Thermochimica Acta, 118 (1987) 237–252
Elsevier Science Publishers B.V., Amsterdam – Printed in The Netherlands

CORRELATION OF THE SPECTROSCOPIC AND THERMODYNAMIC PROPERTIES OF SOLUTIONS OF ETHANOL WITH NON-ASSOCIATING COMPONENTS BY MEANS OF THE UNIQUAC ASSOCIATED-SOLUTION MODEL

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(Received 10 February 1987)

ABSTRACT

The UNIQUAC associated-solution model is used to correlate the spectroscopic and thermodynamic properties of solutions of ethanol in a non-associating component in terms of three self-association constants of open-chain hydrogen-bonded groups, one self-association constant of cyclic groups and one enthalpy for formation of the hydrogen bonds. This model gives a better prediction of the vapour–liquid equilibrium and excess enthalpy than the association model of Nagata and Tamura for ternary solutions of ethanol with two non-associating components.

INTRODUCTION

A number of alcohol association models, employing up to four equilibrium constants, were tested to fit the vapour pressures for ethanol + η-hexadecane [1]. Stokes [2] chose a model based on mole fraction statistics to explain the thermodynamic, spectroscopic and dielectric properties of dilute solutions for ethanol + cyclohexane. The model assumes the presence of open-chain and closed cyclic hydrogen-bonded groups with allowance for a non-polar interaction term. Another similar model based on volume fraction statistics [3] was used for the vapour pressures and excess enthalpies of ethanol + *n*-hexadecane.

The UNIQUAC associated-solution model usually uses a single association contant for the self-association of ethanol molecules over most of the

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0040-6031/87/$03.50

concentration range [4]. The two-constant UNIQUAC associated-solution model, where only the dimerization constant is different and the other association constants of linear polymerization are equal, was employed in the correlation and prediction of excess enthalpies of alcohol–hydrocarbon mixtures [5]. The previous papers and our preliminary study may suggest that at least four association constants are necessary for the quantitative description of the activity coefficients, excess enthalpies and IR spectroscopic behaviour of dilute solutions of ethanol in saturated hydrocarbons.

In this paper, we apply the UNIQUAC associated-solution model with four self-association constants to describe the spectroscopic and thermodynamic properties of binary solutions of ethanol and one non-associating component as well as possible. We also compare the predictive ability of the present model with that of the association model having four self-association constants defined in terms of mole fraction [6] in estimating ternary vapour–liquid equilibrium (VLE) and excess enthalpy for ethanol solutions by use of binary parameters alone.

MODEL DESCRIPTION

For a ternary mixture containing one alcohol A and two non-associating components B and C, we present here the basic equations of the activity coefficients and excess enthalpy. As described in the previous papers [2,3,5], the present UNIQUAC associated-solution model assumes that open chains of any length and closed cyclic groups for alcohol molecules are formed according to the following reactions:

$$A_1 + A_1 = A_2 \qquad K_{A_2} = \frac{\Phi_{A_2}}{\Phi_{A_1}^2}\left(\frac{1}{2}\right) \tag{1}$$

$$A_2 + A_1 = A_3 \qquad K_{A_3} = \frac{\Phi_{A_3}}{\Phi_{A_2}\Phi_{A_1}}\left(\frac{2}{3}\right) \tag{2}$$

$$A_i + A_1 = A_{i+1} \qquad K_A = \frac{\Phi_{A_{i+1}}}{\Phi_{A_i}\Phi_{A_1}}\left(\frac{i}{i+1}\right) \text{ for } i \geqslant 3 \tag{3}$$

$$A_i(\text{open}) = A_i(\text{cyclic}) \qquad K_{cy} = \frac{\Theta}{i} = \frac{\Phi_{A_i(\text{cyclic})}}{\Phi_{A_i(\text{open})}} \text{ for } i \geqslant 5 \tag{4}$$

where Φ is the segment fraction and Θ is a constant.

Additionally, we include two solvation equilibria between the terminal hydroxyl group of alcohol chains and solvating molecules:

$$A_i + B_1 = A_iB \qquad K_{AB} = \frac{\Phi_{A_iB}}{\Phi_{A_i}\Phi_{B_1}}\left(\frac{i}{ir_A + r_B}\right) \text{ for all } i \geqslant 1 \tag{5}$$

$$A_i + C_1 = A_iC \qquad K_{AC} = \frac{\Phi_{A_iC}}{\Phi_{A_i}\Phi_{C_1}}\left(\frac{i}{ir_A + r_C}\right) \text{ for all } i \geqslant 1 \tag{6}$$

where r is the pure-component structural constant.

The van't Hoff equation fixes the temperature dependence of the equilibrium constants and the enthalpy of the hydrogen bond h_A and the enthalpies of complex formation h_{AB} and h_{AC} are assumed to be independent of chain length and temperature:

$$\begin{aligned} &\partial \ln K_{A_2}/\partial(1/T) = -h_A/R && \partial \ln K_{A_3}/\partial(1/T) = -h_A/R \\ &\partial \ln K_A/\partial(1/T) = -h_A/R && \partial \ln \theta/\partial(1/T) = -h_A/R \\ &\partial \ln K_{AB}/\partial(1/T) = -h_{AB}/R && \partial \ln K_{AC}/\partial(1/T) = -h_{AC}/R \end{aligned} \tag{7}$$

The activity coefficients of the components A and B are expressed by

$$\begin{aligned} \ln \gamma_A = {} & \ln\left(\frac{\Phi_{A_1}}{\Phi^0_{A_1}x_A}\right) + \frac{r_A}{V^0_A} - \frac{r_A}{V} - \left(\frac{Z}{2}\right)q_A\left[\ln\left(\frac{\Phi_A}{\theta_A}\right) + 1 - \frac{\Phi_A}{\theta_A}\right] \\ & + q_A\left[1 - \ln\left(\sum_J \theta_J \tau_{JA}\right) - \sum_J \frac{\theta_J \tau_{AJ}}{\sum_K \theta_K \tau_{KJ}}\right] \end{aligned} \tag{8}$$

$$\begin{aligned} \ln \gamma_B = {} & \ln\left(\frac{\Phi_{B_1}}{x_B}\right) + 1 - \frac{r_B}{V} - \left(\frac{Z}{2}\right)q_B\left[\ln\left(\frac{\Phi_B}{\theta_B}\right) + 1 - \frac{\Phi_B}{\theta_B}\right] \\ & + q_B\left[1 - \ln\left(\sum_J \theta_J \tau_{JB}\right) - \sum_J \frac{\theta_J \tau_{BJ}}{\sum_K \theta_K \tau_{KJ}}\right] \end{aligned} \tag{9}$$

$\ln \gamma_C$ is given by exchanging the subscript B in eqn. (9) with C. The surface fraction θ_I, the segment fraction Φ_I and the binary parameter τ_{JI}, which is related to energy parameter a_{JI}, are defined by

$$\theta_I = q_I x_I / \sum_J q_J x_J \tag{10}$$

$$\Phi_I = r_I x_I / \sum_J r_J x_J \tag{11}$$

$$\tau_{JI} = \exp(-a_{JI}/T) \tag{12}$$

The excess Gibbs free energy of the ternary mixture is given by

$$\frac{g^E}{RT} = x_{\mathrm{A}} \ln\left(\frac{\Phi_{\mathrm{A}_1}}{\Phi^0_{\mathrm{A}_1} x_{\mathrm{A}}}\right) + x_{\mathrm{B}} \ln\left(\frac{\Phi_{\mathrm{B}_1}}{x_{\mathrm{B}}}\right) + x_{\mathrm{C}} \ln\left(\frac{\Phi_{\mathrm{C}_1}}{x_{\mathrm{C}}}\right) + \frac{x_{\mathrm{A}} r_{\mathrm{A}}}{V^0_{\mathrm{A}}} + x_{\mathrm{B}} + x_{\mathrm{C}}$$

$$- \frac{\sum\limits_I x_I r_I}{V} + \left(\frac{Z}{2}\right) \sum_I q_I x_I \ln\left(\frac{\theta_I}{\Phi_I}\right) - \sum_I q_i x_I \ln\left(\sum_J \theta_J \tau_{JI}\right) \tag{13}$$

The monomer segment fractions Φ_{A_1}, Φ_{B_1} and Φ_{C_1} are simultaneously solved from the following mass balance equations:

$$\Phi_{\mathrm{A}} = \Phi_{\mathrm{A}_1}\left(1 + K_{\mathrm{AB}} \Phi_{\mathrm{B}_1} r_{\mathrm{A}} + K_{\mathrm{AC}} \Phi_{\mathrm{C}_1} r_{\mathrm{A}}\right)$$

$$\times \left[1 + 2K_{\mathrm{A}_2} \Phi_{\mathrm{A}_1} + K_{\mathrm{A}_2} K_{\mathrm{A}_3} \Phi^2_{\mathrm{A}_1} (3 - 2z)/(1 - z)^2\right]$$

$$+ \Theta K_{\mathrm{A}_2} K_{\mathrm{A}_3} K^2_{\mathrm{A}} \Phi^5_{\mathrm{A}_1}/(1 - z) \tag{14}$$

$$\Phi_{\mathrm{B}} = K_{\mathrm{AB}} \Phi_{\mathrm{B}_1} \Phi_{\mathrm{A}_1} r_{\mathrm{B}} \left[1 + K_{\mathrm{A}_2} \Phi_{\mathrm{A}_1} + K_{\mathrm{A}_2} K_{\mathrm{A}_3} \Phi^2_{\mathrm{A}_1}/(1 - z)\right] + \Phi_{\mathrm{B}_1} \tag{15}$$

$$\Phi_{\mathrm{C}} = K_{\mathrm{AC}} \Phi_{\mathrm{C}_1} \Phi_{\mathrm{A}_1} r_{\mathrm{C}} \left[1 + K_{\mathrm{A}_2} \Phi_{\mathrm{A}_1} + K_{\mathrm{A}_2} K_{\mathrm{A}_3} \Phi^2_{\mathrm{A}_1}/(1 - z)\right] + \Phi_{\mathrm{C}_1} \tag{16}$$

The true molar volume of the ternary mixture is

$$\frac{1}{V} = \frac{\Phi_{\mathrm{A}_1}}{r_{\mathrm{A}}} \left[1 + K_{\mathrm{A}_2} \Phi_{\mathrm{A}_1} + \frac{K_{\mathrm{A}_2} K_{\mathrm{A}_3} \Phi^2_{\mathrm{A}_1}}{(1 - z)}\right]$$

$$- \frac{\Theta K_{\mathrm{A}_2} K_{\mathrm{A}_3}}{K^3_{\mathrm{A}} r_{\mathrm{A}}} \left[\ln(1 - z) + z + \frac{z^2}{2} + \frac{z^3}{3} + \frac{z^4}{4}\right]$$

$$+ \left(K_{\mathrm{AB}} \Phi_{\mathrm{B}_1} \Phi_{\mathrm{A}_1} + K_{\mathrm{AC}} \Phi_{\mathrm{C}_1} \Phi_{\mathrm{A}_1}\right) \left[1 + K_{\mathrm{A}_2} \Phi_{\mathrm{A}_1} + \frac{K_{\mathrm{A}_2} K_{\mathrm{A}_3} \Phi^2_{\mathrm{A}_1}}{(1 - z)}\right] + \frac{\Phi_{\mathrm{B}_1}}{r_{\mathrm{B}}} + \frac{\Phi_{\mathrm{C}_1}}{r_{\mathrm{C}}} \tag{17}$$

where $z = K_{\mathrm{A}} \Phi_{\mathrm{A}_1}$.

In pure alochol, eqns. (14) and (17) reduce to

$$1 = \Phi^0_{\mathrm{A}_1} + 2K_{\mathrm{A}_2} {\Phi^0_{\mathrm{A}_1}}^2 + K_{\mathrm{A}_2} K_{\mathrm{A}_3} {\Phi^0_{\mathrm{A}_1}}^3 (3 - 2z^0)/(1 - z^0)^2$$

$$+ \Theta K_{\mathrm{A}_2} K_{\mathrm{A}_3} K^2_{\mathrm{A}} {\Phi^0_{\mathrm{A}_1}}^5/(1 - z^0) \tag{18}$$

$$\frac{1}{V^0_{\mathrm{A}}} = \frac{\Phi^0_{\mathrm{A}_1}}{r_{\mathrm{A}}} \left[1 + K_{\mathrm{A}_2} \Phi^0_{\mathrm{A}_1} + \frac{K_{\mathrm{A}_2} K_{\mathrm{A}_3} {\Phi^0_{\mathrm{A}_1}}^2}{(1 - z^0)}\right]$$

$$- \frac{\Theta K_{\mathrm{A}_2} K_{\mathrm{A}_3}}{K^3_{\mathrm{A}} r_{\mathrm{A}}} \left[\ln(1 - z^0) + z^0 + \frac{{z^0}^2}{2} + \frac{{z^0}^3}{3} + \frac{{z^0}^4}{4}\right] \tag{19}$$

The molar excess enthalpy of the mixture is expressed as the sum of the chemical and physical contributions [5].

$$h^{\mathrm{E}} = h^{\mathrm{E}}_{\mathrm{chem}} + h^{\mathrm{E}}_{\mathrm{phys}} \tag{20}$$

$$\begin{aligned} h^{\mathrm{E}}_{\mathrm{chem}} = {} & \frac{h_{\mathrm{A}} K_{\mathrm{A}_2} \Phi^2_{\mathrm{A}_1} x_{\mathrm{A}}}{\Phi_{\mathrm{A}}} \left(1 + K_{\mathrm{AB}} r_{\mathrm{A}} \Phi_{\mathrm{B}_1} + K_{\mathrm{AC}} r_{\mathrm{A}} \Phi_{\mathrm{C}_1}\right) \left[1 + \frac{K_{\mathrm{A}_3} \Phi_{\mathrm{A}_1} (2 - z)}{(1 - z)^2}\right] \\ & + \frac{h_{\mathrm{A}} K_{\mathrm{A}_2} K_{\mathrm{A}_3} K^2_{\mathrm{A}} \Theta \Phi^5_{\mathrm{A}_1} x_{\mathrm{A}}}{\Phi_{\mathrm{A}} (1 - z)} + \frac{r_{\mathrm{A}} \Phi_{\mathrm{A}_1} x_{\mathrm{A}}}{\Phi_{\mathrm{A}}} \left(h_{\mathrm{AB}} K_{\mathrm{AB}} \Phi_{\mathrm{B}_1} + h_{\mathrm{AC}} K_{\mathrm{AC}} \Phi_{\mathrm{C}_1}\right) \\ & \times \left[1 + K_{\mathrm{A}_2} \Phi_{\mathrm{A}_1} + \frac{K_{\mathrm{A}_2} K_{\mathrm{A}_3} \Phi^2_{\mathrm{A}_1}}{(1 - z)}\right] - x_{\mathrm{A}} h_{\mathrm{A}} K_{\mathrm{A}_2} \Phi^{0\,2}_{\mathrm{A}_1} \left[1 + \frac{K_{\mathrm{A}_3} \Phi^0_{\mathrm{A}_1} (2 - z^0)}{(1 - z^0)^2}\right] \\ & - \frac{x_{\mathrm{A}} h_{\mathrm{A}} K_{\mathrm{A}_2} K_{\mathrm{A}_3} K^2_{\mathrm{A}} \Theta \Phi^{0\,5}_{\mathrm{A}_1}}{(1 - z^0)} \end{aligned} \tag{21}$$

$$h^{\mathrm{E}}_{\mathrm{phys}} = -R \sum_I q_I x_I \frac{\sum_J \theta_J \dfrac{\partial \tau_{JI}}{\partial (1/T)}}{\sum_J \theta_J \tau_{JI}} \tag{22}$$

The energy parameters are assumed to be linearly dependent on temperature.

$$a_{JI} = C_I + D_I (T - 273.15) \tag{23}$$

The IR spectroscopic data provide the ratio of the number of free hydroxyl groups to the stoichiometric number of alcohol molecules. We define this ratio as β:

$$\begin{aligned} \beta & = \frac{\sum_{i=1}^{\infty} x_{\mathrm{A}_i(\mathrm{linear})}}{\sum_{i=1}^{\infty} i x_{\mathrm{A}_i(\mathrm{linear})} + \sum_{i=5}^{\infty} i x_{\mathrm{A}_i(\mathrm{cyclic})}} \\ & = \frac{1 + K_{\mathrm{A}_2} \Phi_{\mathrm{A}_1} + K_{\mathrm{A}_2} K_{\mathrm{A}_3} \Phi^2_{\mathrm{A}_1} + K_{\mathrm{A}_2} K_{\mathrm{A}_3} K_{\mathrm{A}} \Phi^3_{\mathrm{A}_1} / (1 - z)}{1 + 2 K_{\mathrm{A}_2} \Phi_{\mathrm{A}_1} + K_{\mathrm{A}_2} K_{\mathrm{A}_3} \Phi^2_{\mathrm{A}_1} \left[(3 - 2z)/(1 - z)^2 + \Theta z^2/(1 - z)\right]} \end{aligned} \tag{24}$$

PARAMETER DETERMINATION

Many combinations of K_{A_2}, K_{A_3}, K_{A}, and Θ were tested to find the equilibrium constants from the spectroscopic and thermodynamic data. Those values of K_{A_2}, K_{A_3}, K_{A} and Θ, which are best for ethanol +

cyclohexane, are not best for ethanol + n-hexadecane. Finally, at 50 °C we chose the following compromised set of equilibrium constants, which are able to reproduce the data for these mixtures as well as possible: $K_{A_2} = 25$, $K_{A_3} = 85$, $K_A = 70$ and $\Theta = 10$. The value of h_A is set as -23.2 kJ mol^{-1}, which is the enthalpy of dilution of ethanol in n-hexane at 25 °C [7].

In the parameter estimation from binary VLE data, a computer program, based on the maximum likelihood principle as described by Prausnitz et al. [8], and eqns. (25) and (26) were used:

$$P\phi_I y_I = \gamma_I x_I P_I^s \phi_I^s \exp\left[v_I^L (P - P_I^s)/RT\right] \tag{25}$$

$$\ln \phi_I = \left(2\sum_J y_I B_{IJ} - \sum_I \sum_J y_I y_J B_{IJ}\right)\frac{P}{RT} \tag{26}$$

where P is the total pressure, ϕ is the vapour-phase fugacity coefficient, where the second virial coefficients B_{IJ} were estimated using the Hayden–O'Connell correlation [9], y is the vapour-phase mole fraction, P^s is the pure-component vapour pressure which was taken from the original references of VLE or calculated from the Antoine equation [10,11], v^L is the pure-component liquid molar volume estimated by the modified Rackett equation [12] and R is the universal gas constant. The pure-component molecular structural constants r and q were calculated in accordance with the method of Vera et al. [13] and are given in Table 1. The following objective function was minimized to obtain an optimum set of the energy parameters in VLE data reduction:

$$F = \sum_{i=1}^{N}\left[\frac{(P_i - \hat{P}_i)^2}{\sigma_P^2} + \frac{(T_i - \hat{T}_i)^2}{\sigma_T^2} + \frac{(x_i - \hat{x}_i)^2}{\sigma_x^2} + \frac{(y_i - \hat{y}_i)^2}{\sigma_y^2}\right] \tag{27}$$

where a circumflex represents an estimated true value corresponding to each measured data point. The estimated standard deviations for the measured variables were taken as $\sigma_P = 1$ Torr, $\sigma_T = 0.05$ °C, $\sigma_x = 0.001$ and $\sigma_y = 0.003$.

TABLE 1

Molecular structural constants for pure components

Component	r	q
Ethanol	1.69	1.55
Benzene	2.56	2.05
Cyclohexane	3.18	2.55
n-Hexane	3.61	3.09
n-Hexadecane	9.01	7.41
Toluene	3.10	2.48
p-Xylene	3.65	2.92
2-Butanone	2.60	2.28
Chloroform	2.30	2.04
Ethyl acetate	2.79	2.43

The simplex method [14] was used in fitting the model to h^E, $h^E/x_A x_B$ and $g^E/x_A x_B$ data.

CALCULATED RESULTS AND DISCUSSIONS

Reproduction of binary experimental data

Table 2 gives the solvation equilibrium constants and the enthalpies of complex formation. The values of K_{AB} obtained in this work are generally

TABLE 2

Solvation constants and enthalpies of complex formation

Mixture (A + B)	K_{AB} (temp.(°C))	$-h_{AB}$ (kJ mol^{-1})
Ethanol + benzene	1.4(50)	8.3
Ethanol + toluene	1.4(50)	8.3
Ethanol + *p*-xylene	1.4(50)	8.3
Ethanol + 2-butanone	20(25)	21
Ethanol + chloroform	3(50)	13
Ethanol + ethyl acetate	7(70)	17

TABLE 3

Results of $g^E/x_A x_B$ and $h^E/x_A x_B$ data reduction

Data type	Temp. (°C)	No. of data points	Absolute arith. mean deviation (J mol^{-1})	C_A (K)	C_B (K)	D_A	D_B	Ref.
Ethanol (A) + cyclohexane (B)								
g^E	6.73	27	2.3	22.36	50.65			15
	25	27	3.4	2.68	70.40			
	45	27	4.6	−28.35	101.98			
h^E	6.73	27	7.0	1534.71	32.83	5.0515	−0.2536	15
	25	27	4.0	1128.26	63.34	3.6181	−0.1239	
	45	27	5.4	842.15	111.75	2.4434	0.0731	
Ethanol (A) + *n*-hexadecane (B)								
g^E	52.1	33	12.6	130.16	−44.65			3
h^E	52.1	60	13.1	1263.76	366.19	4.1232	0.9633	3
Ethanol (A) + *p*-xylene (B)								
g^E	13.3	25	3.8	152.94	−77.64			16
	25	25	4.1	155.76	−77.59			
	35	25	4.2	157.44	−77.26			
	45	25	4.6	164.17	−80.40			
h^E	13.3	25	3.0	577.81	174.39	2.1501	0.7910	16
	25	25	3.9	95.86	340.29	0.3966	1.3395	
	35	25	3.5	208.65	310.55	0.7870	1.2104	
	45	25	3.8	67.89	423.28	0.2330	1.6119	

TABLE 4

Results of vapour–liquid equilibrium data reduction

Mixture (A + B)	Temp. (°C)	No. of data points	Root-mean square deviations				Parameters (K)		Ref.
			δP (Torr)	δT (°C)	δx ($\times 10^3$)	δy ($\times 10^3$)	a_{AB}	a_{BA}	
Ethanol + benzene	25	11	0.47	0.01	0.6	5.1	−44.77	109.91	17
	50	5	0.76	0.03	0.5	4.5	68.19	−3.75	18
Ethanol + 2-butanone	25	12	1.04	0.01	0.5	4.6	300.98	−153.51	17
Ethanol + chloroform	35	27	2.39	0.05	2.2	8.9	−235.95	377.22	19
Ethanol + cyclohexane	50	5	0.44	0.02	0.3	4.7	3.39	66.76	20
Ethanol + *n*-hexane	35	9	1.06	0.03	1.0	7.5	−42.45	119.44	21
Ethanol + toluene	50	5	0.54	0.01	0.1	3.5	163.75	−79.40	20
Benzene + cyclohexane	39.99	7	0.30	0.01	0.2	1.9	−5.72	74.58 [a]	22
2-Butanone + benzene	25	10	1.03	0.00	0.3	2.5	−143.79	222.80 [a]	17
Chloroform + *n*-hexane	35	9	0.96	0.03	0.3	2.8	33.59	43.32 [a]	21
Toluene + cyclohexane	50	5	0.68	0.01	0.3	2.9	−80.32	141.30 [a]	20

[a] Taken from ref. 4.

TABLE 5

Results of excess enthalpy data reduction at 25 ° C

Mixture (A + B)	No. of data points	Absolute arith. mean deviation (J mol^{-1})	Parameters				Ref.
			C_A (K)	C_B (K)	D_A	D_B	
Ethanol + benzene	10	1.9	247.92	179.91	0.4195	0.9445	23
Ethanol + cyclohexane	20	1.9	279.43	214.69	0.7587	0.4856	24
Ethanol + ethyl acetate	13	9.7	631.90	134.07	2.5583	−0.2928	25
Ethanol + toluene	10	5.8	99.42	273.99	0.2303	1.2747	23
Ethanol + *p*-xylene	16	8.2	413.72	115.82	1.5781	0.5099	26
Benzene + cyclohexane	24	1.1	129.04	65.35	0.0963	−0.1206 [a]	24
Ethyl acetate + cyclohexane	15	4.1	256.96	178.03	−0.0794	0.1520	27
Toluene + cyclohexane	12	3.2	86.58	22.96	−0.0806	−0.0021 [a]	28
p-Xylene + cyclohexane	19	3.3	29.46	18.07	−0.9439	0.7911 [a]	26

[a] Taken from ref. 26.

smaller than those described previously and the values of h_{AB} are the same as the previous ones [4]. Tables 3–5 list detailed results obtained in binary data reduction and the magnitude of the deviations between the calculated and experimental values is nearly the same as that of the mole fraction

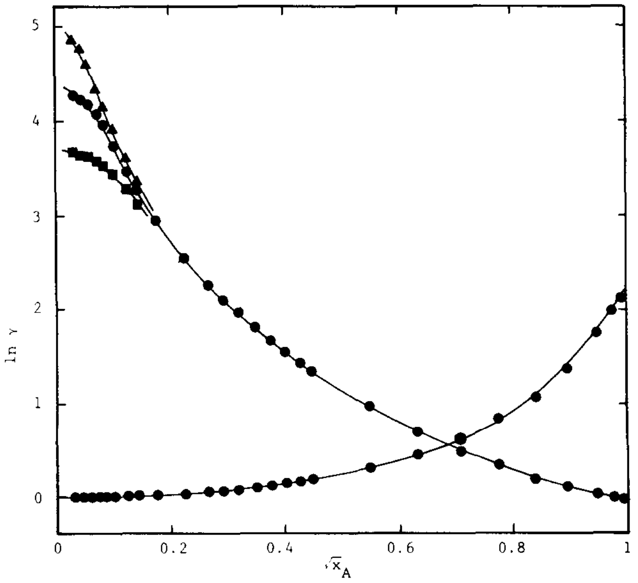

Fig. 1. Activity coefficients for ethanol (A) + cyclohexane (B). Calculated: (———). Experimental data of Stokes and Adamson [15]: ▲, 6.7 ° C; ●, 25 ° C: ■, 45 ° C. Experimental data at 6.7 and 45 ° C are shown at only very low concentrations of ethanol.

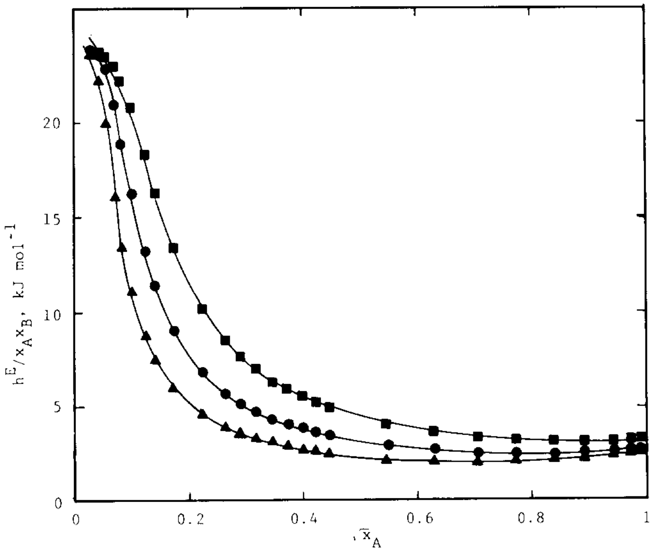

Fig. 2. Excess molar enthalpies of ethanol (A) + cyclohexane (B). Calculated: (———). Experimental data of Stokes and Adamson [15]: ▲, 6.7 °C; ●, 25 °C; ■, 45 °C.

model [6]. Figures 1–7 show a good comparison between the calculated results and the experimental values.

Prediction of ternary properties from binary data

Table 6 indicates predicted VLE results derived from three different approaches: the one-constant UNIQUAC associated-solution model [4], the

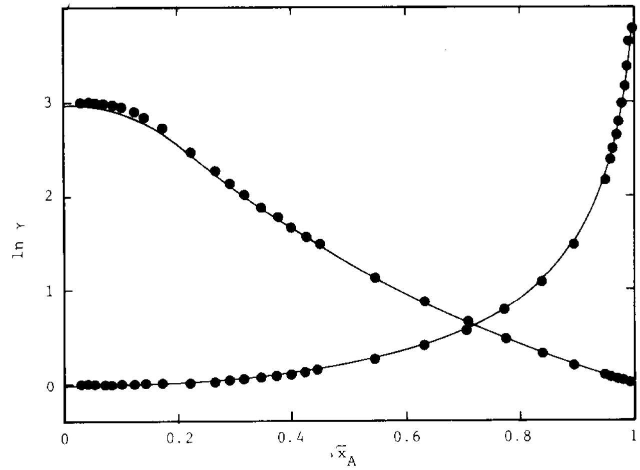

Fig. 3. Activity coefficients for ethanol (A) + *n*-hexadecane (B). Calculated: (———). Experimental data of French et al. [3]: ●, 52.1 °C.

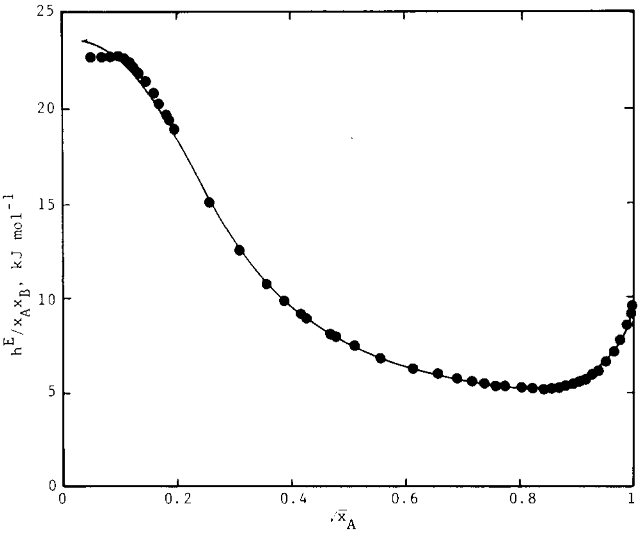

Fig. 4. Excess molar enthalpies of ethanol (A) + n-hexadecane (B). Calculated: (———). Experimental data of French et al. [3]: ●, 52.1° C.

four-constant UNIQUAC associated-solution model and the four-constant mole fraction model [6]. For ethanol + chloroform + n-hexane the present model gives best results and for ethanol + 2-butanone + benzene the three models give similar good results. These results suggest that increasing the number of the association constants in the UNIQUAC associated-solution model reduces the deviations between calculated and experimental values

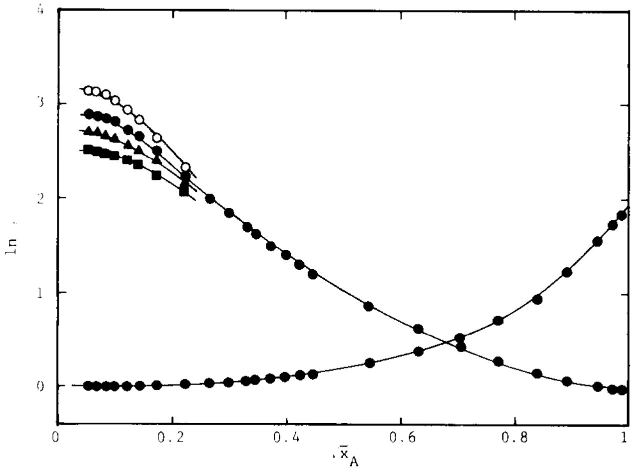

Fig. 5. Activity coefficients for ethanol (A) + *p*-xylene (B). Calculated: (———). Experimental data of Stokes and French [16]: ○, 13.3° C; ●, 25° C; ▲, 35° C; ■, 45° C. Experimental data at 13.3, 35 and 45° C are shown at only very low concentrations of ethanol.

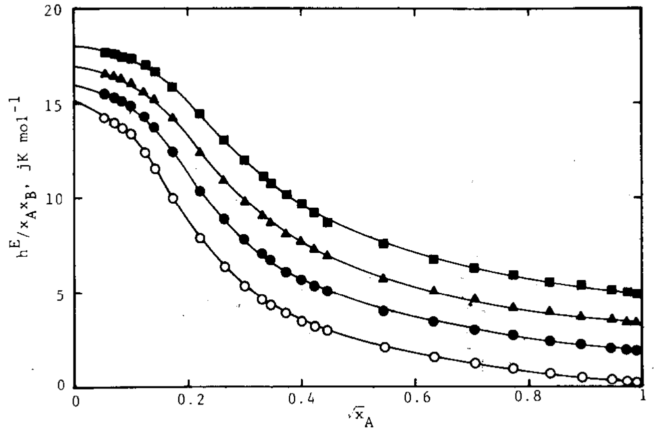

Fig. 6. Excess molar enthalpies for ethanol (A) + *p*-xylene (B). Calculated: (———). Experimental data of Stokes and French [16]: ○, 13.3° C; ●, 25° C; ▲, 35° C; ■, 45° C. It should be noted that the ordinate for the 13.3° C curve is displaced downwards by 1 kJ and those for the 35 and 45° C curves are displaced upwards by 1 and 2 kJ respectively to avoid overlap.

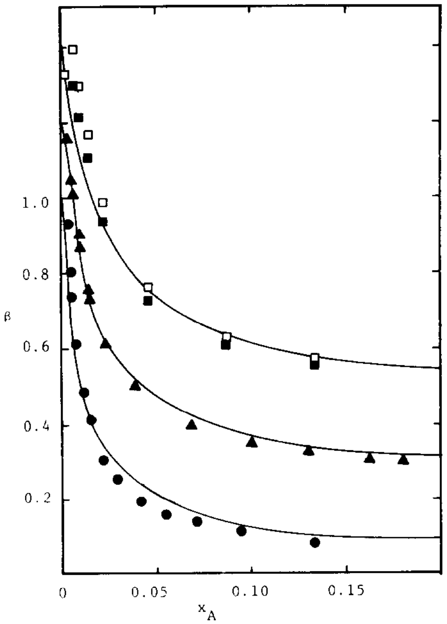

Fig. 7. IR spectroscopic data for the fraction of free OH groups for ethanol (A) + cyclohexane (B). Calculated: (———). Experimental data of Sassa and Katayama [29]: ●, 15° C; ▲, 25° C; □, 35° C. It should be noted that the ordinates for the 25 and 35° C curves are displaced upwards by 0.2 and 0.4 respectively to avoid overlap. ■, Data at 35° C reduced by 10% to adjust for suggested extrapolation error.

TABLE 6

Predicted results for ternary vapour–liquid equilibria

Mixture	Temp. (°C)	No. of data points	Absolute arith. mean deviation						Ref.
			Vapour mole fraction			Pressure (Torr)			
			I [a]	II [b]	III [c] ($\times 10^3$)	I	II	III	
Ethanol +				6.6	10.6				
benzene +	50	19		3.5	4.8		6.1	7.2	18
cyclohexane				6.7	8.4				
Ethanol +			4.2	6.0	6.5				
2-butanone +	25	33	3.1	3.0	4.6	2.1	0.9	0.9	17
benzene			2.2	5.2	4.5				
Ethanol +			8.1	7.1	11.0				
chloroform +	35	36	6.9	5.5	11.9	5.4	2.6	9.6	30
n-hexane			8.4	6.5	12.3				
Ethanol +				7.7	7.3				
toluene +	50	19		3.5	4.5		4.7	3.4	20
cyclohexane				6.4	5.2				

[a] I, one-constant UNIQUAC associated-solution model [4].
[b] II, four-constant UNIQUAC associated-solution model.
[c] III, four-constant mole fraction model [6].

for some mixtures and the present model seems to show a slightly better overall performance than the mole fraction model while both models use four association constants. Predicted results for ternary excess enthalpies are given in Table 7, which confirms that the present model works better than the mole fraction model does, and increasing the number of association constants from two to four does not improve the ability of the UNIQUAC

TABLE 7

Predicted results for ternary excess enthalpies at 25 °C

Mixture	No. of data points	Absolute arith. mean deviation (J mol^{-1})			Ref.
		I [a]	II [b]	III [c]	
Ethanol + benzene					
+ cyclohexane	18	14.5	16.7	14.1	31
Ethanol + ethyl acetate					
+ cyclohexane	51		15.2	26.8	27
Ethanol + toluene					
+ cyclohexane	8	14.8	14.2	26.7	31
Ethanol + *p*-xylene					
+ cyclohexane	59	9.1	12.8	17.2	26

[a] I, two-constant UNIQUAC associated-solution model [5].
[b] II, four-constant UNIQUAC associated-solution model.
[c] III, four-constant mole fraction model [6].

associated-solution model in predicting ternary excess enthalpies of alcohol mixtures, although the two-constant UNIQUAC associated-solution model gives better predicted results than the one-constant UNIQUAC associated-solution model [26].

LIST OF SYMBOLS

A, B, C	alcohol and active non-associating components
a_{IJ}	binary interaction energy parameter
B_{IJ}	second virial coefficient
C_I, D_I	coefficients of eqn. (23)
F	objective function as defined by eqn. (27)
g^E	excess molar Gibbs free energy
h^E	excess molar enthalpy
h_A	enthalpy of hydrogen bond
h_{AB}, h_{AC}	enthalpies of complex formation between unlike molecules
K_A	association constant of open-chain i-mer formation for $i > 3$
K_{A_2}	association constant of dimerization
K_{A_3}	association constant of open-chain trimer formation
K_{cy}	association constant of cyclization of open-chain i-mer as defined by Θ/i for $i > 4$
K_{AB}, K_{AC}	solvation constants to form chemical complexes A_iB and A_iC for $i \geqslant 1$
P	total pressure
P_I^s	saturation pressure of pure component I
q_I	molecular geometric area parameter of pure component I
R	universal gas constant
r_I	molecular geometric volume parameter of pure component I
T	absolute temperature
V	true molar volume of the mixture
v_I^L	molar liquid volume of pure component I
x_I	liquid-phase mole fraction of component I
y_I	vapour-phase mole fraction of component I
Z	coordination number set as 10
z	coefficient as defined by $K_A\Phi_{A_1}$

Greek letters

β	coefficient as defined by eqn. (24)
γ_I	activity coefficient of component I
Θ	coefficient as defined by eqn. (4)
θ_I	surface fraction of component I
σ_P, σ_T, σ_x, σ_y	standard deviations in pressure, temperature, liquid-phase mole fraction and vapour-phase mole fraction respectively

τ_{IJ}	coefficient as defined by $\exp(-a_{IJ}/T)$
Φ_I	segment fraction of component I
Φ_{A_1}, Φ_{B_1}, Φ_{C_1}	monomer segment fractions of components A, B and C
ϕ_I	vapour-phase fugacity coefficient of component I
ϕ_I^s	vapour-phase fugacity coefficient of pure component I at system temperature T and vapour pressure P_I^s

Subscripts

A, B, C	alcohol and non-associating components
A_1, B_1, C_1	monomers of components A, B and C
A_i	alcohol i-mer
AB, AC	complexes containing alcohol open-chain i-mer and component B or C
chem	chemical
I, J, K	components
phys	physical

Superscripts

0	pure-liquid reference state
$\hat{}$	calculated property
E	excess
s	saturation

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