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THERMODYNAMICS OF METHANOL + HEPTANONE SOLUTIONS

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ABSTRACT

The excess Gibbs energy of methanol + heptanone systems at 298.15 and 323.15 K have been calculated previously from experimental VLE data. The capability of several theoretical models for predicting VLE data as well as the activity coefficients, has been checked. The simplest models considered are those that assume a random distribution of unlike interactions. The Margules, Van Laar and Scatchard models are tested. Introducing some non-randomness into the distribution of interactions, we have models like those of Wilson, NRTL ($\alpha = 0.3$), NRTL (α free), UNIQUAC and Heil. The Wilson model, which is the simplest of those examined, gives the best results, indicating that there are important factors which have not been considered in all these models.

Models based on group contributions (ASOG, UNIFAC and Barker) have also been checked; these yielded poor results. The models which consider some chemical association of one or both components give better predictions. Nevertheless, there are still some contributions to the excess Gibbs energy which remain unexplained in this kind of mixture.

INTRODUCTION

The excess Gibbs energy, G^E, of systems containing methanol + heptanone, have been reported previously [1,2]. These systems show interesting thermodynamical behavior. Since they are formed from polar molecules, some molecular interactions may occur preferentially in these systems. On the other hand, the alcohol may form relatively strong hydrogen bonds which may explain some chemical association of, at least, one component. This paper is concerned with the capability of the available theoretical models to predict the vapor–liquid equilibrium (VLE) data for these systems. Several models have been checked in order to predict the experimental G^E data obtained in our laboratory. Chemical models which assume a random and non-random distribution of interactions between unlike molecules have been discussed and compared with the results of models which assume group contributions or chemical associations.

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TABLE 1

Model parameters and standard deviations of the variables for several random and non-random rigid-lattice molecular models

$\sigma(T) < 10^{-3}$ K in all cases studied here

Model	System					
	2-H	3-H	4-H	2-H	3-H	4-H
	298.15 K			323.15 K		
Margules						
A	0.5016 ± 0.0019	0.5418 ± 0.0007	0.4517 ± 0.0082	0.4501 ± 0.0015	0.4742 ± 0.0048	0.4508 ± 0.0022
B	0.5920 ± 0.0015	0.6475 ± 0.0005	0.6732 ± 0.0024	0.4990 ± 0.0010	0.5823 ± 0.0029	0.6217 ± 0.0007
D	0.0923 ± 0.0054	0.1845 ± 0.0017	0.1791 ± 0.0071	0.0461 ± 0.0040	0.1471 ± 0.114	0.1259 ± 0.0033
$\sigma(p)$ (Pa)	11	4	12	18	59	10
$\sigma(x) \times 10^5$	2	1	1	10	31	3
Van Laar						
A	0.4968 ± 0.0009	0.5295 ± 0.0025	0.4156 ± 0.0031	0.4480 ± 0.0013	0.4625 ± 0.0019	0.4266 ± 0.0012
B	0.5964 ± 0.0009	0.6577 ± 0.0027	0.6764 ± 0.0024	0.4999 ± 0.0010	0.5920 ± 0.0018	0.6236 ± 0.0008
D	0.0697 ± 0.0026	0.1429 ± 0.0071	0.0172 ± 0.0062	0.0370 ± 0.0037	0.1046 ± 0.0049	0.0240 ± 0.0024
$\sigma(p)$ (Pa)	7	17	10	15	27	10
$\sigma(x) \times 10^5$	1	4	1	10	13	3
Scatchard						
A	0.4533 ± 0.0059	0.4722 ± 0.0082	0.3906 ± 0.0029	0.4056 ± 0.0061	0.4151 ± 0.0054	0.3310 ± 0.0033
B	0.8207 ± 0.0392	0.9219 ± 0.0543	0.7090 ± 0.0110	0.6894 ± 0.0408	0.8054 ± 0.0330	0.6708 ± 0.0122
D	0.4055 ± 0.0309	0.4396 ± 0.0426	0.1482 ± 0.0099	0.3627 ± 0.0316	0.3603 ± 0.0263	0.1831 ± 0.0109
$\sigma(p)$ (Pa)	83	111	23	185	160	79
$\sigma(x) \times 10^5$	19	29	3	111	101	35
Wilson						
$\lambda_{21} - \lambda_{11}$ [a]	4385 ± 6	4372 ± 25	3751 ± 24	4704 ± 11	4394 ± 17	4261 ± 26
$\lambda_{12} - \lambda_{22}$ [a]	-664 ± 17	-401 ± 28	357 ± 31	-1289 ± 10	-609 ± 17	-161 ± 23
$\sigma(p)$ (Pa)	8	35	31	27	69	60
$\sigma(x) \times 10^5$	2	10	4	15	31	21

NRTL						
$\alpha = 0.3$						
$g_{21} - g_{11}$ [a]	2098 ± 223	920 ± 43	459 ± 49	1263 ± 73	881 ± 36	816 ± 59
$g_{12} - g_{22}$ [a]	1360 ± 271	2670 ± 50	3232 ± 46	1892 ± 73	2591 ± 31	2932 ± 54
$\sigma(p)$ (Pa)	262	80	111	120	240	298
$\sigma(x) \times 10^4$	5	2	1	6	8	11
NRTL						
α	-0.7217 ± 0.0088	-0.4755 ± 0.0329	-0.8505 ± 0.0059	-0.6038 ± 0.0095	-1.1104 ± 0.0127	-0.9201 ± 0.0083
$g_{21} - g_{11}$ [a]	1544 ± 4	1876 ± 29	1803 ± 3	1478 ± 4	1465 ± 6	1719 ± 4
$g_{12} - g_{22}$ [a]	961 ± 3	838 ± 30	537 ± 7	1024 ± 3	952 ± 6	805 ± 4
$\sigma(p)$ (Pa)	12	74	12	17	41	35
$\sigma(x) \times 10^4$	0	2	0	1	2	1
UNIQUAC						
$u_{21} - u_{11}$ [a]	2297 ± 80	2811 ± 55	1360 ± 119	2840 ± 64	2468 ± 94	2207 ± 57
$u_{12} - u_{22}$ [a]	5 ± 63	-234 ± 25	605 ± 75	-358 ± 39	-79 ± 50	110 ± 41
$\sigma(p)$ (Pa)	435	213	431	646	735	708
$\sigma(x) \times 10^4$	9	6	8	39	48	33
HEIL						
τ_{21}	0.9600 ± 0.0164	0.9145 ± 0.0266	0.7256 ± 0.0125	0.9568 ± 0.0182	0.8317 ± 0.0261	0.7440 ± 0.0194
τ_{21}	-0.4097 ± 0.0188	-0.3071 ± 0.0327	-0.0517 ± 0.0158	-0.4975 ± 0.0190	-0.2890 ± 0.0352	-0.1228 ± 0.0290
$\sigma(p)$ (Pa)	90	151	61	206	357	243
$\sigma(x) \times 10^4$	2	3	1	10	17	9
UNIQUAC-MOD						
$u_{21} - u_{11}$ [a]	2532 ± 51	2663 ± 61	2899 ± 84	2271 ± 42	2266 ± 30	3663 ± 54
$u_{12} - u_{22}$ [a]	5619 ± 91	6168 ± 120	6548 ± 224	5185 ± 95	6241 ± 44	5664 ± 85
$\sigma(p)$ (Pa)	180	182	187	318	356	580
$\sigma(x) \times 10^4$	4	4	2	14	17	19

[a] J mole^{-1}.

RESULTS AND DISCUSSION

The regression procedure

The experimental values of the total vapor pressure as a function of composition of binary systems containing methanol + 2-heptanone (2-H), methanol + 3-heptanone (3-H) and methanol + 4-heptanone (4-H) have been reported at 298.15 K [1] and 323.15 K [2]. This experimental information has been used to determine the values of the adjustable parameters of several empirical models listed in Table 1. The regression method used in all cases, is based on the maximum likelihood principle. It has been described by Prausnitz et al. [3] when it is applied to the UNIQUAC model. This regression method provides the uncertainty of the parameters and the standard deviation of the variables, $\sigma(x)$ and $\sigma(p)$, for the mole fraction and pressure, respectively, where σ is the standard deviation between the experimental value and the so-called calculated "true" values of each experimental variable.

Other additional information, such as molar volumes, second virial coefficients, etc., of each component is given in refs. 1 and 2.

The calculated G^E values were fitted to the equation

$$\frac{G^E}{RTx(1-x)} = \frac{\sum_{i=0}^{m} A_i(2x-1)^i}{1+\sum_{j=1}^{m} B_j(2x-1)^j} \tag{1}$$

where RT is the thermal energy, x is the mole fraction of methanol and A_i and B_j are the adjustable parameters. We will refer to the G^E values obtained from eqn. (1) as experimental when they are compared with the G^E values predicted by any of the models.

For all three systems studied here at both temperatures, a (1/1) approximant [eqn. (1)] has been found to be the most adequate equation to fit the experimental data, according to the objective criteria developed previously [1,2].

Random distribution models

Since the G^E values for the methanol + heptanone systems give an almost symmetrical curve for G^E vs. x [1,2], we may assume that the empirical models derived from the Wohl equation [4] could fit our data. We have chosen, if possible, the model with three parameters in order to compare the results with those obtained from eqn. (1). The notation used by Hâla [5] has been adopted.

Table 1 gives the results of the Margules, Van Laar and Scatchard models with three parameters. It may be observed that the Van Laar and Margules models fit the data very satisfactorily. The standard deviations, $\sigma(x)$ and $\sigma(p)$, are of the same magnitude as those obtained from eqn. (1). This agreement, which is surprising in systems formed by polar molecules, may be due to the fact that both the Margules and Van Laar equations may be derived analytically from eqn. (1). Since other more sophisticated models are not able to reproduce the experimental data as well as these two do, we have to consider that the similarity of these equations is the reason for such a good agreement. We will use the standard deviations for the Van Laar and Margules models as a relative estimation of the scattering of the experimental data.

The results for the Scatchard model, which cannot be derived from eqn. (1), may be illustrative of the results of a random distribution model applied to the methanol + heptanone systems.

Non-random distribution models

The assumption of different molecular interactions between like and unlike pairs of molecules, introduces the non-randomness hypothesis into the model, which was first enunciated by Wilson [6]. This model proposes that there are different compositions around the molecules of both components according to the nature of its interactions (local composition concept). Renon and Prausnitz [7] combined the local composition concept with Scott's two-fluid model [8] to obtain the NRTL equation which has been checked in two forms: firstly, assuming $\alpha = 0.3$, as was recommended by the authors [7], and, secondly, allowing α to vary like one more adjustable parameter.

Finally, Abrams and Prausnitz [9], generalizing Guggenheim's [10] quasi-chemical hypothesis, obtained the UNIQUAC equation which has been checked in two different forms: firstly, the original equation [9], and, secondly, the same equation using the geometrical parameters of methanol modified by Anderson and Prausnitz [11] (UNIQUAC-MOD). We have also checked the Heil and Prausnitz [12] model, which mainly applies to polymer solutions.

For all the non-random models, the notation used by Renon and Prausnitz [7] and Abrams and Prausnitz [9] has been adopted. For the sake of brevity, we have not reproduced the equations of these models which are widely known in the literature.

Table 1 gives the results for Wilson, NRTL ($\alpha = 0.3$), NRTL (α free), UNIQUAC, Heil and UNIQUAC-MOD equations. The Wilson model reproduced the data most accurately. None of the two-parameter equations gave good results with the systems studied here. It is interesting to note the difference between the NRTL ($\alpha = 0.3$) and NRTL (α free) models, where the introduction of the third variable gives a considerable improvement in the results.

TABLE 2

Parameters of eqn. (2) for several models

Model	Parameter	System					
		2-H		3-H		4-H	
		a_i	b_i	a_i	b_i	a_i	b_i
Wilson	$\lambda_{21} - \lambda_{11}$	−8743	2408679	−3090	801608	−6339	1996313
	$\lambda_{12} - \lambda_{22}$	8508	−1229390	4656	−84785	10343	−1965482
NRTL	$g_{21} - g_{11}$	8237	−2050267	1649	304457	15335	4008042
$\alpha = 0.3$	$g_{12} - g_{22}$	−8695	3217996	416	150302	5074	−1375838
UNIQUAC	$u_{21} - u_{11}$	−4687	1398961	1769	−597352	−5973	1907674
	$u_{12} - u_{22}$	9316	−2092660	−1623	1321883	12308	−3264242
UNIQUAC-MOD	$u_{21} - u_{11}$	−842	1005864	7112	−281334	12774	−2944370
	$u_{12} - u_{22}$	9	1672587	−2467	1529993	−4879	3406836

Using the Wilson model, it is possible to correlate the parameter values from 2-heptanone to 4-heptanone and from 298.15 to 323.15 K. The parameter $(\lambda_{21} - \lambda_{11})$ decreases from 2-H to 4-H and increases with temperature. The parameter $(\lambda_{12} - \lambda_{22})$ is always negative except for 4-H at 298.15 K; it increases from 2-H to 4-H and decreases with temperature. This may suggest that the methanol–ketone interactions are more likely than the ketone–ketone interactions. Nevertheless, at 298.15 K, 4-H would be more likely to interact with itself than with methanol. This behavior may be a consequence of hydrogen bonding between methanol and heptanone molecules, although the experimental dipole moments [13] do not differ very much from one to another (2.61, 2.81 and 2.74 D at 295.15 K for 2-, 3- and 4-heptanone, respectively).

The parameters for the Wilson equation and other non-random equations are strongly correlated to one another. As was discussed by Fabries and Renon [14], strong correlation is common whenever the two adjustable parameters represent energy differences. It is also common that, when both

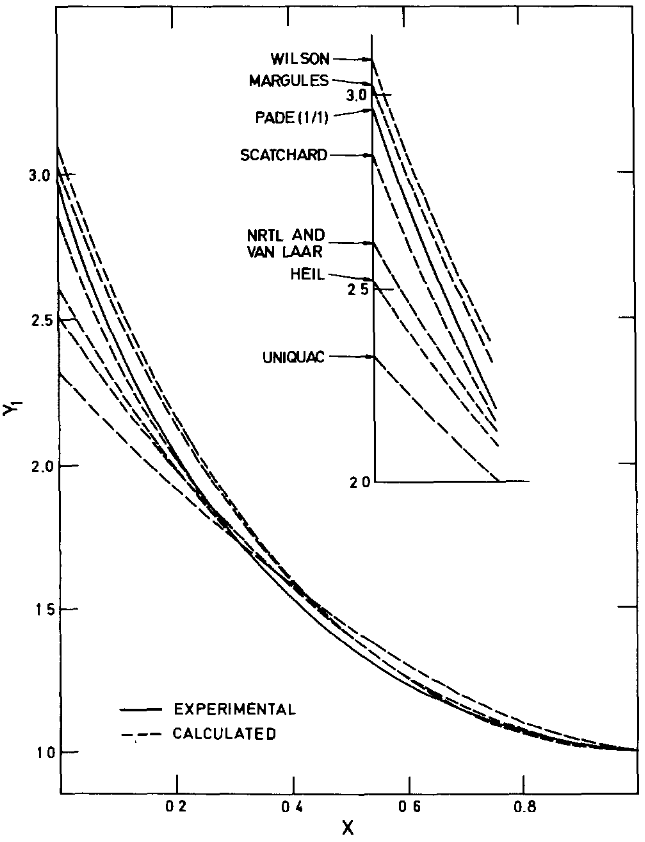

Fig. 1. Activity coefficient of methanol in the methanol + 3-heptanone systems at 323.15 K. The experimental curve corresponds to the values obtained from eqn. (1).

parameters are related, we may find other solutions [11,14]. Nevertheless, it has not been possible to find a negative value of the parameter $(\lambda_{12}-\lambda_{22})$ in Wilson's equation for the 4-H system at 298.15 K.

Dohnal et al. [15] have used Wilson's equation to correlate experimental G^E, H^E and C_p^E data. They found that it is possible to assume a temperature dependence for any parameter, θ_i, in the form

$$\theta_i = a_i + b_i/T \tag{2}$$

Table 2 gives the values of the parameters a_i and b_i for each system and model.

Other authors have found that Wilson's equation reproduces the data with some advantages over other models, e.g. Dohnal et al. [16] for the methanol + acetonitrile system, Rao et al. [17] for *n*-alcohol + chlorobenzene systems, and Wolff and Shadriakhy [18] for the 1-hexanol + *n*-hexane system. They found that Wilson's equation is usually better than the NRTL ($\alpha = 0.3$) equation, and that this is better than the Redlich–Kister equation up to four parameters. Nevertheless, for the systems studied in this paper, the Redlich–Kister equation with three parameters [eqn. (1) for 2/0 degree] gives better results than the NRTL ($\alpha = 0.3$) equation in all cases.

Figure 1 shows the activity coefficient of methanol, γ_1, as a function of composition for the 3-H system at 323.15 K using different models. The

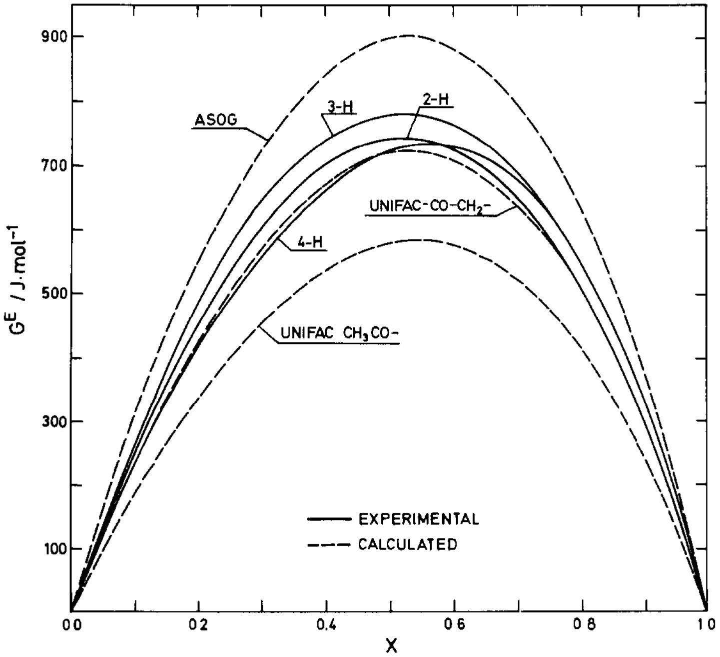

Fig. 2. Excess Gibbs energy of methanol + heptanone systems at 298.15 K. The experimental curves correspond to eqn. (1) while the calculated curves are the predictions made by means of a model.

enlarged figure allows us to identify the results. The values of the activity coefficient at infinite dilution, γ_1^∞, may fluctuate by up to 25% between the different models.

Prausnitz et al. [3] have applied the UNIQUAC model to some methanol + ketone systems showing that the parameter $(u_{21}-u_{11})$ is very sensitive to temperature, and always increases with temperature. They also observed a more complicated dependence with temperature for the $(u_{12}-u_{22})$ parameter. The parameter values given in Table 1 agree with these conclusions in all but the 3-H system. This may be why the UNIQUAC equation presents one of the worst predictions in Fig. 1.

Group contribution models

Models which assume the additive contributions of the functional groups of each molecule, have been successfully applied to VLE data and its prediction. Kojima and Tochigi [19] proposed the ASOG method and Fredenslund et al. [20], calculated the parameters for the UNIFAC method.

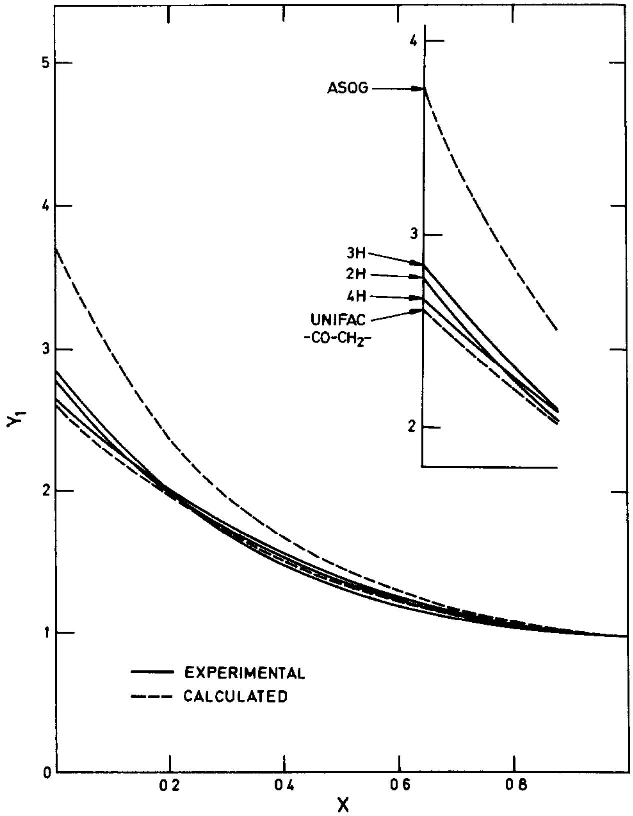

Fig. 3. Activity coefficient of methanol in the methanol + heptanone systems at 323.15 K. The experimental curves correspond to eqn. (1).

Making use of the parameter values given in refs. 19 and 20, we have calculated the G^E values for the systems studied here. Figure 2 shows the values calculated at 298.15 K by means of the ASOG and UNIFAC methods compared with the experimental values [eqn. (1)]. The UNIFAC method has been applied with two different group contributions for the ketone. In the 2-H system, it is possible to consider the groups $-COCH_3$ or $-COCH_2-$; this leads to different results. It may be observed in Fig. 2, that both the ASOG and UNIFAC methods are not able to distinguish the isomeric systems. Figure 3 shows the activity coefficient of methanol, γ_1, for our systems at 323.15 K. Our conclusions are similar to those obtained from Fig. 2.

The model proposed by Barker et al. [21,22] has also been checked. The contributions of $-CH_3$ and $-OH$ groups for methanol and $-CH_3$, $-CH_2-$ and $-CO-$ groups for the ketones were considered. Following Goates et al. [23], we have considered three external contacts per group. The number of lattice sites, r, of each molecule have been calculated proportional to their molar volume, V, viz.

$$\frac{r_i}{r_j} = \frac{V_i}{V_j} \tag{3}$$

The total number of contacts per molecule, zq_i, is calculated from

$$r_i = \frac{zq_i}{2} - 1 \tag{4}$$

The resulting number of contacts of each group, Q_i, are: 3 for the $-CH_3$ group, as was postulated for methanol [21], 2 for the $-CH_2-$ group and 5.5 for the $-CO-$ group. Since the methyl and methylene groups in the methanol and ketone molecules are considered to be indistinguishable, we have calculated only one adjustable interaction parameter from our experimental data.

The interaction energy between the $-CH_3$ and $-CO-$ groups has been

TABLE 3

Interaction parameters obtained using Barker's model [21]

T (K)	u_{ij} (J mole^{-1})	
	$-CH_3 \leftrightarrow -CO-$	$-CH_3 \leftrightarrow -OH$
253.15	7553	
268.15	6182	
293.15	4671	
308.15	3447	5902
318.15		6146
323.15		5920
333.15		5923
348.15		6583

TABLE 4

Interaction parameters between the -OH and -CO- groups according to Barker's model [21]

T (K)	$u_{CO \leftrightarrow OH}$ (J mole^{-1})		
	2-H	3-H	4-H
298.15	1208	1278	1201
323.15	957	1033	1070

calculated from the VLE data of the acetone + n-hexane system at different temperatures [24]. Similarly, the interaction energy between the $-CH_3$ and -OH groups was derived from data for the methanol + n-hexane system at different temperatures [24]. By interpolation and some extrapolation, we have adopted the values of 4000 and 2100 J mole^{-1} at 298.15 and 323.15 K, respectively, for the $-CH_3 \leftrightarrow$ -CO- interaction parameter. The value of 6000 J mole^{-1} has been adopted for the $-CH_3 \leftrightarrow$ -OH interaction at both temperatures. Table 3 gives the calculated values of these parameters at the temperatures available.

The interaction parameter corresponding to the -OH and -CO- groups was calculated from the equimolar mixture values of our experimental data.

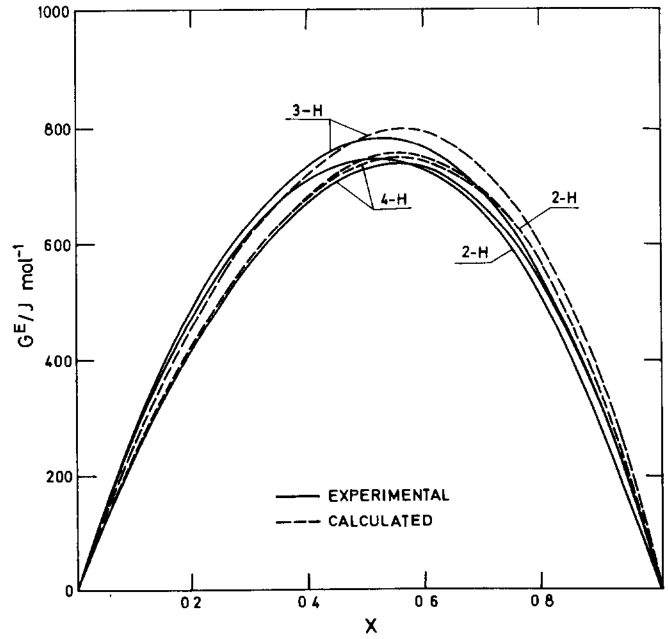

Fig. 4. Excess Gibbs energy of methanol + heptanone systems at 298.15 K. The experimental curves correspond to eqn. (1) while the calculated curves are the values predicted using Barker's model.

Table 4 shows the values obtained for each system at both temperatures. Values for this interaction parameter vary less than 6% at 298.15 K and 11% at 323.15 K.

Figure 4 shows the results at 298.15 K for G^E predicted using the Barker model compared with the experimental curves [eqn. (1)]. The agreement between experimental and calculated values is numerically acceptable but the model is not able to predict how the shape of the curve varies with composition.

As was pointed out by Goates et al. [23], the shape of the G^E curve depends basically on the number of contacts of each group. The results given in Fig. 4 may be improved by recalculating the number of contacts of each group. In any case, the prediction of G^E by the Barker and UNIFAC (with the $-CH_2CO-$ group) methods are good. Both methods are, more or less, equivalent for this family of systems.

Chemical association models

The association of alcohols has been studied by many methods and from different points of view [25,26]. It is well known that solvent polarity is a positive factor in chemical association as well as in the formation of linear polymers in solutions containing alcohols [27]. The Continuous Linear Association Model (CLAM) has been introduced by Renon and Prausnitz [28]. The energy of formation of a hydrogen bond is taken to be 48 kJ mole^{-1} and the association constant of methanol at 323.15 K is 450 [28]. The physical interaction is evaluated using Scatchard's expression [25], viz.

$$G^E(\text{physical}) = \beta\phi_A\phi_K(x_A V_A + x_K V_K) \tag{5}$$

where β is the interaction parameter, ϕ_A and ϕ_K are the volume fractions of alcohol and ketone, respectively, x_A and x_K are the bulk mole fractions and, V_A and V_K are the molar volumes.

TABLE 5

Interaction parameters for the Continuous Linear Association Model with a Scatchard-type physical model

System	β (J cm^{-3})	
	298.15 K	323.15 K
2-H	20.72	16.83
	(21.24)	(17.54)
3-H	23.10	19.44
	(23.65)	(20.91)
4-H	19.57	20.44
	(20.12)	(21.91)

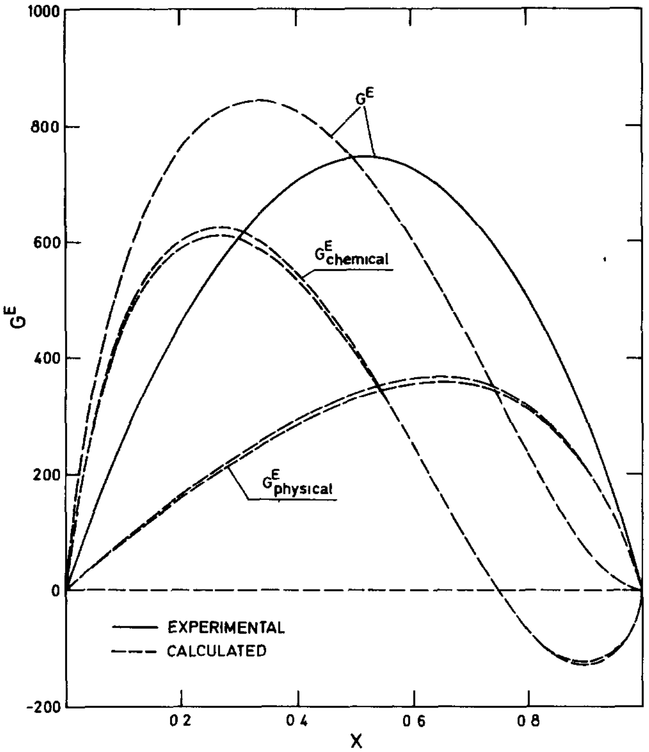

Fig. 5. Excess Gibbs energy of methanol + 2-heptanone systems at 298.15 K. The experimental curve corresponds to the values obtained using eqn. (1). The calculated values are the predictions made with the CLAM model. Two different calculations have been carried out for the physical and chemical contributions to G^E, with the same result for the total G^E.

Fujiwara and Ikenone [29] have satisfactorily explained the NMR spectra of alcohol + hydrocarbon solutions by the CLAM model.

Figure 5 shows the experimental [eqn. (1)] and calculated (CLAM model) G^E curves for the 2-H system at 298.15 K. The physical and chemical contributions to G^E are also shown. The other systems studied in this paper present similar results. Figure 5 shows two different calculations of G^E(physical) and G^E(chemical). In the first calculation, the calculated values were obtained using the association constant given by Renon and Prausnitz [28], and the interaction parameter, β, which reproduces the G^E value of the equimolar mixture. Table 5 gives the values of β used in this calculation. The second calculation of Fig. 5 was performed using the association constant estimated from pure-component data as was proposed by Nath and Bender [30]. The values of β which fit the equimolar values of G^E are enclosed in parentheses in Table 5.

There are almost no differences between both calculations. In any case, the experimental and calculated values of G^E are not in agreement. Tucker

TABLE 6

Interaction parameters and complexation constants obtained using Stokes' association model with NRTL-type physical interactions

	T (K)	System		
		2-H	3-H	4-H
$(g_{21}-g_{11})$	298.15	−867	−729	−2020
(J mole^{-1})	323.15	−825	−702	−274
$(g_{12}-g_{22})$	298.15	1934	2067	4306
J mole^{-1}	323.15	1869	1820	1710
K_{AB}	298.15	43	45	48
	323.15	24	22	26

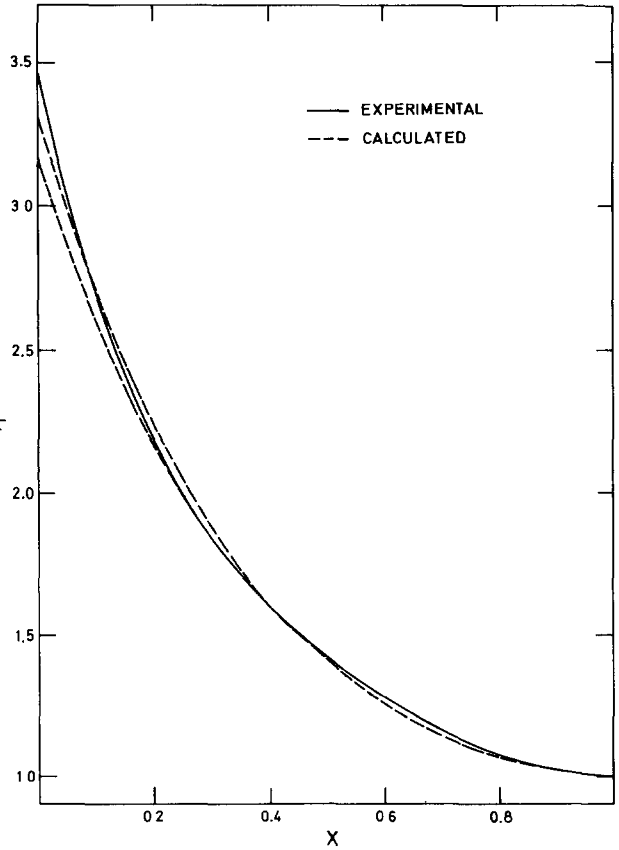

Fig. 6. Activity coefficient of methanol in the methanol + 3-heptanone systems at 323.15 K. The experimental curve corresponds to the values obtained from eqn. (1). The calculated curves are the predictions of the NRTL ($\alpha = 0.3$) model without any association assumption, and the NRTL ($\alpha = 0.3$) model with the association introduced by Nagata and Tamura [37].

and Christian [31] found that the CLAM model was not able to fit the VLE data of the methanol + *n*-hexadecane system in the hydrocarbon-rich mixtures. Chitale and Jose [32] have shown the existence of cyclic associations in the pure alcohol which are not considered in the CLAM model. Fujiwara et al. [33], using spectroscopic data, and Wise et al. [34], using VLE data, have shown the importance of alcohol–solvent association when the solvent is a polar molecule.

Stokes [35] developed an association model which considers dimerization, trimerization, polymerization, cyclation and Scatchard's physical contribution. This model gave good predictions for the VLE data of the ethanol + cyclohexane system [36]. More recently, Nagata and Tamura [37] studied methanol solutions using Stoke's model, and introduced the NRTL ($\alpha = 0.3$) model to estimate the physical contributions.

Using the model of Nagata and Tamura and the values of the constants given in ref. 37, we have calculated the values of the parameters given in Table 6. Figure 6 shows the predicted activity coefficient of methanol, γ_1, in the 3-H system at 323.15 K. The values predicted by the NRTL ($\alpha = 0.3$) model (without association) are also included in Fig. 6. It may be observed that the inclusion of association represents an important improvement in the prediction. It is important to point out that the parameter values given in Table 6 are strongly correlated. So, it is possible to find several sets of parameters which reproduce the results with similar accuracy. This situation reduces the physical significance of the alcohol–solvent association constant, K_{AB}. The lack of heat-of-mixing data bars the calculation of a unique set of parameters.

The almost coincident values of K_{AB} for the three isomeric systems agree with the similar values of the dipolar moments of the parameters. The $(g_{ij} - g_{ii})$ values do not reflect the chemical similarity of the systems.

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