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THERMODYNAMICS OF ASSOCIATED SOLUTIONS. TERNARY LIQUID–LIQUID EQUILIBRIUM FOR SOLUTIONS CONTAINING ACETIC ACID, WATER AND ONE NON-ASSOCIATED COMPONENT

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ABSTRACT

An association model is used to predict ternary liquid–liquid equilibria for six aqueous systems including acetic acid and one non-associated component from binary parameters alone. The model involves the dimerisation constant for acetic acid and the solvation constant between acetic acid and a solvating component with a physical contribution term given by the NRTL equation.

INTRODUCTION

The association model, based on the assumptions of the liquid phase dimerisation of acetic acid molecules and the 1 : 1 solvation of one acetic acid molecule and a solvating one, has been successfully used in reproducing isothermal vapour–liquid equilibria for binary acetic acid–non-polar or polar component systems and predicting isothermal vapour–liquid equilibria for the acetic acid–toluene–*n*-heptane system [1,2]. Furthermore, the same model is able to represent the excess enthalpy data of binary acetic acid–non-polar or polar component mixtures [3,4].

This work presents predicted results on ternary liquid–liquid equilibria for six acetic acid–water–one non-associated component systems obtained from the association model with binary parameters alone.

SOLUTION MODEL

A, B and C represent acetic acid, water and a non-associating component. In a ternary mixture containing these three components there are three

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dimerisation equilibria for the formation of one homodimer A_2 and two heterodimers AB and AC, and their mole fraction equilibrium constants are defined by

$$K_x = \frac{x_{A_2}}{x_{A_1}^2} \qquad \text{for } A_1 + A_1 \rightleftharpoons A_2 \qquad (1)$$

$$K_{AB} = \frac{x_{AB}}{x_{A_1} x_{B_1}} \qquad \text{for } A_1 + B_1 \rightleftharpoons AB \qquad (2)$$

$$K_{AC} = \frac{x_{AC}}{x_{A_1} x_{C_1}} \qquad \text{for } A_1 + C_1 \rightleftharpoons AC \qquad (3)$$

Further, the thermodynamic dimerisation constant for acetic acid is given by

$$K_T = \frac{x_{A_2}^{\star} \gamma_{A_2}^{\star}}{\left(x_{A_1}^{\star} \gamma_{A_1}^{\star}\right)^2} = K_x^{\star} K_\gamma^{\star} = \frac{x_{A_2} \gamma_{A_2}}{\left(x_{A_1} \gamma_{A_1}\right)^2} = K_x K_\gamma \qquad (4)$$

The nominal mole fractions of the three components are related to the monomer mole fractions of the chemical species present in the mixture:

$$x_A = \frac{x_{A_1} + 2K_x x_{A_1}^2 + K_{AB} x_{A_1} x_{B_1} + K_{AC} x_{A_1} x_{C_1}}{x_{A_1} + 2K_x x_{A_1}^2 + 2K_{AB} x_{A_1} x_{B_1} + 2K_{AC} x_{A_1} x_{C_1} + x_{B_1} + x_{C_1}} \qquad (5)$$

$$x_B = \frac{x_{B_1} + K_{AB} x_{A_1} x_{B_1}}{x_{A_1} + 2K_x x_{A_1}^2 + 2K_{AB} x_{A_1} x_{B_1} + 2K_{AC} x_{A_1} x_{C_1} + x_{B_1} + x_{C_1}} \qquad (6)$$

$$x_C = \frac{x_{C_1} + K_{AC} x_{A_1} x_{C_1}}{x_{A_1} + 2K_x x_{A_1}^2 + 2K_{AB} x_{A_1} x_{B_1} + 2K_{AC} x_{A_1} x_{C_1} + x_{B_1} + x_{C_1}} \qquad (7)$$

The sum of the true mole fractions of all the chemical species must be unity:

$$x_{A_1} + x_{A_2} + x_{AB} + x_{B_1} + x_{AC} + x_{C_1}$$
$$= x_{A_1} + K_x x_{A_1}^2 + K_{AB} x_{A_1} x_{B_1} + x_{B_1} + K_{AC} x_{A_1} x_{C_1} + x_{C_1} = 1 \qquad (8)$$

Molecular interactions between the chemical species are described using the NRTL equation [5]. The activity coefficient of any species i is given by

$$\ln \gamma_i = \frac{\sum_i \tau_{ji} G_{ji} x_j}{\sum_k G_{ki} x_k} + \sum_j \frac{x_j G_{ij}}{\sum_k G_{kj} x_k} \left(\tau_{ij} - \frac{\sum_r x_r \tau_{rj} G_{rj}}{\sum_k G_{kj} x_j} \right) \qquad (9)$$

where τ_{ji} and G_{ji} are expressed by

$$\tau_{ji} = a_{ji}/T \qquad (10)$$

$$G_{ji} = \exp(-\alpha_{ji} \tau_{ji}) \qquad (11)$$

According to the model assumptions that reduce the number of adjustable molecular parameters, many molecular interaction parameters are interrelated to each other: $a_{A_1A_2} = a_{A_2A_1} = -100$ K for acetic acid monomer–dimer; for acetic acid–water, $a_{A_1B_1} = 2a_{A_2B_1}$, $a_{B_1A_1} = 2a_{B_1A_2}$, $a_{A_1AB} = a_{ABA_1} = a_{B_1AB} = a_{ABB_1} = 2a_{A_2AB} = 2a_{ABA_2}$; for acetic acid–solvating component, $a_{A_1C_1} = 2a_{A_2C_1}$, $a_{C_1A_1} = 2a_{C_1A_2}$, $a_{A_1AC} = a_{ACA_1} = a_{C_1AC} = a_{ACC_1} = 2a_{A_2AC} = 2a_{ACA_2}$. Values of $a_{B_1C_1}$ and $a_{C_1B_1}$ are obtained from the mutual solubility data of the water–non-associated component systems with a value of $\alpha_{BC} = \alpha_{CB} = 0.25$. For acetic acid–non-polar component mixtures the value of α_{AC} ($= \alpha_{CA}$) is an adjustable parameter and for acetic acid–polar component mixtures α_{AC} is fixed as 0.3. Six remaining binary molecular interactions, which never exist in each binary mixture, are to be fitted to ternary experimental data or to be approximately estimated from the known binary parameters. These parameters are assumed to be $a_{ABC_1} = a_{A_2C_1}$, $a_{C_1AB} = a_{C_1A_2}$, $a_{ACB_1} = a_{A_2B_1}$, $a_{B_1AC} = a_{B_1A_2}$, $a_{ABAC} = (a_{A_2AC} + a_{ABA_2})/2$ and $a_{ACAB} = (a_{ACA_2} + a_{A_2AB})/2$.

The mole fraction equilibrium constant $K_x^\star$ and the enthalpy of hydrogen bond formation $h_A^\star$ for the dimerisation of pure acetic acid are $K_x^\star(20\,°C) = 62$ and $h_A^\star = -26$ kJ mol^{-1} as given by Freedman [6]. This value of $h_A^\star$ fixes

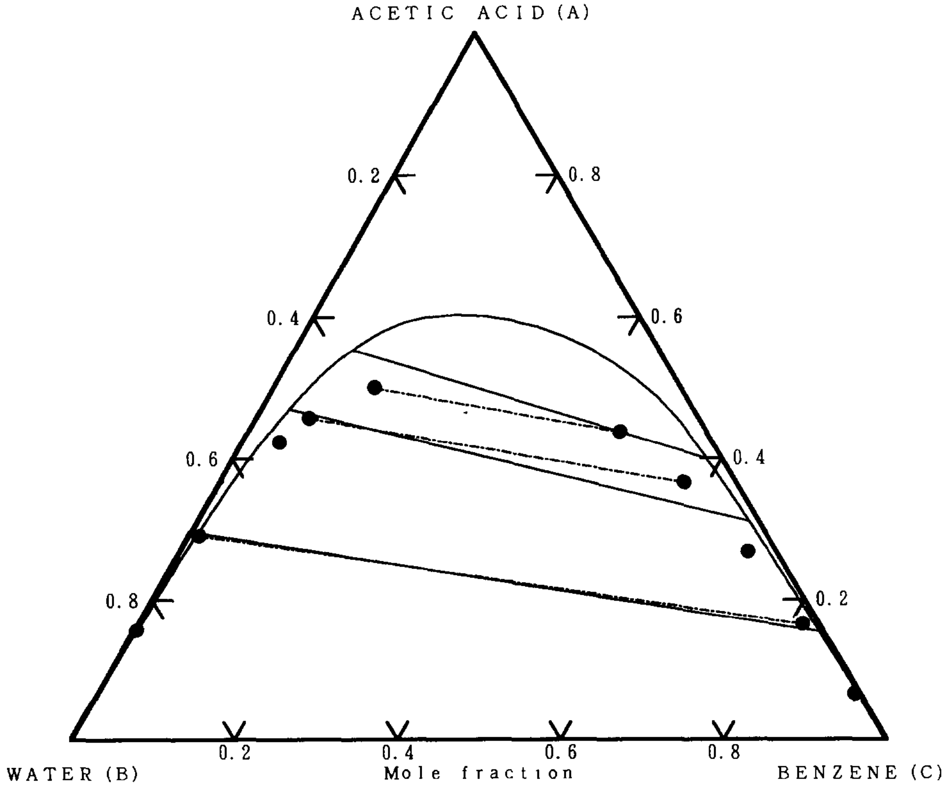

Fig. 1. Liquid–liquid equilibrium for acetic acid–water–benzene at 25 °C: experimental (·–·–·) [17] and calculated (———) tie-lines.

the temperature dependence of $K_x^\star$ by an integrated form of the van't Hoff equation:

$$K_x^\star = K_x^\star(20\,°\mathrm{C})\ \exp[(h_\mathrm{A}^\star/R)(1/293.15 - 1/T)] \tag{12}$$

The thermodynamic dimerisation constant K_T depends on temperature. At any temperature $K_x^\star$ is evaluated, then $x_{\mathrm{A}_1}^\star$ and $x_{\mathrm{A}_2}^\star$ are determined from eqn. (1). $K_\gamma^\star$ is calculated using eqn. (9) with $a_{\mathrm{A}_1\mathrm{A}_2} = a_{\mathrm{A}_2\mathrm{A}_1} = -100$ K and $\alpha_{\mathrm{A}_1\mathrm{A}_2} = \alpha_{\mathrm{A}_2\mathrm{A}_1} = 0.3$ for acetic acid. Finally K_T is given by the product of $K_x^\star$ and $K_\gamma^\star$.

In an associated solution the activity of any nominal component is equal to that of its monomer as pointed out by Prigogine and Defay [7] and the following equations hold for three components:

$$x_\mathrm{A}\gamma_\mathrm{A} = \frac{x_{\mathrm{A}_1}\gamma_{\mathrm{A}_1}}{x_{\mathrm{A}_1}^\star\gamma_{\mathrm{A}_1}^\star} \tag{13}$$

$$x_\mathrm{B}\gamma_\mathrm{B} = x_{\mathrm{B}_1}\gamma_{\mathrm{B}_1} \tag{14}$$

$$x_\mathrm{C}\gamma_\mathrm{C} = x_{\mathrm{C}_1}\gamma_{\mathrm{C}_1} \tag{15}$$

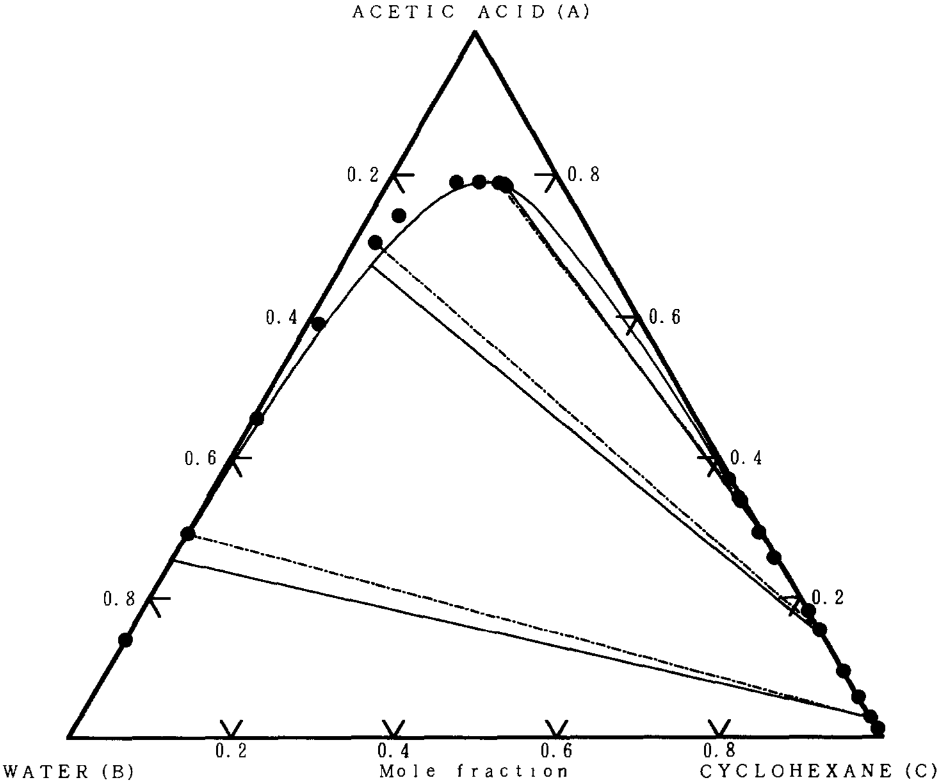

Fig. 2. Liquid–liquid equilibrium for acetic acid–water–cyclohexane at 25 °C: experimental (·–·–·) [18] and calculated (———) tie-lines.

TABLE 1

Calculated results of phase equilibrium data reduction for binary mixtures

System (A–B)	Temperature (°C)	Number of data points (type)	Root-mean-square deviations				Parameters			Variance of fit [a]	Reference
			δP (Torr)	δT (K)	δx ($\times 10^3$)	δy ($\times 10^3$)	$a_{A_1B_1}$ (K)	$a_{B_1A_1}$ (K)	α_{AB}		
Acetic acid–benzene	25	13 (VL)	1.18	0.00	0.0	6.3	120.42	491.61	0.3800	7.51	8
Acetic acid–cyclohexane	25	17 (VL)	0.38	0.00	0.5	7.1	916.41	891.93	0.4280	7.22	9
Acetic acid–tetrachloromethane	20	18 (VL)	0.42	0.00	0.0		369.91	645.98	0.8955	0.21	10
Acetic acid–toluene	30	15 (VL)	0.27	0.00	0.0	4.0	387.66	441.96	0.9602	2.27	11
Acetic acid–2-butanone	68.51	8 (VL) [b]	2.11	0.00	0.7	4.8	−1376.72	2244.68	0.1378	12.26	12
			2.05	0.00	1.0	2.9	−568.28	548.91	2400.84 [c]	9.97	
Acetic acid–ethyl acetate	65	11 (VL)	1.75	0.04	1.5	11.3	−81.25	−141.85	4.694	27.46	13
			1.65	0.03	1.4	10.7	−613.43	757.43	844.65 [c]	24.62	
Acetic acid–water	20	10 (VL)	0.10	0.00	0.2	2.1	756.99	−383.97	−121.49 [c]	0.79	14
Water–benzene	25	1 (MS)					1901.6	1372.0	0.25		15
Water–cyclohexane	25	1 (MS)					3004.1	1992.2	0.25		15
Water–tetrachlomethane	25	1 (MS)					2377.3	1811.9	0.25		15
Water–toluene	25	1 (MS)					2304.5	1493.3	0.25		15
Water–2-butanone	25	1 (MS)					811.18	117.39	0.25		15
Water–ethyl acetate	30	1 (MS)					1094.0	280.81	0.25		15

[a] Variance of fit = (sum of squared, weighted residuals)/(number of degrees of freedom) = F/(number of data points − number of parameters)

[b] One erroneous point rejected.

[c] Refers to a_{A_1AB}(K).

Ternary liquid–liquid equilibrium calculations are performed using the thermodynamic relations for any component in the conjugated phases I and II:

$$(x_i\gamma_i)^{\mathrm{I}} = (x_i\gamma_i)^{\mathrm{II}} \qquad i = \mathrm{A, B, C} \tag{16}$$

The heterodimerisation constants K_{AB} and K_{AC} and the enthalpies of complex formation h_{AB} and h_{AC} are as follows [3,4]: for acetic acid–water $K_{\mathrm{AB}} = 2$ at 20 °C and $h_{\mathrm{AB}} = -14.1$ kJ mol^{-1}; for acetic acid–2-butanone $K_{\mathrm{AC}} = 0.7$ at 55 °C and $h_{\mathrm{AC}} = -12.8$ kJ mol^{-1}; for acetic acid–ethyl acetate $K_{\mathrm{AC}} = 0.6$ at 55 °C and $h_{\mathrm{AC}} = -11.2$ kJ mol^{-1}. These equilibrium constants vary with temperature through the van't Hoff equation.

An iterative method was used to determine the monomer mole fractions of the chemical species in the ternary mixture for any set of the nominal mole fractions of components in such a way as to fulfil eqns. (4)–(7) and (13)–(15). Then the preset values of the nominal mole fractions are checked as to whether they satisfy eqn. (16). If not, the preset values of the nominal

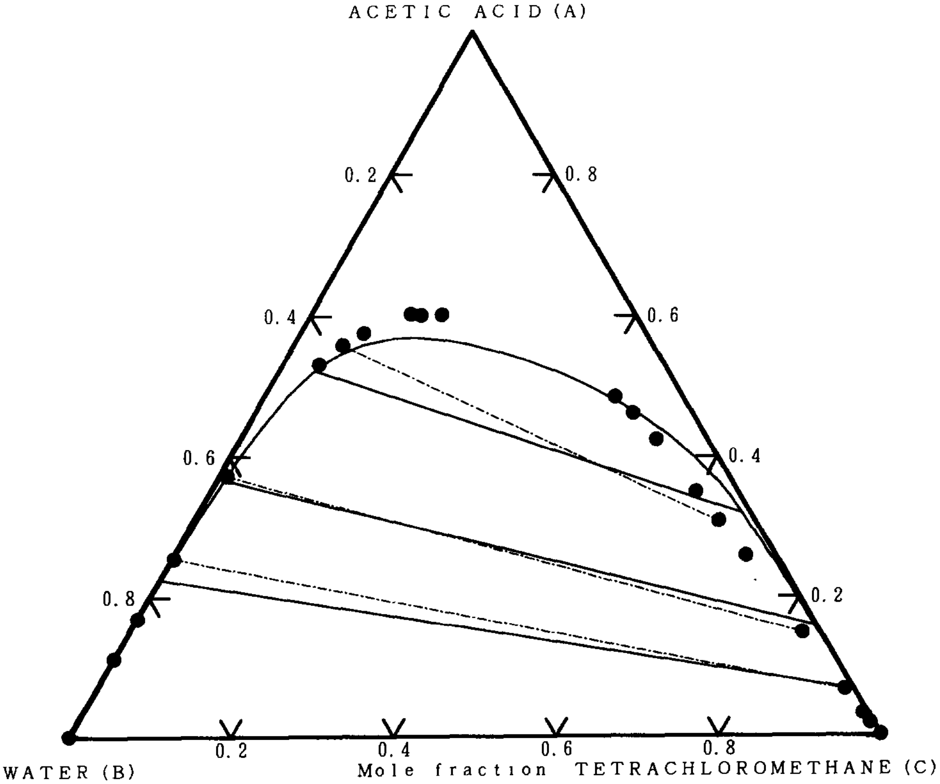

Fig. 3. Liquid–liquid equilibrium for acetic acid–water–tetrachloromethane at 25 °C: experimental (·—·—·) [19] and calculated (———) tie lines.

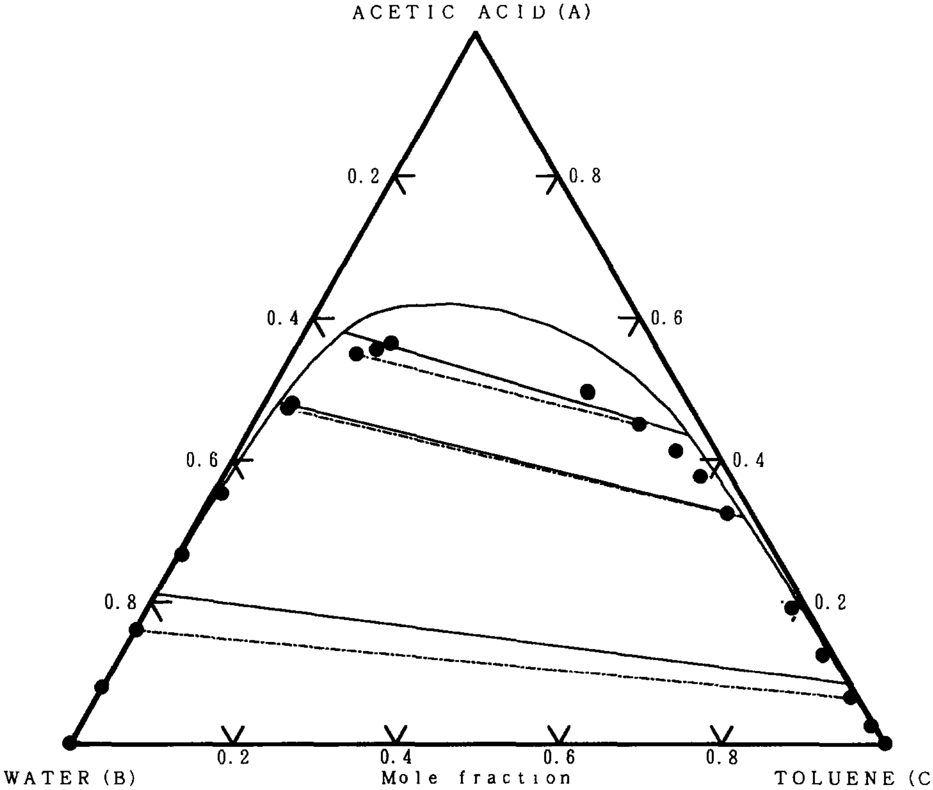

Fig. 4. Liquid–liquid equilibrium for acetic acid–water–toluene at 25 °C: experimental (·–·–·) [17] and calculated (———) tie-lines.

mole fractions are readjusted and another loop starts to find a new set of the mole fractions of the chemical species.

CALCULATED RESULTS AND DISCUSSION

Table 1 gives detailed results of binary phase equilibrium data reduction. The binary parameters from vapour–liquid equilibrium data were taken from previous papers [1,3,4] and those from mutual solubilities were obtained from smoothed values given by Sørensen and Arlt [15]. These parameters were used to calculate ternary liquid–liquid equilibria.

Experimental ternary liquid–liquid equilibrium data sets are available from the compilation of Sørensen and Arlt [16], for acetic acid–water–benzene at 25 °C [17], for acetic acid–water–cyclohexane at 25 °C [18], for acetic acid–water–tetrachloromethane at 25 °C [19], for acetic acid–water–toluene at 25 °C [17], for acetic acid–water–2-butanone at 25 °C [20] and for acetic acid–water–ethyl acetate at 30 °C [21]. Figures 1–6 illustrate reasonable agreement between the experimental and calculated solubility envelopes.

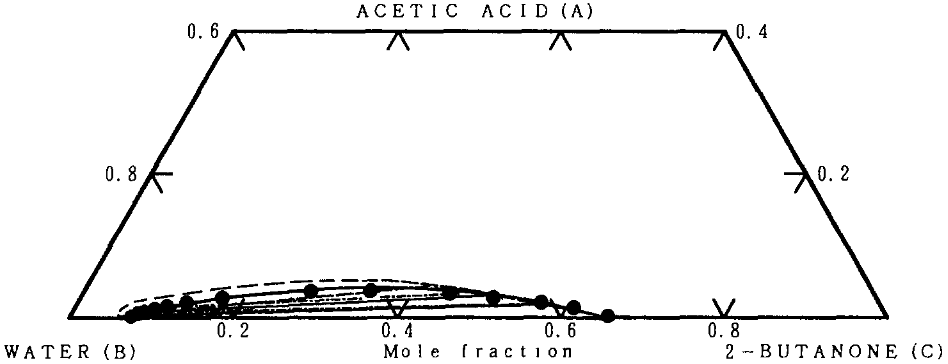

Fig. 5. Liquid–liquid equilibrium for acetic acid–water–2-butanone at 25 °C: experimental (·–·–·) [20] and calculated (———, $K_{AC} \neq 0$; — — —, $K_{AC} = 0$) tie-lines.

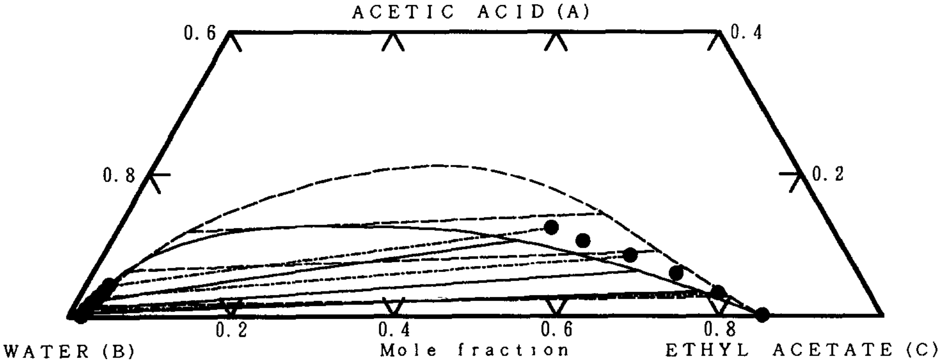

Fig. 6. Liquid–liquid equilibrium for acetic acid–water–ethyl acetate at 30 °C: experimental (·–·–·) [21] and calculated (———, $K_{AC} \neq 0$; — — —, $K_{AC} = 0$) tie-lines.

Incorporating the solvation constant between acetic acid and 2-butanone or ethyl acetate gives smaller envelopes as shown in Figs. 5 and 6.

It may be concluded that the association model used is able to predict ternary liquid–liquid equilibria for mixtures containing acetic acid, water and a non-associated component with sufficient accuracy.

LIST OF SYMBOLS

A, B, C	acetic acid, water and a non-associated component
a_{ji}	NRTL binary interaction parameter for the j–i pair
F	objective function used in vapour–liquid equilibrium data reduction (refs. 1, 2)
G_{ji}	coefficient as defined by $\exp(-\alpha_{ji}\tau_{ji})$
h_A	enthalpy of hydrogen bond formation for acetic acid

h_{AB}, h_{AC}	enthalpies of complex formation
K_{AB}, K_{AC}	heterodimerisation constants
K_T	thermodynamic equilibrium constant
K_x	liquid phase mole fraction dimerisation constant as defined by $x_{A_2}/x_{A_1}^2$
K_γ	activity coefficient ratio as defined by $\gamma_{A_2}/\gamma_{A_1}^2$
R	universal gas constant
T	absolute temperature
x_i	liquid phase mole fraction of chemical species i

Greek letters

α_{ji}	non-randomness parameter for the j–i pair
γ_i	activity coefficient of component i or species i
δP, δT	root-mean-square deviations in pressure and temperature
δx, δy	root-mean-square deviations in liquid phase and vapour phase mole fractions
τ_{ji}	coefficient as defined by a_{ji}/T

Subscripts

A_1, A_2	monomer and dimer of acetic acid
AB, AC	1 : 1 complexes of acetic acid with water and a solvating component
B_1, C_1	monomers of water and a non-associating component
i, j, k, r	chemical molecular species or components

Superscript

$*$	pure liquid reference state

REFERENCES

1 I. Nagata and T. Satoh, Thermochim. Acta, 132 (1988) 53.
2 I. Nagata and T. Satoh, Thermochim. Acta, 138 (1989) 207.
3 I. Nagata, Thermochim. Acta, 168 (1990) 213.
4 I. Nagata and T. Tanimura, Thermochim. Acta, 168 (1990) 218.
5 H. Renon and J.M. Prausnitz, AIChE J., 14 (1968) 135.
6 E. Freedman, J. Chem. Phys., 21 (1953) 1784.
7 I. Prigogine and R. Defay, Chemical Thermodynamics, Longmans Greens, London, 1954, Chap. 26.
8 F. Hovorka and D. Dreisbach, J. Am. Chem. Soc., 56 (1934) 1664.
9 B.S. Lark, T.S. Banipal, S. Singh and R.C. Palta, J. Chem. Eng. Data, 29 (1984) 277.
10 G. Miksch, F. Ratkovics and F. Kohler, J. Chem. Thermodyn., 1 (1969) 257.
11 N.P. Markuzin and L.M. Pavlova, Zh. Prikl. Khim. (Leningrad), 44 (1971) 311.

12 P. Rasmussen, L. Kierkegaard and A. Fredenslund, Chemical Engineering with Per Søltoft, Teknisk Forlag a-s, Copenhagen, 1977, p. 129.

13 E.A. Macedo and P. Rasmussen, J. Chem. Eng. Data, 27 (1982) 463.

14 W.S. Lazeeva and N.P. Markuzin, Zh. Prikl. Khim. (Leningrad), 46 (1973) 360.

15 J.M. Sørensen and W. Arlt, Liquid–Liquid Equilibrium Data Collection, Binary Systems, Chemistry Data Series, Vol. V, Part 1, DECHEMA, Frankfurt am Main, 1979, pp. 6, 217, 224, 341, 384, 448.

16 J.M. Sørensen and W. Arlt, Liquid–Liquid Equilibrium Data Collection, Ternary Systems, Chemistry Data Series, Vol. V, Part 2. DECHEMA, Frankfurt am Main, 1980, pp. 4, 219, 220, 257, 259, 293.

17 K. Fuse and A. Iguchi, Kagaku Kogaku, 35 (1971) 107.

18 K. Fuse and A. Iguchi, Kagaku Kogaku, 34 (1970) 1226.

19 K. Fuse and A. Iguchi, Kagaku Kogaku, 34 (1971) 1001.

20 K. Fuse and A. Iguchi, Kagaku Kogaku, 35 (1971) 477.

21 V.R. Sohoni and U.R. Warhadpande, Ind. Eng. Chem., 44 (1952) 1428.