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THE PREDICTION OF VAPOR–LIQUID EQUILIBRIUM FROM HEAT OF MIXING DATA FOR BINARY NITRILE–ALCOHOL MIXTURES

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ABSTRACT

A continuous linear association model for the excess Gibbs energy (g^E) previously used for alcohol–alcohol solutions has been applied to binary nitrile–alcohol mixtures. The method of Hanks, Gupta and Christensen has been used to predict vapor–liquid equilibria (VLE) from heat of mixing (h^E) data for these mixtures. Results are compared with those obtained for other models widely used in the literature. The predictions made using the new model agree well with the experimental VLE data.

INTRODUCTION

Vapor–liquid equilibrium (VLE) data are essential in the design of chemical processes which usually include separation operations. These processes very often occur under conditions of temperature and pressure for which VLE data are not available. Since obtaining new data requires considerable experimental skill and time, much attention has been given to the development of estimation procedures [1,2]. The data required for the application of these procedures and the accuracy of the prediction made vary from one method to another.

The prediction of VLE data for the nitrile–alcohol binary systems is studied in this paper. Several models for the excess Gibbs energy (g^E) widely used in the literature [3–6] and a continuous linear association model recently proposed [7] were considered. The new model has been shown to adequately describe [7,8] alcohol–alcohol mixtures.

The prediction method used has been developed by Hanks et al. [9] and provides a simultaneous description of the excess Gibbs energy and excess enthalpy (h^E). The parameters of the g^E model are evaluated by curve-fitting experimental binary isothermal h^E data to the algebraic equation for h^E derived from the g^E model by application of the Gibbs–Helmholtz relation.

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The method (here called the HGC method) has been shown to be successful in the calculation of both isothermal and isobaric VLE data for a variety of non-associating binary hydrocarbon mixtures [9–13] and for several types of associating mixtures [8,14,15].

MODELS FOR THE EXCESS GIBBS ENERGY

A continuous linear association model for alcohol–alcohol solutions was recently derived and used in conjunction with the HGC method to satisfactorily represent g^E and h^E data simultaneously [7]. Since nitriles are known to be associated to a great extent, their mixtures with alcohols can also be expected to be described by this model. Its expressions for g^E and h^E contain three parameters; two of them, K_A and K_B, have the physical significance of the equilibrium constants for self-association processes of components A and B, respectively, while the third one, β, is an interaction energy parameter. The reported value for the equilibrium constant of acetonitrile at a certain temperature is much lower than those determined for the constants of the alcohols [16–18]. This indicates that alcohols are more strongly associated than the nitriles. On the other hand, different authors have obtained different values of the self-association constants for alcohols [19]. These values even vary sometimes with the nature of the other component. For this reason, we chose to treat K_A, K_B, and β, as adjustable parameters whose values are determined from experimental data. Linear association complexes of the type A_mB_n are not considered and the model is treated as an effective semiempirical curve-fitting form.

The excess Gibbs energy is given by

$$\begin{aligned} g^E = {} & \beta\phi_A\phi_B(x_A v_A + x_B v_B) \\ & + RT\left[x_A \ln(\phi_{A_1}/\phi^*_{A_1}x_A) + x_B \ln(\phi_{B_1}/\phi^*_{B_1}x_B)\right. \\ & \left. + x_A K_A(\phi_A\phi_{A_1} - \phi^*_{A_1}) + x_B K_B(\phi_B\phi_{B_1} - \phi^*_{B_1})\right] \end{aligned} \tag{1}$$

where x_A and x_B are the mole fractions, ϕ_A and ϕ_B are the volume fractions, and v_A and v_B are the molar volumes of components A and B, respectively. ϕ_{A_1} and ϕ_{B_1} are the volume fractions of monomers in the solution which are given by

$$\phi_{A_1} = \frac{1 + 2K_A\phi_A - \sqrt{1 + 4K_A\phi_A}}{2K_A^2\phi_A} \tag{2}$$

$$\phi_{B_1} = \frac{1 + 2K_B\phi_B - \sqrt{1 + 4K_B\phi_B}}{2K_B^2\phi_B} \tag{3}$$

$\phi^*_{A_1}$ and $\phi^*_{B_1}$ are the volume fractions in the pure components which may be obtained from the expressions for ϕ_{A_1} and ϕ_{B_1} by setting ϕ_A and ϕ_B equal to one, respectively.

The excess enthalpy may be written as

$$h^E = \beta'\phi_A\phi_B(x_Av_A + x_Bv_B) - x_A\Delta h^0\left(\frac{1-\phi_A}{\sqrt{1+4K_A\phi_A}} + \frac{\sqrt{1+4K_A\phi_A} - \sqrt{1+4K_A}}{2K_A}\right) - x_B\Delta h^0\left(\frac{1-\phi_B}{\sqrt{1+4K_B\phi_B}} + \frac{\sqrt{1+4K_B\phi_B} - \sqrt{1+4K_B}}{2K_B}\right) \quad (4)$$

where

$$\beta' = \beta - T\frac{d\beta}{dT} \quad (5)$$

and

$$\Delta h^0 = T^2\partial(R \ln K)/\partial T \quad (6)$$

where K may be either K_A or K_B. The value of Δh^0 has been assumed to be $-25\,100$ J mol^{-1} [20].

In a previous paper [7], we mentioned several attempts to develop g^E models for associating mixtures. Pouchly and Zivny [21] also derived a model for a mixture of two alcohols assuming that the mixture contains linear association complexes A_n, B_n and A_mB_n. They have applied their model to represent g^E and h^E data for the 1-butanol (1) + 2-methyl-2-propanol (2), 1-butanol (1) + 2-methyl-1-propanol (2), and methanol (1) + 2-methyl-2-propanol (2) systems. The model has several parameters which have to be either evaluated or adjusted from data for a particular mixture.

Nagata et al. [18,22] derived modified versions of the associated solutions theories proposed by other authors [16,23] which assume two kinds of self-association for one of the components (dimerization and chain association) and the formation of binary complexes between the associating component and an active non-associating component of the binary or ternary mixture. Other types of complexes can be also assumed for ternary mixtures [24]. The physical interaction term is assumed to be given by the UNIQUAC or NRTL equations [4,6]. The association equilibrium constants and standard enthalpy changes are evaluated for a particular mixture and the model contains two adjustable energy parameters which are assumed to change linearly with temperature. Nagata et al. correlated separately binary VLE and h^E data using a two-parameter equation for g^E and a four-parameter equation for h^E. When the model is applied to systems formed by acetonitrile and a hydrocarbon (benzene, toluene, carbon tetrachloride or n-heptane) [22,24], the acetonitrile is considered as the associating component. When the model is applied to systems formed by acetonitrile and an alcohol

[18,22,25], the acetonitrile is considered as the active non-associating component. Nagata's model satisfactorily explains the behavior of both types of mixtures. Since VLE and h^E data are correlated separately, we can only compare the results of fitting this model to h^E data of systems formed by acetonitrile with those of Table 2 of the present work. Deviations between experimental and calculated values of h^E are of similar magnitude.

The non-random two liquid (NRTL) model [4] was also used and is described by the following equations

$$\frac{g^E}{RT} = x_A x_B \left[\frac{\tau_A^\alpha G_A}{x_B + x_A \tau_A^\alpha} + \frac{\tau_B^\alpha G_B}{x_A + x_B \tau_B^\alpha} \right] \tag{7}$$

$$\frac{h^E}{RT} = \frac{g^E}{RT} - \alpha x_A x_B \left[\frac{x_A \tau_B^\alpha G_B^2}{\left(x_A + x_B \tau_B^\alpha\right)^2} + \frac{x_B \tau_A^\alpha G_A^2}{\left(x_B + x_A \tau_A^\alpha\right)^2} \right] \tag{8}$$

where $\tau_A = \exp(-G_A)$, $\tau_B = \exp(-G_B)$, $G_A = (g_{AB} - g_{BB})/RT$, and $G_B = (g_{BA} - g_{AA})/RT$. α, $(g_{AB} - g_{BB})$ and $(g_{BA} - g_{AA})$ are three adjustable parameters which are assumed to be independent of temperature. We will refer to the parameters $(g_{AB} - g_{BB})$ and $(g_{BA} - g_{AA})$ as Δg_{AB} and Δg_{BA}, respectively.

The local effective mole fraction (LEMF) model [5] is essentially the NRTL model with $\alpha = -1$ and has two adjustable parameters, $(g_{AB} - g_{BB})$ and $(g_{BA} - g_{AA})$.

The Wilson equation [3] was also tested. The algebraic equation for h^E derived from this g^E model assuming that the energy parameters are not dependent on temperature is not able to correlate h^E data for the nitrile–alcohol systems. This could be expected since Hanks et al. [12] had already pointed out the limitations of this equation as a result of a parametric analysis. Dohnal et al. [26,27] used the Wilson equation with energy parameters dependent on temperature to simultaneously represent VLE and h^E data for the acetonitrile (1) + ethanol (2) and acetonitrile (1) + 1-propanol (2) systems. The disadvantage of this approach is the higher number of adjustable parameters required (four for the first system and six for the second).

Excess enthalpies for the nitrile–alcohol systems could not be fitted by the equation for h^E derived from the UNIQUAC model [6]. As has already been pointed out, Nagata et al. [18,22,24,25] found that this model is adequate for describing the physical interactions in these mixtures while an associate–solution theory is required to give a proper account of the chemical interactions taking place.

PREDICTION METHOD

The usual approach to VLE correlation or prediction is to obtain experimental information such as total pressure, p, liquid composition, x, and very often vapor composition, y, at constant temperature or pressure. From these data the liquid-phase activity coefficients, γ_j, may be calculated and the excess Gibbs energy is computed using the well-known equation

$$g^{E} = RT \sum_{j=1}^{n} x_j \ln \gamma_j \tag{9}$$

The excess Gibbs energy data are then curve-fitted to some semiempirical model, $g^{E}(x_j, C_1 \ldots C_k)$, where C_k are the adjustable parameters which are usually assumed to be temperature independent [3–6,28].

The excess enthalpy, h^{E}, is related to g^{E} by the Gibbs–Helmholtz relation

$$h^{E} = -T^{2}\partial(g^{E}/T)/\partial T \tag{10}$$

Frequently, a model is not able to correlate g^{E} and h^{E} data simultaneously. If g^{E} data are used to determine the parameter values, C_k, there is an error magnification effect inherent to the differentiation process of eqn. (10).

The HGC method used in this paper reverses the order of this process by obtaining an algebraic equation for the heat of mixing, $h^{E}(x_j, C_1 \ldots C_k)$, which is derived from a given g^{E} model by application of eqn. (10). The values for $C_1 \ldots C_k$ are determined by curve-fitting of h^{E} data. These C_k values are then used in the original g^{E} model to calculate the activity coefficients, γ_j, from which the x–y data are finally predicted.

This prediction method was applied to all the models for g^{E} described above. All the parameters were assumed to be temperature independent. The opposite assumption increases the number of parameters and usually leads to equations so complex as to be of little practical use. The Wilson formulation [29] of the Redlich–Kwong equation of state was used to take into account the non-ideality of the vapor in VLE calculations.

RESULTS AND DISCUSSION

A survey of the literature revealed six binary nitrile–alcohol systems for which VLE data and h^{E} data are available simultaneously. These systems are listed in Table 1, together with the source of data. Most h^{E} data have been measured at 298.15 K and atmospheric pressure. The system acetonitrile (1) + ethanol (2) had h^{E} data available at 293.15, 298.15, 308.15 and 318.15 K, and the system acetonitrile (1) + 1-propanol (2) had h^{E} data available at 298.15, 308.15 and 318.15 K. In most cases there are many data points to be fitted to the algebraic equation for h^{E}. Values of h^{E} are endothermic with a maximum at a mole fraction close to 0.5 whose value ranges from 1100 to 2000 J mol^{-1} (see Figs. 1–5).

Table 2 shows the temperature at which h^{E} data have been measured, the values of parameters, the standard deviation, σ, between experimental and calculated values of h^{E}, and the percentage of this standard deviation with

TABLE 1

Binary systems studied and source of experimental data

System No.	Components	References	
		h^E data	VLE data
I	Acetonitrile (1)+Methanol (2)	30, 31	32–35
II	+Ethanol (2)	26, 30, 31, 36, 37	26, 35, 36, 38–40
III	+1-Propanol (2)	27, 30, 31	27, 35, 41
IV	+2-Propanol (2)	30, 31	42
V	+1-Butanol (2)	30, 31, 43	35
VI	Propanenitrile (1)+2-Propanol (2)	37	35

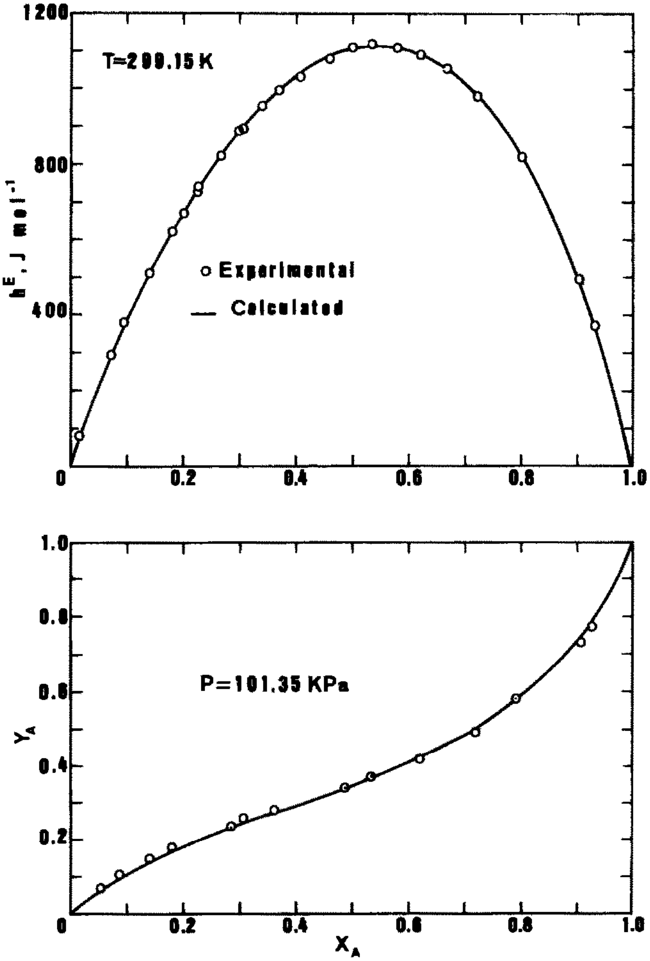

Fig. 1. Comparison of calculated and experimental data for the system acetonitrile (1)+ methanol (2). Solid curves are calculated from eqns. (1) and (4).

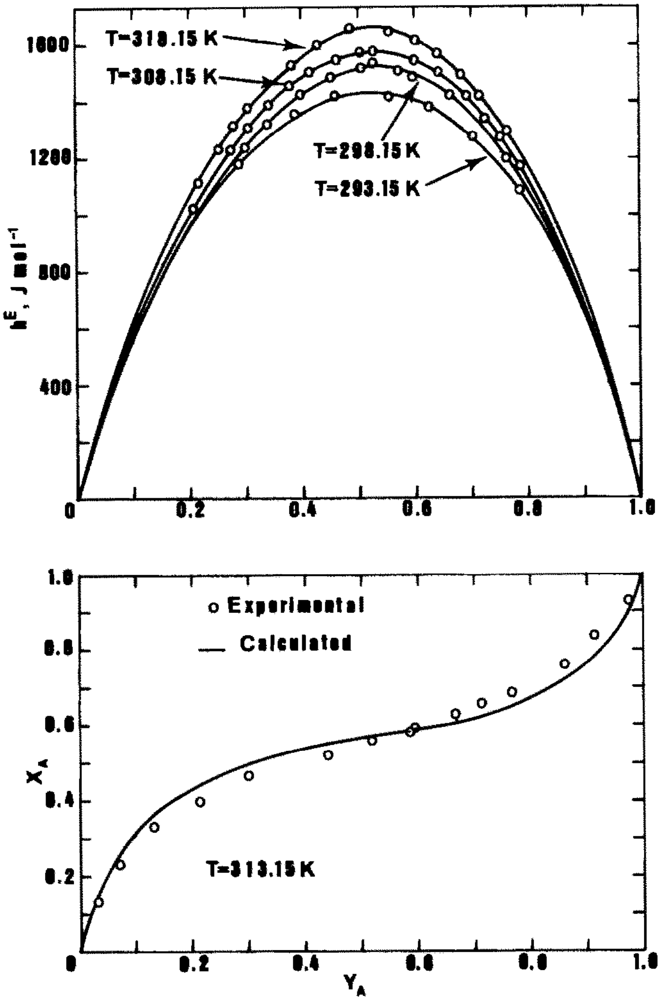

Fig. 2. Comparison of calculated and experimental data for the system acetonitrile (1) + ethanol (2). Solid curves are calculated from eqns. (1) and (4) using the 298.15 K set of parameters. Some experimental h^E data have been omitted for the sake of clarity.

respect to the highest value of h^E, for each of the different models used. The fits are good in all cases. Values of $\sigma/h^E_{\mathrm{max}}$ are lower for the association model and the NRTL model. Values of the LEMF model parameters increase slightly with temperature for the two systems which had h^E data available at more than one temperature. In the case of the acetonitrile (1) + 1-propanol (2) system, values for the parameters K_A and K_B of the association model and Δg_{AB}, Δg_{BA} and α of the NRTL model do not change appreciably with temperature. Values of β' increase moderately with temperature. This is also true for the acetonitrile (1) + ethanol (2) system when values of parameters are adjusted from data taken at 298.15, 308.15

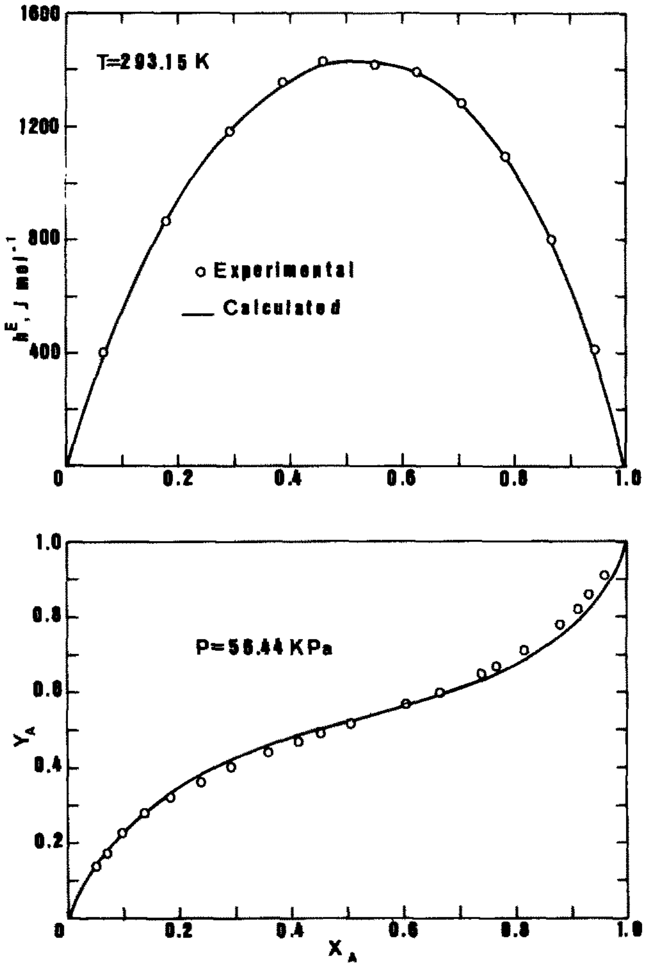

Fig. 3. Comparison of calculated and experimental data for the system acetonitrile (1)+ethanol (2). Solid curves are calculated from eqns. (1) and (4) using the 293.15 K set of parameters.

and 318.15 K. However, values for parameters K_A, K_B, β', Δg_{AB}, Δg_{BA} and α obtained from data taken at 293.15 K for this system do not follow the same pattern. This could be related to the variations of the excess enthalpy with temperature. The 293.15 K set of data has a maximum of ~ 1425 J mol^{-1}. The 298.15, 308.15 and 318.15 K sets of data which have been reported by different authors have maxima of approximately 1550, 1575 and 1650 J mol^{-1}, respectively. As can be seen in Fig. 2, these values correspond to moderate increases of the excess enthalpy with temperature except for the large difference observed between the 293.15 and 298.15 K sets of data. The observed variations of the values of the parameters with temperature do not enable us to extrapolate their values to a higher temperature.

Table 3 gives the results of VLE predictions. The conditions of the VLE

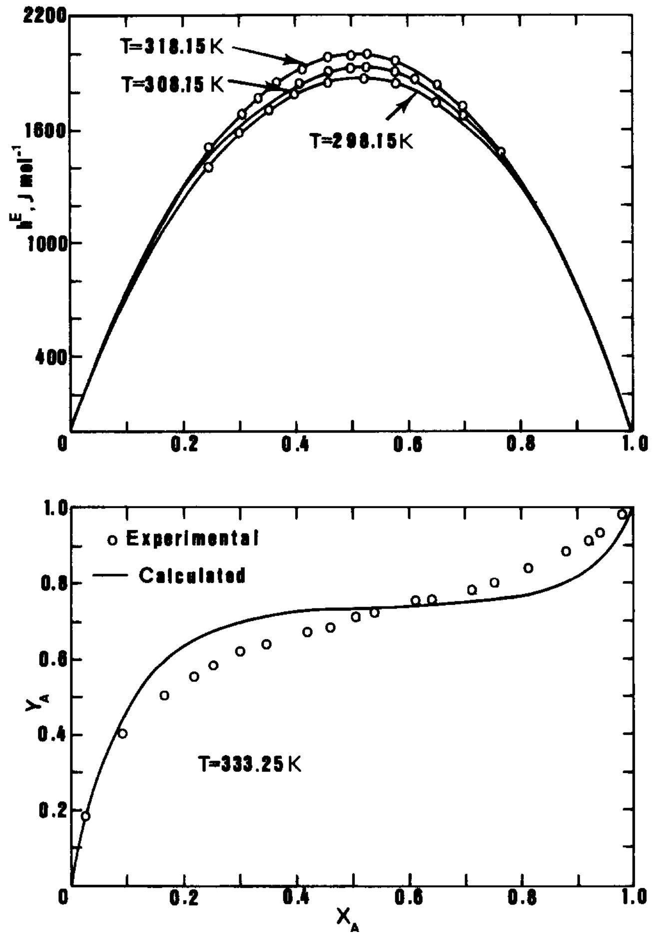

Fig. 4. Comparison of calculated and experimental data for the system acetonitrile (1)+1-propanol (2). Solid curves are calculated from eqns. (1) and (4) using the 298.15 K set of parameters. Some experimental h^E data have been omitted for the sake of clarity.

data are indicated. When the data are isothermal, both the temperature and the range of total pressures are indicated. When the data are isobaric, the pressure and the temperature interval are stated. If h^E data for a system were taken at only one temperature, there is only one set of parameters available to predict VLE data under any conditions. In this case, the temperature of the h^E data is indicated in Table 3 under the heading "set of parameters".

The mean deviation of y_1 has been chosen as the criterion to examine the accuracy of the VLE predictions and is given in Table 3. Values for the maximum deviation are also reported in order to complement the information provided by the mean deviation. When experimental values of y_1 were not available, the mean deviations of the total pressure were calculated and are expressed in kPa. The source of VLE data is indicated in the last column of Table 3.

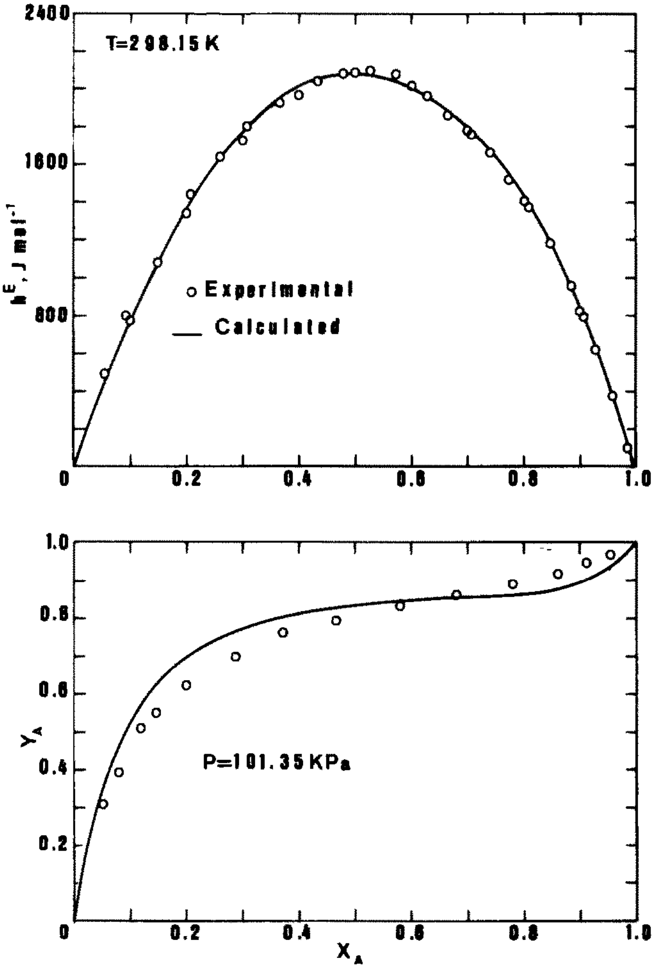

Fig. 5. Comparison of calculated and experimental data for the system acetonitrile (1)+1-butanol (2). Solid curves are calculated from eqns. (1) and (4).

Values for the molar volumes were taken from Timmermans [44] and from the Handbook for Chemistry and Physics [45]. Some molar volumes used in the calculation of isobaric VLE data had to be estimated using the method of Gunn and Yamada [46]. Application of Wilson's formulation of the Redlich–Kwong equation [29] requires the knowledge of the critical constants and acentric factors for pure components. Values for these parameters have been taken from Reid et al. [47]. Values for the pure components' vapor pressures were also taken from Reid et al. [47] except for the cases in which these values were reported together with total pressure measurements of the mixtures.

Predictions of Table 3 correspond to the association model and the LEMF model. Predictions made using the NRTL model were always less accurate

TABLE 2

Calculated values of the parameters and comparison of experimental and calculated h^E data

System No.:	I	II				III			IV	V	VI
T (K):	298.15	293.15	298.15	308.15	318.15	298.15	308.15	318.15	298.15	298.15	298.15
Parameters of eqn. (4)											
$K_A \times 10^2$	12.469	21.428	14.421	16.292	15.569	23.274	24.233	25.063	19.948	31.678	37.378
$K_B \times 10^2$	26.351	34.196	25.388	26.486	23.297	24.881	25.530	22.563	15.202	22.704	37.545
β' (J cm^3)	35.958	49.177	62.909	64.220	70.214	71.737	73.658	76.540	85.564	71.157	47.708
σ (J mol^{-1}) [a]	1.9	1.2	1.3	0.9	0.5	2.2	1.5	1.1	2.2	1.9	0.5
σ/h^E_{max}(%)	0.6	0.7	0.9	0.6	0.5	1.0	0.5	0.5	0.7	1.0	0.3
Parameters of NRTL equation											
Δg_{AB} (J mol^{-1})	4672.3	6241.0	5930.3	6108.7	6045.1	6821.9	7088.2	6930.3	6445.3	7224.7	7250.5
Δg_{BA} (J mol^{-1})	2829.5	5006.5	4313.3	4693.4	4761.3	5735.8	5990.3	6116.6	5324.6	6487.2	7250.5
α	0.2657	0.2204	0.1991	0.2014	0.1940	0.1634	0.1654	0.1627	0.1337	0.1456	0.1882
σ (J mol^{-1}) [a]	2.4	1.8	1.4	0.9	0.5	2.8	0.6	0.5	2.3	1.8	0.2
σ/h^E_{max} (%)	0.5	0.9	0.9	0.6	0.5	1.0	0.2	0.2	0.8	1.0	0.1
Parameters of LEMF equation											
Δg_{AB} (J mol^{-1})	1183.8	1599.5	1637.2	1712.8	1822.7	1982.0	2039.2	2141.7	2103.8	2180.9	1980.0
Δg_{BA} (J mol^{-1})	1638.1	1831.8	1922.9	1992.3	2026.7	2149.3	2217.5	2242.7	2217.6	2250.2	1980.0
σ (J mol^{-1}) [a]	2.4	2.5	3.8	2.6	2.8	8.4	8.4	7.4	13	11	2.8
σ/h^E_{max}(%)	0.9	1.2	2.1	1.9	2.0	3.4	3.5	3.5	4.7	4.3	1.5

[a] Standard deviation between experimental and calculated h^E values.

TABLE 3

Summary of VLE predictions from h^E data

System No.	T (K)	P (kPa)	Set of parameters (K)	Association model vapor composition		LEMF model vapor composition		Ref.
				Mean deviation	Maximum deviation	Mean deviation	Maximum deviation	
I	303.15	13–22	298.15	0.036	0.063	0.045	0.1	32
	326.04	41–67	298.15	0.017	0.028	0.033	−0.059	34
	328.15	49–73	298.15	0.018	0.026	0.037	0.088	33
	336.46	56–90	298.15	0.015	0.023	0.025	−0.052	34
	312–324	37.54	298.15	0.021	−0.032	0.032	−0.061	34
	322–335	56.45	298.15	0.015	0.026	0.026	−0.050	34
	332–346	86.05	298.15	0.016	0.029	0.024	−0.048	34
	336–350	101.35	298.15	0.011	0.019	0.038	0.081	35
II	293.15	8–10	293.15	0.26 [a]	−0.85 [a]	1.4 [a]	1.8 [a]	36
			298.15	0.50 [a]	0.62 [a]	1.8 [a]	2.1 [a]	
	293.15	9–11	293.15	0.26 [a]	−0.49 [a]	1.5 [a]	1.7 [a]	40
			298.15	0.44 [a]	0.54 [a]	1.8 [a]	2.0 [a]	
	303.15	10–18	293.15	0.17 [a]	−0.43 [a]	2.5 [a]	2.9 [a]	36
			298.15	1.1 [a]	1.5 [a]	3.0 [a]	3.4 [a]	
	313.15	17–27	293.15	1.4 [a]	2.5 [a]	4.9 [a]	6.5 [a]	36
			298.15	3.1 [a]	4.5 [a]	5.6 [a]	7.2 [a]	
	313.15	20–29	293.15	0.010	0.020	0.049	0.092	38
			298.15	0.028	0.054	0.057	0.109	
	323.15	29–42	293.15	0.72 [a]	1.3 [a]	5.3 [a]	6.1 [a]	39
			298.15	3.1 [a]	4.0 [a]	6.3 [a]	7.1 [a]	

	343.15	69–92	293.15	3.8 [a]	5.5 [a]	12 [a]	14 [a]	40
			298.15	9.4 [a]	12 [a]	14 [a]	16 [a]	
	393.15	297–450	293.15	45 [a]	60 [a]	65 [a]	80 [a]	40
			298.15	72 [a]	92 [a]	73 [a]	89 [a]	
	324–332	45.35	293.15	0.017	0.037	0.057	0.102	26
			298.15	0.040	0.073	0.065	0.118	
	330–336	56.44	293.15	0.018	0.035	0.060	0.096	26
			298.15	0.043	0.072	0.069	0.112	
	335–341	69.48	293.15	0.018	0.042	0.054	0.099	26
			298.15	0.040	0.078	0.061	0.114	
	341–348	86.05	293.15	0.019	0.050	0.052	0.105	26
			298.15	0.041	0.085	0.059	0.120	
	346–352	101.35	293.15	0.025	0.043	0.054	0.095	35
			298.15	0.046	0.078	0.061	0.110	
III	328.15	21–42	298.15	0.059	−0.081	0.081	−0.191	41
	333.25	24–51	298.15	0.059	−0.104	0.073	−0.177	27
	351.22	51–94	298.15	0.081	−0.138	0.094	−0.191	27
	325–344	37.54	298.15	0.060	−0.111	0.082	−0.177	27
	336–352	56.44	298.15	0.062	−0.113	0.077	−0.191	27
	348–363	86.05	298.15	0.075	−0.115	0.098	−0.161	27
	353–367	101.35	298.15	0.068	−0.121	0.083	−0.177	35
IV	323.15	28–40	298.15	0.117	0.168	0.123	−0.199	42
V	355–380	101.35	298.15	0.052	−0.087	0.082	−0.188	35
VI	355–365	101.35	298.15	0.071	0.124	0.099	0.181	35

[a] Mean deviations in the total pressure expressed in kPa.

and have been omitted. In order to examine the accuracy of the predictions when experimental values of y_1 are not reported, values for the total pressure mean deviation should be compared with the corresponding interval.

When two or more sets of h^E data taken at different temperatures are available for a system, VLE data at a certain temperature can be predicted using different sets of parameters. Since for most cases values of the parameters do not change appreciably with temperature, the accuracy of the predictions is not significantly affected by the set of parameters used and deviations corresponding to the 298.15 K set are reported in Table 3. However, results for the 293.15 K set of parameters of the acetonitrile (1) + ethanol (2) system are also reported because more precise VLE predictions are always obtained for the three models used. As has been pointed out above, these discrepancies could be related to the variations of the excess enthalpy with temperature reported for this system.

Values of the y_1 mean deviation or of total pressure mean deviation are lower when the model based on the association of both components is used. Figures 1–5 show some typical examples of the results obtained for this model.

Predictions are poorer when the difference in size of both components increases. A similar trend was observed when the model was used to describe alcohol–alcohol systems but deviations were always lower (0.01–0.04). The model is now severely tested by trying to represent the behavior of a mixture whose components are associated to a different degree. Nevertheless, the model seems to be more effective than other models widely used in the literature. The HGC prediction method also led to more accurate predictions for other types of binary mixtures. However, results can be considered satisfactory given the difficulties involved in simultaneously representing by a unique set of parameters h^E and VLE data for nitrile–alcohol systems.

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