe a meaningful decrease in the $C_{\mathrm{ch},1}^{\mathrm{DIS}}$ coefficients for mixtures with cycloheptane or cyclooctane. In the case of the cyclopentanol + cycloheptane system, this may be related to the unexpected flattening of the $G^E(x_1)$ curve.

Finally, it is noteworthy that the interaction parameters for 1-alkanol + cyclohexane mixtures are valid for systems with other cycloalkanes, because previously these had been considered not to form a homologous series in terms of c-CH_2 groups [14]. The $C_{\mathrm{ch},2}^{\mathrm{DIS}}$ coefficient for the methanol + cyclopentane mixture may be due to the H^E data being measured close to the critical point.

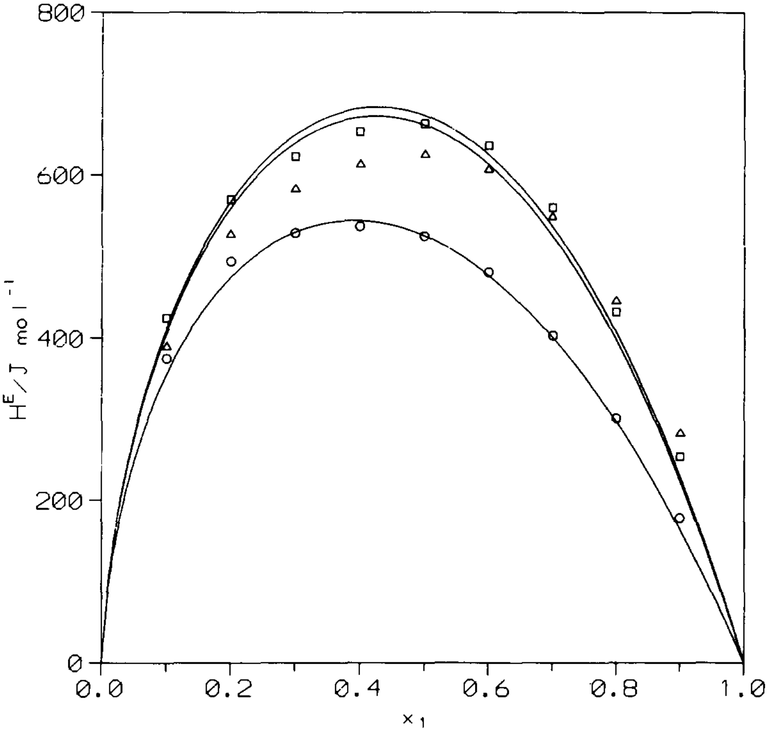

Fig. 6. Comparison of theory with experiment for the molar excess enthalpy H^E at 298.15 K of ethanol(1) + cycloalkane(2) mixtures: full lines, predicted values; points experimental results [26]: ○, cyclopentane; □, cycloheptane; Δ, cyclooctane.

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