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Application of DISQUAC to binary liquid organic mixtures containing 1-alkanols and CCl_4

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Abstract

The data available in the literature on vapour–liquid equilibria (VLE), molar excess Gibbs energies G^E, molar excess enthalpies H^E, activity coefficients γ_i^∞, and partial molar excess enthalpies $H_i^{E,\infty}$ at infinite dilution of 1-alkanol(1) + tetrachloromethane(2) mixtures are examined on the basis of the DISQUAC group contribution model.

The components of the mixtures are characterized by three types of surface groups: hydroxyl (OH group), alkane (CH_3 or CH_2 groups), and tetrachloromethane (CCl_4 group). The alkane/CCl_4 and alkane/hydroxyl interaction parameters are available in the literature. The parameters for the hydroxyl/CCl_4 interactions are reported in this work.

The model provides a good description of the VLE and of the related G^E data. For the H^E data, surprising larger discrepancies are encountered for systems containing 1-propanol or 1-butanol. The temperature dependence of the H^E values is fairly well represented. Predictions for the natural logarithms of the activity coefficients at infinite dilution and on $H_i^{E,\infty}$ are similar to those for other 1-alkanol(1) + organic solvent(2) mixtures.

INTRODUCTION

The theoretical treatment of alcoholic solutions is of interest when investigating the ability of any model to describe the non-ideal behaviour of such solutions.

For this reason, we are engaged in a systematic study of 1-alkanol(1) + organic solvent(2) mixtures using DISQUAC [1, 2], a group contribution method.

Up to now, we have investigated binary systems containing 1-alkanols and *n*-alkanes [3–5], benzene or toluene [3, 4, 6], cyclohexane [3, 7], or 1-alkanols [8]. In these works, each alcohol is considered separately in order to report a characteristic set of interaction parameters for each of them, which takes into account their different degrees of association.

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In our approach, a good representation of the phase equilibria, VLE [5-7], liquid-liquid, LLE [4, 7], or solid-liquid [7, 9], and of the excess functions G^E and H^E, or the excess heat capacity C_p^E, is obtained [5-8]. It is noteworthy that DISQUAC describes fairly well the temperature dependence of these excess functions [5-7], even that of the C_p^E [6].

The more important limitations of the model are related to prediction of (a) the shape of the calculated H^E and LLE curves which are not as flat as the experimental ones close to the critical point [4, 7], which seems to be a general trend of the model [2, 7]; and (b) the partial molar excess quantities at infinite dilution, particularly $H_i^{E,\infty}$ [5-7].

The study of binary mixtures involving 1-alkanols and tetrachloromethane is particularly interesting because, compared with those containing different non-polar solvents such as *n*-hexane or benzene, their heats of mixing are exothermic at high alcohol concentrations for the lower alcohols at lower temperatures. This indicates an interaction between the hydroxylic oxygen or hydrogen and the chlorine of the CCl_4. This behaviour is more pronounced with the lower 1-alkanols due to the greater number of such interactions in comparison with other long-chain alcohols. Moreover, it is also more pronounced at higher alcohol concentrations and at lower temperatures because of the relative absence of the opposing effect due to dissociation of the alcohol [10].

The purpose of this paper is to test the ability of DISQUAC to represent these general features of 1-alkanol + CCl_4 mixtures. To this end, we report the interaction parameters for the hydroxyl/CCl_4 interactions.

Previously, this type of system has been investigated by Dacre and Benson (1963) [11] in terms of the quasi-lattice theory developed by Barker [12].

ESTIMATION OF THE INTERACTION PARAMETERS

The molecules under study, i.e. 1-alkanols and tetrachloromethane, are regarded as possessing three types of surface: (1) type a (CH_3 or CH_2 groups in 1-alkanols); (2) type h (OH group in 1-alkanols); (3) type d (CCl_4 group in tetrachloromethane).

The equations used to calculate G^E and H^E are the same as in other cases [5]. The temperature dependence of the interaction parameters is expressed in terms of the dispersive (DIS) or quasi-chemical (QUAC) interchange coefficients $C_{st,l}^{DIS}$ and $C_{st,l}^{QUAC}$ where $s, t = \mathrm{a, d, h}$, and $l = 1$ (Gibbs energy), 2 (enthalpy), or 3 (heat capacity). For the QUAC part, the coordination number used is $z = 4$.

The geometrical parameters, relative volumes r_i, total surfaces q_i, and surface fractions α_{si} ($s = \mathrm{a, h}$), for the alkanols investigated in this work have been calculated on the basis of the group volumes and surfaces recommended by Bondi [13], arbitrarily taking the volume and surface of methane as unity. The relative molecular volume of an OH group

TABLE 1

Dispersive interchange coefficients $C^{DIS}_{ad,l}(n)$ ($l = 1$, Gibbs energy; $l = 2$, enthalpy) for the contact (a, d) (type a, aliphatic; type d, CCl_4); n is the number of heavy atoms, C and O, in the 1-alkanol [16, 17]

l		$C^{DIS}_{ad,l}$						
	n	≤5	6	8	10	12	14	16
1		0.093	0.096	0.097	0.105	0.114	0.123	0.130
2		0.180	0.181	0.190	0.200	0.212	0.227	0.245

is $r_{OH} = 0.46963$, and the relative area $q_{OH} = 0.50345$. For the $-CH_3$ group, these two values are 0.79848 and 0.73103, respectively; and for the $-CH_2-$ group, they are 0.59755 and 0.46552 [14]. For the tetrachloromethane molecule, the geometrical parameters are $r_i = 3.0543$, $q_i = 2.5104$, $\alpha_{ni} = 0$, and $\alpha_{di} = 1$ [15].

The general procedure used by us in the fitting of any set of interaction parameters has been described in detail previously [5, 8]; for the adjustment of the third interchange coefficients, see also, for example, refs. 6 and 7.

The three types of surface generate three pairs of contacts: (a, d), (a, h) and (d, h).

TABLE 2

Interchange coefficients, dispersive $C^{DIS}_{hd,l}$ and quasichemical $C^{QUAC}_{hd,l}$ ($l = 1$, Gibbs energy; $l = 2$, enthalpy, $l = 3$, heat capacity), for the contacts (h, d) (type h, OH in 1-alkanols; type d, CCl_4). The coordination number used for the QUAC part is $z = 4$; m is the number of carbon atoms in the 1-alkanol

m	$C^{DIS}_{hd,1}$	$C^{DIS}_{hd,2}$	$C^{DIS}_{hd,3}$	$C^{QUAC}_{hd,1}$	$C^{QUAC}_{hd,2}$	$C^{QUAC}_{hd,3}$
1	0.90	−0.33	−9.10	12.20	14.00	62.50
2	1.30	−1.45	−9.10	12.20	20.50	62.50
3	1.78	−1.55	−19.00	12.20	20.50	62.50
4	2.35	−1.40	−19.00	12.20	20.50	62.50
5	3.10[a]	−0.90[a]	−27.00[a]	12.20	20.50	62.50
6	4.10[a]	−0.40[a]	−27.00[a]	12.20	20.50	62.50
7	5.50[a]	0.15[a]	−35.00[a]	12.20	20.50	62.50
8	7.20	0.55	−35.00	12.20	20.50	62.50
10	12.05[a]	2.15	−42.00	12.20	20.50	62.50
12	18.40[a]	6.65[a]	−42.00[a]	12.20	20.50	62.50
14	26.20[a]	17.50[a]	−42.00[a]	12.20	20.50	62.50
16	35.20[a]	39.50[a]	−42.00[a]	12.20	20.50	62.50

[a] Estimated value.

TABLE 3

Comparison of some experimental (exp.) coordinates of azeotropes: pressure (P_{az}), temperature (T_{az}) and mole fraction (x_{1az}) for 1-alkanol(1) + tetrachloromethane(2) mixtures with values calculated (calc.) using the coefficients from Tables 1 and 2 (present work) and from Tables 1 and 3 [5, 6]; *m* is the number of carbon atoms in the 1-alkanol

m	T_{az}/K	P_{az}/kPa		x_{1az}		Source of data
		Exp.	Calc.	Exp.	Calc.	
1	298.15	27.212	27.138	0.4894	0.5019	Yasuda et al., 1975 [29]
	303.15	34.680	34.367	0.502	0.4900	Góral et al., 1990 [30]
	328.15	171.95	171.30	0.5844	0.5907	Wolff and Hoeppel, 1968 [31]
2	318.15	46.809	46.442	0.324	0.327	Barker et al., 1953 [32]
	338.15	101.39	100.12	0.393	0.400	Barker et al., 1953 [32]
3	308.15	24.916	25.267	0.0919	0.0969	Paraskevopoulos and Missen, 1962 [33]
	343.15	89.529	89.476	0.1600	0.1547	Papousek et al., 1959 [34]
4	308.15	23.278	23.426	0.0118	0.0181	Paraskevopoulos and Missen, 1962 [33]

(i) The non-polar alkane/CCl_4 (a, d) interactions are represented by dispersive parameters (Table 1). A careful examination [16] has shown that the $C_{ad,l}^{DIS}$ parameters increase with increasing chain length of the *n*-alkane. This increase is attributed to conformational changes, or changes in molecular order, when *n*-alkanes are mixed with the globular molecule, such as tetrachloromethane (the Patterson effect [18]).

Due to the size of the OH group, we have taken the *n*-alkane with one CH_2 more as the homomorph to the 1-alkanol under consideration.

(ii) The polar alkane/alkanol (a, h) interactions are represented by DIS and QUAC parameters reported previously [5, 6]. We have shown that both depend on the alcohol. So, $C_{ah,1}^{DIS}$ increases regularly with the length of the 1-alkanol; the reverse behaviour is encountered for $C_{ah,3}^{DIS}$, which is constant from 1-dodecanol; $C_{ah,2}^{DIS}$ decreases as far as propanol, and then increases regularly. However, $C_{ah,1}^{QUAC}$ and $C_{ah,3}^{QUAC}$ are constant, and $C_{ah,2}^{QUAC}$ varies in a similar way to the maximum of the H^E for 1-alkanol + *n*-alkane mixtures, being constant from 1-decanol. When SLE data are considered, it is shown that $C_{ah,1}^{DIS}$ and $C_{ah,2}^{DIS}$ are constant from 1-octadecanol [9].

As a matter of interest, we must point out that the QUAC coefficients are equal to those for the OH/C_6H_{12} contacts, a behaviour which seems to be rather general because it is also encountered in mixtures of ethers [19], ketones, [20], organic carbonates [21] or chloroalkanes [15], with *n*-alkanes or cyclohexane.

(iii) The polar alkanol/CCl_4 (h, d) interactions are represented by parameters which are considered, as usual, to be chain-length dependent, in

TABLE 4

Molar excess Gibbs energies $G^E(T; x_1 = 0.5)$ for 1-alkanol(1) + tetrachloromethane(2) mixtures at various temperatures (T/K) and equimolar composition. Comparison of experimental results (exp.) with values calculated (calc.) using the coefficients from Tables 1 and 2 (present work) and from Tables 1 and 3 [5, 6]; m is the number of carbon atoms in the 1-alkanol

m	T/K	G^E/J mol^{-1}		Source of data
		Exp.	Calc.	
1	293.15	1297	1292	Góral et al., 1988 [35]
		1323		Wolff and Hoeppel, 1968 [31]
	298.15	1315 [a]	1311	Matteoli and Lepori, 1986 [36]
		1296		Yasuda et al., 1975 [29]
	303.15	1338	1330	Góral et al., 1990 [30]
	308.15	1361	1347	Scatchard and Ticknor, 1952 [37]
		1255		Moelwyn-Hughes and Missen, 1957 [38]
	323.15	1415	1393	Wolff and Hoeppel, 1968 [31]
	328.15	1427	1406	Scatchard and Ticknor, 1952 [37]
	343.15	1463	1432	Wolff and Hoeppel, 1968 [31]
2	298.15	1137 [a]	1138	Matteoli and Lepori, 1986 [36]
	318.15	1172	1187	Barker et al., 1953 [32]
	338.15	1204	1199	Barker et al., 1953 [32]
3	293.15	1028	948	Markuzin and Sokolova, 1966 [39]
	298.15	960 [a]	959	Matteoli and Lepori, 1986 [36]
	308.15	934	979	Paraskevopoulos and Missen, 1962 [33]
	343.15	1034	1004	Papousek et al., 1959 [34]
4	298.15	896 [a]	888	Matteoli and Lepori, 1986 [36]
	308.15	946	905	Paraskevopoulos and Missen, 1962 [33]
8	293.15	604	559	Platford, 1977 [40]
	333.15	547 [a]	559	Paraskevopoulos and Missen, 1962 [33]

[a] System used in the estimation of the interchange coefficients.

order to take into account the different degrees of association of each alcohol.

For mixtures of a polar molecule (characteristic group: X) and benzene or tetrachloromethane (characteristic group: s), this dependence is, of course, a function of the nature of the polar group X. If X is Cl [22, 23], Br [17], I [24], F [25] or the carbonate group [26, 27], the $C^{\mathrm{DIS}}_{\mathrm{Xs},l}$ coefficients change with the length of the polar molecule, and the $C^{\mathrm{QUAC}}_{\mathrm{Xs},l}$ coefficients are taken as being equal to zero. If X is the alkanol group, the DIS and QUAC parameters present, respectively, inductive and steric effects [28]. However, for the hydroxyl/aromatic contacts, only the inductive effect is encountered, while there is no steric effect for the QUAC parameters, these now being different to zero [6].

TABLE 5

Molar excess enthalpies $H^E(T;\ x_1 = 0.3)$ for 1-alkanol(1) + tetrachloromethane(2) mixtures at various temperatures (T/K) and $x_1 = 0.3$. Comparison of experimental results (exp.) with values calculated (calc.) using the coefficients from Tables 1 and 2 (present work) and from Tables 1 and 3 [5, 6]; m is the number of carbon atoms in the 1-alkanol

m	T/K	H^E/J mol^{-1}		Source of data
		Exp.	Calc.	
1	273.15	100	115	Otterstedt and Missen, 1962 [10]
	293.15	266	252	Otterstedt and Missen, 1962 [10]
	298.15	290 [a]	302	Nagata and Tamura, 1983 [41]
		310		Dacre and Benson, 1963 [11]
	308.15	433	427	Otterstedt and Missen, 1962 [10]
	323.15	668	684	Otterstedt and Missen, 1962 [10]
2	288.15	255	215	Luo et al., 1985 [42]
	298.15	381 [a]	375	Luo et al., 1985 [42]
		394		Nagata and Tamura, 1984 [43]
		412		Tai et al., 1972 [44]
	308.15	558	584	Luo et al., 1985 [42]
		539		Otterstedt and Missen, 1962 [10]
3	273.15	171	254	Otterstedt and Missen, 1962 [10]
	293.15	429	386	Otterstedt and Missen, 1962 [10]
	298.15	475 [a]	440	Nagata and Tamura, 1986 [45]
	308.15	641	582	Otterstedt and Missen, 1962 [10]
	323.15	884	889	Otterstedt and Missen, 1962 [10]
4	288.15	271	351	Luo et al., 1985 [42]
	298.15	463 [a]	450	Luo et al., 1985 [42]
		503		Dacre and Benson, 1963 [11]
	308.15	663	588	Luo et al., 1985 [42]
		632		Otterstedt and Missen, 1962 [10]
8	273.15	364	423	Otterstedt and Missen, 1962 [10]
	293.15	498	486	Otterstedt and Missen, 1962 [10]
	298.15	530 [a]	520	Dacre and Benson, 1963 [11]
	308.15	631	615	Otterstedt and Missen, 1962 [10]
	323.15	836	834	Otterstedt and Missen, 1962 [10]
10	288.15	459	477	Kardo-Sysoeva et al., 1977 [46]
	303.15	587 [a]	571	Kardo-Sysoeva et al., 1977 [46]
	318.15	727	746	Kardo-Sysoeva et al., 1977 [46]

[a] System used in the estimation of the interchange coefficients.

In view of the differences observed in the evolution of the interchange coefficients for this class of (X, s) contacts, we decided to describe the (h, d) contacts by DIS and QUAC parameters, but while trying to keep the latter constant for the whole set of 1-alkanols. That is, we proceeded as

TABLE 6

Natural logarithms of activity coefficients at infinite dilution $\ln \gamma_i^\infty$ in 1-alkanol(1) + tetrachloromethane(2) mixtures at various temperatures (T). Comparison of experimental results (exp.) with values calculated (calc.) using the coefficients from Tables 1 and 2 (present work) and from Tables 1 and 3 [5, 6]; m is the number of carbon atoms in the 1-alkanol

m	T/K	$\ln \gamma_1^\infty$		$\ln \gamma_2^\infty$		Source of data
		Exp.	Calc.	Exp.	Calc.	
1	293.15	4.27 [a]	4.51	2.13	2.15	Wolff and Hoeppel, 1968 [31]
	298.15	3.87 [a]	4.41	2.07	2.15	Matteoli and Lepori, 1986 [36]
		3.59 [a]		2.04		Yasuda et al., 1975 [29]
	303.15	3.96 [a]	4.30	2.13	2.15	Wolff and Hoeppel, 1968 [31]
	308.15	4.47 [b]	4.19	1.98 [c]	2.15	Paraskevopoulos and Missen, 1962 [33]
	323.15	3.47 [a]	3.84	2.10	2.15	Wolff and Hoeppel, 1968 [31]
	328.15	2.54 [a]	3.71	1.94	2.14	Scatchard and Ticknor, 1952 [37]
2	298.15	3.55 [a]	4.23	1.59	1.64	Matteoli and Lepori, 1986 [36]
	318.15	3.02 [a]	3.61	1.55	1.63	Barker et al., 1953 [32]
3	298.15	3.18 [a]	4.01	1.22	1.25	Matteoli and Lepori, 1986 [36]
	308.15	4.87 [b]	3.70	1.11 [c]	1.25	Paraskevopoulos and Missen, 1962 [33]
	314.9	2.77 [d]	3.49	–	1.24	Trampe and Eckert, 1990 [47]
	329.0	2.48 [d]	3.05	–	1.22	Trampe and Eckert, 1990 [47]
	332.8	–	2.93	1.16 [d]	1.22	Trampe and Eckert, 1990 [47]
	338.8	2.28 [d]	2.75	–	1.20	Trampe and Eckert, 1990 [47]
	343.1	–	2.61	1.14 [d]	1.19	Trampe and Eckert, 1990 [47]
	344.2	2.17 [d]	2.58	–	1.19	Trampe and Eckert, 1990 [47]
	352.9	–	1.84	1.13 [d]	1.18	Trampe and Eckert, 1990 [47]
	369.6	–	4.33	1.11 [d]	1.08	Trampe and Eckert, 1990 [47]
4	293.15	–	4.08	0.98 [e]	1.11	Thomas et al., 1982 [48]
	298.15	2.78 [a]	3.92	1.13	1.11	Matteoli and Lepori, 1986 [36]
	308.15	3.22 [b]	3.62	1.09 [c]	1.10	Paraskevopoulos and Missen, 1962 [33]
	359.6	–	2.05	0.95 [d]	0.98	Trampe and Eckert, 1990 [47]
8	293.15	–	3.58	0.55 [e]	0.60	Thomas et al., 1982 [48]
	333.15	3.84 [b]	2.35	0.76 [c]	0.54	Paraskevopoulos and Missen, 1962 [33]
12	308.15	–	3.01	0.39 [f]	0.40	Alessi et al., 1982 [49]
	326.15	–	2.38	0.34 [f]	0.34	Alessi et al., 1982 [49]
	333.15	–	2.14	0.28 [f]	0.32	Alessi et al., 1982 [49]
14	317.95	–	2.35	0.15 [f]	0.20	Alessi et al., 1982 [49]
	329.15	–	1.81	0.14 [f]	0.11	Alessi et al., 1982 [49]
	348.95	–	0.92	0 [f]	–0.03	Alessi et al., 1982 [49]

[a] From reduction data using the Wilson equation. [b] From an exponential equation for G^E in the region of high dilution in alcohol. [c] From a Redlich–Kister equation for G^E in the region of high dilution in CCl_4. [d] From a differential boiling-point technique. [e] From gas–liquid chromatography. [f] From gas–liquid chromatography using the retention time method.

TABLE 7

Partial molar excess enthalpies of 1-alkanol(1) + tetrachloromethane(2) mixtures at infinite dilution $H_i^{E,\infty}$, and at various temperatures T. Comparison of experimental results (exp.) with values calculated using the coefficients from Tables 1 and 2 (present work) and from Tables 1 and 3 [5, 6]; m is the number of carbon atoms in the 1-alkanol

m	T/K	$H_1^{E,\infty}$/J mol^{-1}		$H_2^{E,\infty}$/J mol^{-1}		Source of data
		Exp.	Calc.	Exp.	Calc.	
1	273.15	20920	9940	−1171	−421	Otterstedt and Missen, 1962 [10]
	293.15	16736	14539	−795	−348	Otterstedt and Missen, 1962 [10]
	298.15	–	15675	−636	−265	Trampe and Eckert, 1991 [50]
	308.15	23012	17921	−318	−1	Otterstedt and Missen, 1962 [10]
	323.15	18828	21210	318	685	Otterstedt and Missen, 1962 [10]
2	283.15	18200	19215	–	−904	Stokes and Burfitt, 1973 [51]
	298.15	18400	22570	−820	−339	Stokes and Burfitt, 1973 [51]
	308.15	18828	24732	841	246	Otterstedt and Missen, 1962 [10]
	318.15	18300	26813	–	1045	Stokes and Burfitt, 1973 [51]
3	273.15	18828	17725	−1448	308	Otterstedt and Missen, 1962 [10]
	293.15	25104	21743	−586	302	Otterstedt and Missen, 1962 [10]
	298.15	17200	22700	–	364	Trampe and Ekert, 1991 [50]
	308.15	20920	24538	−113	583	Otterstedt and Missen, 1962 [10]
	323.15	18828	27057	510	1205	Otterstedt and Missen, 1962 [10]
4	308.15	16736	24477	4	792	Otterstedt and Missen, 1962 [10]
8	273.15	16736	18683	377	997	Otterstedt and Missen, 1962 [10]
	293.15	25104	22167	669	950	Otterstedt and Missen, 1962 [10]
	308.15	16736	24511	966	1104	Otterstedt and Missen, 1962 [10]
	323.15	20920	26516	1205	1480	Otterstedt and Missen, 1962 [10]

for the 1-alkanol + benzene mixtures. The final parameters are listed in Table 2.

Naturally, they behave very similarly to those of the hydroxyl/aromatic contacts. We note the inductive effect in the DIS parameters, and that the $C_{\mathrm{hd},2}^{\mathrm{QUAC}}$ value of methanol is different from the normal value of this parameter for the other alcohols. This exemplifies the difference between methanol and the remaining alcohols in the mixtures under study, a behaviour which has been already pointed out by Dacre and Benson [11] in their study of these systems using Barker's theory [12].

RESULTS AND DISCUSSION

Tables 3–7 and Figs. 1–5 show numerical and graphical comparisons, respectively, between experimental data and DISQUAC predictions. As usual,

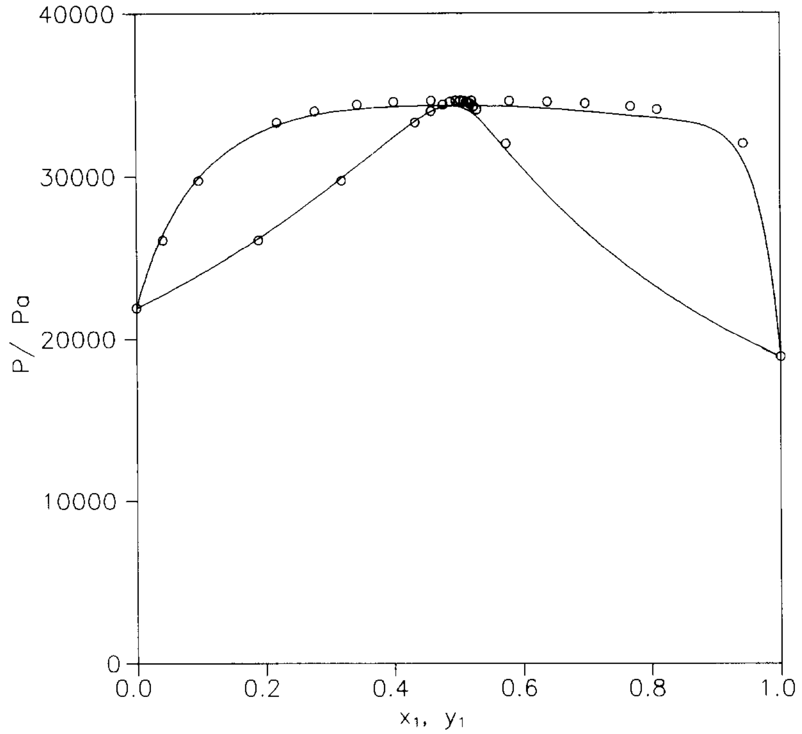

Fig. 1. Comparison of theory with experiment of the isothermal vapour–liquid phase equilibrium diagram of CCl_4 + methanol at 303.15 K: total pressure P vs. x_1 or y_1 (the mole fractions of CCl_4 in the liquid and vapour phases, respectively). Full lines, predicted values; points, experimental results [30].

the model yields a good description of the concentration dependence of the VLE data (see Table 3 and Fig. 1), and of the related G^E values (Table 4, Fig. 2).

The experimental curves of H^E against the mole fraction are very asymmetrical. For the lower alcohols, they present a positive part which is, moreover, rather flat, and an exothermic region at high alcohol concentrations (see the introductory section). This complex behaviour is fairly well represented by DISQUAC for those systems containing methanol or ethanol (Fig. 3). However, with the standard coordination number used ($z = 4$) and our interchange coefficients, the model cannot reproduce the exothermic part of the H^E curve for 1-propanol or 1-butanol + CCl_4 mixtures. Certainly, it is possible to obtain s-shaped H^E curves for these systems, although in this case they become very shifted to the region of low concentration in alcohol, and a worse overall representation is then obtained. For mixtures involving higher 1-alkanols, such as 1-octanol or 1-decanol, the shape of the H^E curves is again fairly well represented by DISQUAC (Fig. 4). Thus, new measurements for H^E for systems containing

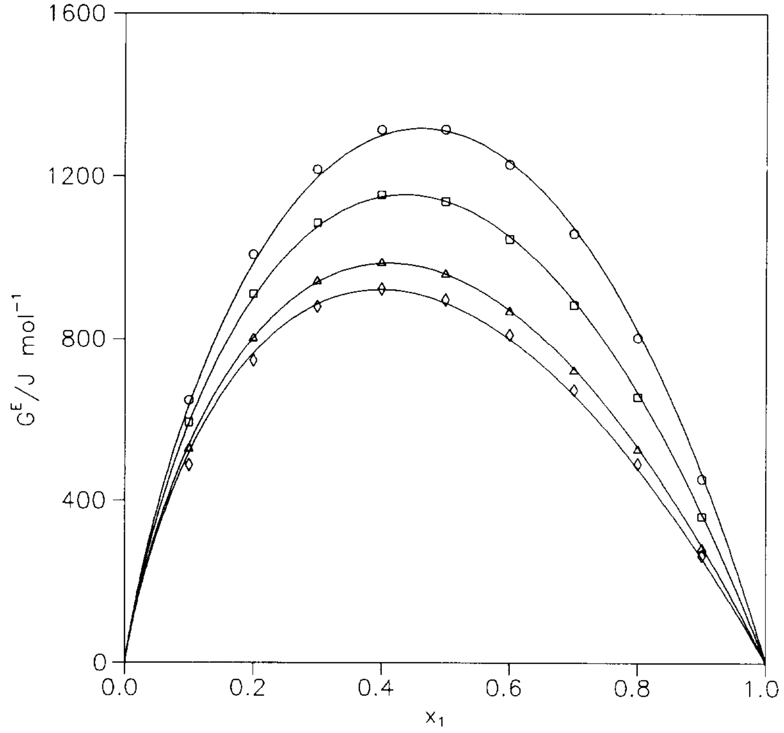

Fig. 2. Comparison of theory with experiment for the molar excess Gibbs energy G^E at 298.15 K of 1-alkanol + CCl_4 mixtures. Full lines, predicted values; points, experimental results: ○, methanol; □, ethanol; △, 1-propanol; ◇, 1-butanol [36].

1-propanol and 1-butanol are needed to test the ability of the model to represent H^E curves for such mixtures.

The more severe tests of any theoretical model are related to its ability to reproduce the temperature dependence of H^E, C_p^E and partial molar excess quantities at infinite dilution.

For the mixtures under study, the model describes fairly well the change with temperature of the excess enthalpy (Table 5, Fig. 5). When the temperature is decreased, larger discrepancies are found because the asymmetry of the H^E curves is then more marked.

Unfortunately, we have not found direct calorimetric data on C_p^E. Otterstedt and Missen [10] report values for this quantity obtained from an equation used to correlate H^E values at different temperatures. As an example, for the methanol + CCl_4 mixture we compare "experimental" with calculated values at equimolar composition and at 273.15, 293.15, 308.15 and 323.15 K. Under these conditions, the values given by Otterstedt and Missen are (in J mol^{-1} K^{-1}) 7.9, 8.8, 11.7 and 16.7; while the DISQUAC values are, respectively, 2.9, 7.7, 12.7 and 19.2, in the same units.

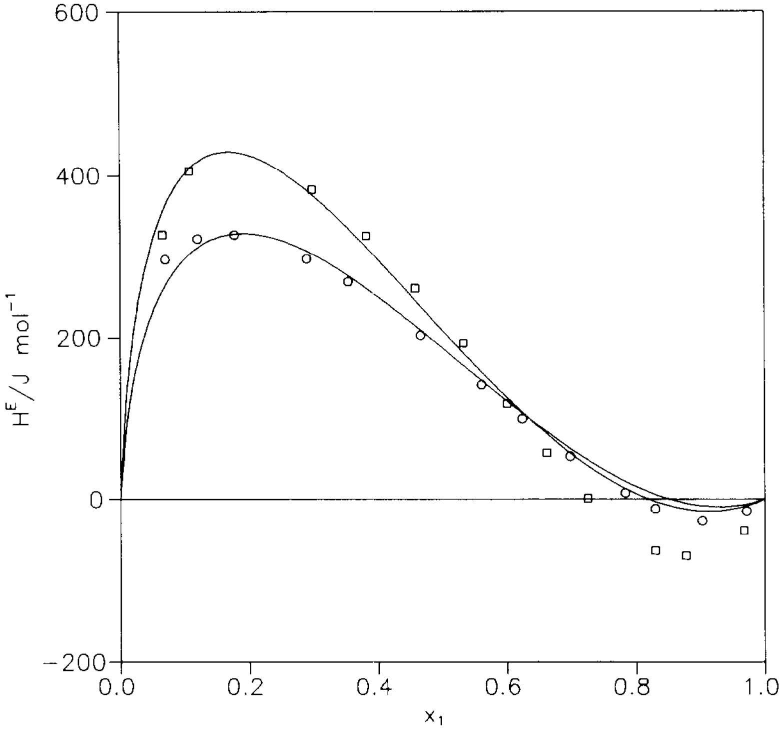

Fig. 3. Comparison of theory with experiment for the molar excess enthalpy H^E at 298.15 K of 1-alkanol + CCl_4 mixtures. Full lines, predicted values; points, experimental results: ○, methanol [41]; □, ethanol [42].

Table 6 shows a comparison between experimental and theoretical values of $\ln \gamma_i^\infty$. We note that $\ln \gamma_2^\infty$ is well reproduced and that the differences $\Delta \ln \gamma_1^\infty$ ($\ln \gamma_1^\infty$(calc) $- \ln \gamma_1^\infty$(exp)) are positive and somewhat large. Such differences are similar to those encountered in 1-alkanol(1) + cyclohexane(2) systems [7] (mean value of $\Delta \ln \gamma_1^\infty$, 22%); and larger than when benzene or toluene is the second compound [6] (mean value of $\Delta \ln \gamma_1^\infty$, 15%). These results are related, at least in part, to the predictions given by the model for 1-alkanol(1) + *n*-alkane(2) mixtures [5], which present a mean value of $\Delta \ln \gamma_1^\infty$ close to 10%, due, to some extent, to the combinatorial term used (Flory–Huggins equation), which, as known, overestimates the combinatorial entropy. In the case of systems containing cyclohexane, $\Delta \ln \gamma_1^\infty$ is increased because the calculated G^E curves are shifted to the region of low concentration in alcohol [7]. However, Fig. 2 shows that the symmetry of these curves for the mixtures under study is well represented by DISQUAC; thus, one would expect lower values of $\Delta \ln \gamma_1^\infty$. The large values obtained for this quantity in the investigated mixtures could be related to: (a) a quasi-chemical contribution of the 1-alkanol which is really less than anticipated (probably a general trend in alcoholic solu-

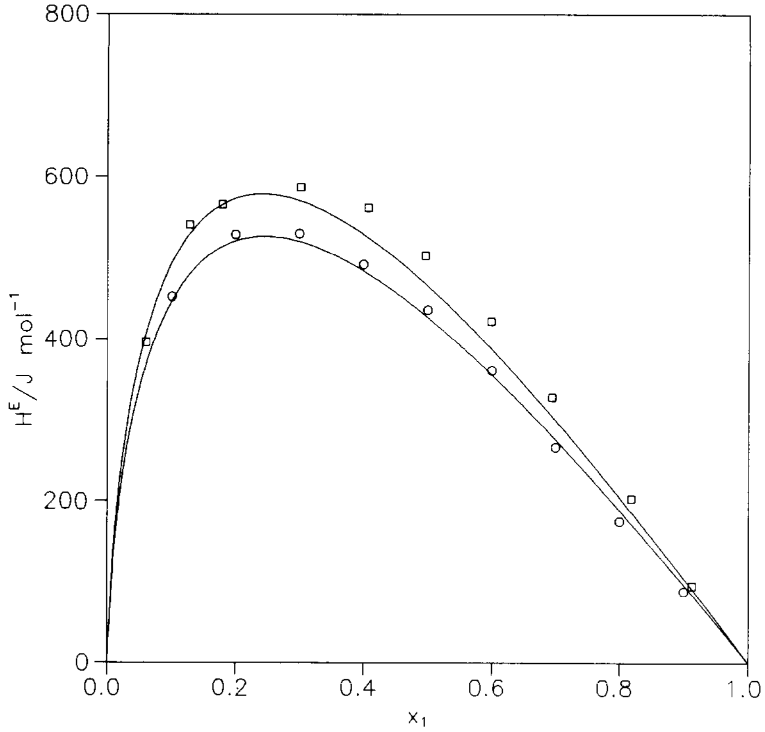

Fig. 4. Comparison of theory with experiment for the molar excess enthalpy H^E at temperature T of 1-alkanol + CCl_4 mixtures. Full lines, predicted values; points, experimental results: ○, 1-octanol (298.15 K) [11]; □, 1-decanol (303.15 K) [46].

tions); and (b) to some experimental inaccuracies [33]. We note that the partial molar excess quantities of mixtures containing 1-alkanols and organic solvents typically increase very steeply with increasing mole fraction of the organic solvent, and their experimental determination becomes rather difficult.

For this reason, the $H_1^{E,\infty}$ values from Otterstedt and Missen [10] (Table 7) should be taken with caution, because they are obtained from only a few H^E data in the dilute alcohol region. Data derived by Stokes and Burfitt [51] were obtained from a high enough number of H^E measurements at very high dilution of one component, and show, as with other 1-alkanol(1) + organic solvent(2) mixtures, the constancy of $H_1^{E,\infty}$ with temperature. In contrast, $H_2^{E,\infty}$ depends strongly on temperature, at least for systems involving the lower alcohols. This indicates that when increasing the temperature, H^E becomes positive over the whole range of mole fraction. DISQUAC predictions are similar to those for 1-alkanol(1) + n-alkane(2), or + cyclohexane(2) mixtures [5, 7], but show, as in the latter case, an unexpected strong dependence of $H_1^{E,\infty}$ on temperature.

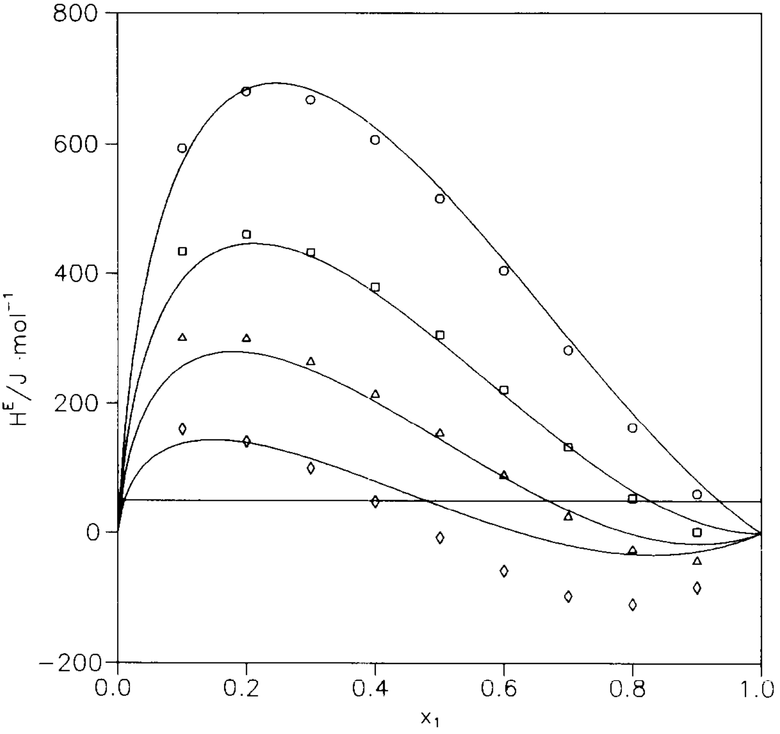

Fig. 5. Comparison of theory with experiment for the molar excess enthalpy H^E at temperature T of methanol + CCl_4 mixtures. Full lines, predicted values; points, experimental results: ◇, 273.15 K; △, 293.15 K; □, 308.15 K; ○, 323.15 K [10].

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