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Thermodynamics of liquid mixtures of acids: phase equilibria and excess molar enthalpies of acetic acid mixtures with active non-associating components

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Abstract

Vapour–liquid equilibria and excess molar enthalpies of binary solutions of acetic acid with water, 2-butanone, methyl acetate and ethyl acetate are calculated using the UNIQUAC associated-solution model, which takes into account the autodimerization of acetic acid and the heteroassociation of unlike molecules. Prediction of ternary liquid–liquid equilibria for the acetic acid + water + nonassociating component systems are demonstrated from the same model with only binary parameters. The calculated results agree well with the experimental values.

LIST OF SYMBOLS

A, A_1, A_2	acid, acid monomer and acid dimer
a_{JI}	binary interaction parameter for J–I pair
AB	1:1 chemical complex involving acid and active component
B, B_1	nonassociating component and nonassociating component monomer
B^F_{II}	free contribution to second virial coefficient of component I
C_{JI}, D_{JI}	coefficients of eqn. (14)
F	objective function as defined by eqn. (22)
H^E	excess molar enthalpy
h_A	enthalpy of hydrogen bond formation for acid dimer
h_{AB}	enthalpy of complex formation between components A and B
K_A	equilibrium constant of acid dimer formation
K_{AB}	solvation constant between components A and B
N	number of experimental data points
P	total pressure

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P^s_I	saturated vapour 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 acid mixture given by eqn. (10)
V^o_A	true molar volumes of pure acid given by eqns. (11)
v^L_I	pure liquid molar volume of component I
x_I	liquid-phase mole fraction of component I
y_I	vapour-phase mole fraction of component I
y_{I_1}	vapour-phase mole fraction of monomeric component I
Z	lattice coordinate number, here set as 10

Greek letters

γ_I	activity coefficient of component I
θ_I	surface fraction of component I
σ_P, σ_T, σ_x, σ_y	standard deviations in pressure, temperature, liquid and vapour compositions, respectively
τ_{JI}	coefficient as defined by $\exp(-a_{JI}/T)$
Φ_I	segment fraction of component I
Φ_{I_1}	monomer segment fraction of component I
$\Phi^o_{I_1}$	monomer segment fraction of pure acid given by eqn. (12)
ϕ_I	fugacity coefficient of component I at P and T
ϕ^s_I	fugacity coefficient of pure component I at P^s_I and T

Subscripts

A	acid
A_1, A_2	acid monomer and acid dimer
AB	binary 1:1 complex between components A and B
B	non-associating component
chem	chemical
I, J, K	components I, J and K
phys	physical

Superscripts

^{o}	pure liquid reference state
*	50°C

INTRODUCTION

The UNIQUAC associated-solution model has been successfully applied to describe vapour–liquid equilibria and excess molar enthalpies of alkanoic acid + hydrocarbon mixtures, under the assumption that the acid self-associates to form dimers in the vapour and liquid phases [1, 2]. The same model has been extended to represent vapour–liquid equilibrium and excess molar enthalpy data for acid + alcohol mixtures [3].

In this paper, based on the UNIQUAC associated-solution model, we study the vapour–liquid equilibria and excess molar enthalpies of binary mixtures of acetic acid + water, +2-butanone, +methyl acetate and +ethyl acetate and the prediction of ternary liquid–liquid equilibria of acetic acid solutions including water and a non-associated component from binary parameters alone.

SOLUTION MODEL

We assume that in the liquid phase acetic acid (A) forms cyclic dimers by autoassociation, and acetic acid and an active non-associating component (B) solvate to yield 1:1 chemical complexes. the equilibrium constants for self-association and solvation, K_A and K_{AB}, are defined by

$$K_A = \frac{\Phi_{A_2}}{\Phi_{A_1}^2}\frac{1}{2} \qquad \text{for } A_1 + A_1 = A_2$$

$$= K_A^* \exp\left[-\frac{h_A}{R}\left(\frac{1}{T} - \frac{1}{T^*}\right)\right] \tag{1}$$

$$K_{AB} = \frac{\Phi_{AB}}{\Phi_{A_1}\Phi_{B_1}}\frac{1}{r_A + r_B} \qquad \text{for } A_1 + B_1 = AB$$

$$= K_{AB}^* \exp\left[-\frac{h_{AB}}{R}\left(\frac{1}{T} - \frac{1}{T^*}\right)\right] \tag{2}$$

where Φ is the segment fraction, h_A the enthalpy of hydrogen bond for dimer formation, h_{AB} the enthalpy of complex formation and superscript * denotes a reference temperature, here equal to 50°C.

Binary systems

Activity coefficient

The UNIQUAC associated-solution model provides the following expressions of the activity coefficients for acetic acid (A) and the active non-associated component (B)

$$\ln \gamma_A = \ln\left(\frac{\Phi_{A_1}}{\Phi_{A_1}^{\circ}}\right) + r_A\left(\frac{1}{V_A^{\circ}} - \frac{1}{V}\right) - \left(\frac{Z}{2}\right)q_A\left[\ln\left(\frac{\Phi_A}{\theta_A}\right) + 1 - \frac{\Phi_A}{\theta_A}\right]$$

$$+ q_A\left[1 - \ln\left(\sum_J \theta_J \tau_{JA}\right) - \sum_J \frac{\theta_J \tau_{AJ}}{\sum_K \theta_K \tau_{KJ}}\right] \tag{3}$$

$$\ln \gamma_B = \ln\left(\frac{\Phi_B}{x_B}\right) + 1 - \frac{r_B}{V} - \left(\frac{Z}{2}\right)q_B\left[\ln\left(\frac{\Phi_B}{\theta_B}\right) + 1 - \frac{\Phi_B}{\theta_B}\right]$$

$$+ q_B\left[1 - \ln\left(\sum_J \theta_J \tau_{JB}\right) - \sum_J \frac{\theta_J \tau_{BJ}}{\sum_K \theta_K \theta_{KJ}}\right] \tag{4}$$

where Z is the lattice coordination number, here set as 10, and the segment fraction Φ_I, the surface fraction θ_I, the binary coefficient τ_{JI} related to the binary interaction parameter a_{JI} are expressed by

$$\Phi_I = r_I x_I \Big/ \sum_J r_J x_J \tag{5}$$

$$\theta_I = q_I x_I \Big/ \sum_J q_J x_J \tag{6}$$

$$\tau_{JI} = \exp(-a_{JI}/T) \tag{7}$$

The monomer segment fractions of both components are simultaneously solved from eqns. (8) and (9).

$$\begin{aligned}\Phi_A &= \Phi_{A_1} + \Phi_{A_2} + \Phi_{AB} r_A / r_{AB} \\ &= \Phi_{A_1} + 2K_A \Phi_{A_1}^2 + K_{AB} \Phi_{A_1} \Phi_{B_1} r_A \end{aligned} \tag{8}$$

$$\begin{aligned}\Phi_B &= \Phi_{B_1} + \Phi_{AB} r_B / r_{AB} \\ &= \Phi_{B_1} + K_{AB} \Phi_{A_1} \Phi_{B_1} r_B \end{aligned} \tag{9}$$

where $r_{AB} = r_A + r_B$ is assumed.

The true molar volume of the mixture is given by

$$\frac{1}{V} = \frac{\Phi_{A_1}}{r_A}(1 + K_A \Phi_{A_1}) + \frac{\Phi_{B_1}}{r_B} + K_{AB} \Phi_{A_1} \Phi_{B_1} \tag{10}$$

At pure acid state V_A° and $\Phi_{A_1}^\circ$ are given by eqns. (11) and (12)

$$\frac{1}{V_A^\circ} = \frac{1 - K_A \Phi_{A_1}^{\circ 2}}{r_A} \tag{11}$$

$$\Phi_{A_1}^\circ = [-1 + (1 + 8K_A)^{0.5}]/4K_A \tag{12}$$

Excess molar enthalpy

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

$$\begin{aligned} H^E &= H_{\text{chem}}^E + H_{\text{phys}}^E \\ &= h_A x_A K_A \left(\frac{\Phi_{A_1}^2}{\Phi_A} - \Phi_{A_1}^{\circ 2} \right) + \frac{h_{AB} K_{AB} \Phi_{A_1} \Phi_{B_1} r_A x_A}{\Phi_A} \\ &\quad - R \sum_I q_I x_I \frac{\sum_J \theta_J \dfrac{\partial \tau_{JI}}{\partial (1/T)}}{\sum_J \theta_J \tau_{JI}} \end{aligned} \tag{13}$$

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

$$a_{JI} = C_{JI} + D_{JI}(T - 273.15) \qquad (14)$$

Ternary systems

In a ternary mixture containing acid (A) and two active non-associating components (B and C), we assume additional complex formation between acid and component C.

$$K_{AC} = \frac{\Phi_{AC}}{\Phi_{A_1}\Phi_{C_1}} \frac{1}{r_A + r_C} \qquad \text{for } A_1 + C_1 = AC$$

$$= K^*_{AC} \exp\left[-\frac{h_{AC}}{R}\left(\frac{1}{T} - \frac{1}{T^*}\right)\right] \qquad (15)$$

The monomer segment fractions, Φ_{A_1}, Φ_{B_1} and Φ_{C_1}, are given by simultaneous solution of the following mass balance equations:

$$\Phi_A = \Phi_{A_1} + 2K_A\Phi^2_{A_1} + K_{AB}\Phi_{A_1}\Phi_{B1}r_A + K_{AC}\Phi_{A_1}\Phi_{C_1}r_A \qquad (16)$$

$$\Phi_B = \Phi_{B_1} + K_{AB}\Phi_{A_1}\Phi_{B_1}r_B \qquad (17)$$

$$\Phi_C = \Phi_{C_1} + K_{AC}\Phi_{A_1}\Phi_{C_1}r_C \qquad (18)$$

The true molar volume V of the ternary mixture is expressed by

$$\frac{1}{V} = \frac{\Phi_{A_1}}{r_A}(1 + K_A\Phi_{A_1}) + \frac{\Phi_{B_1}}{r_B} + K_{AB}\Phi_{A_1}\Phi_{B_1} + \frac{\Phi_{C_1}}{r_C} + K_{AC}\Phi_{A_1}\Phi_{C_1} \qquad (19)$$

The activity coefficient of component C is obtained by changing the subscript B in eqn. (4) to the subscript C.

CALCULATED RESULTS

Table 1 shows the molecular structural parameters of pure components, r and q, which were estimated according to the method of Vera et al. [4].

Vapour–liquid equilibrium data were reduced using the thermodynamic

TABLE 1

Molecular structural parameters for pure components

Component	r	q	Component	r	q
Acetic acid	1.78	1.62	Methyl acetate	2.25	2.00
Benzene	2.56	2.05	Toluene	3.10	2.48
2-Butanone	2.60	2.28	Tetrachloromethane	2.71	2.37
Cyclohexane	3.18	2.55	Water	0.73	1.19
Ethyl acetate	2.79	2.43			

TABLE 2

Solvation parameters for binary mixtures

System (A + B)	K_{AB} at 323.15 K	$-h_{AB}$/kJ mol^{-1}
Acetic acid + water	60	23.4
Acetic acid + 2-butanone	40	22.0
Acetic acid + ethyl acetate	40	20.5
Acetic acid + methyl acetate	40	20.5

relation

$$P\phi_I y_I = \gamma_I x_I \phi_I^s P_I^s \left[\frac{v_I^L(P - P_I^s)}{RT}\right] \tag{20}$$

where P is the total pressure, ϕ_I the fugacity coefficient of component I, y_I the vapour-phase mole fraction of component I, P_I^s the pure component vapour pressure taken from the original vapour–liquid equilibrium data set, v_I^L the pure-liquid molar volume estimated from the modified Rackett equation [5]. The fugacity coefficient ϕ_I is calculated from the chemical theory of vapour imperfections [6].

$$\phi_I = \frac{y_{I_1}}{y_I}\exp\left(\frac{PB_{II}^F}{RT}\right) \tag{21}$$

where y_{I_1} is the vapour-phase monomer mole fraction of component I and B_{II}^F the free contribution to the second virial coefficient [7]. The association parameters of acetic acid were taken from Tamura and Nagata [1]: $K_A = 14651.2$ at 50°C and $-h_A = 44.5$ kJ mol^{-1}. The solvation parameters are shown in Table 2.

The computer program described by Prausnitz et al. [8] was used to seek an optimum set of the energy parameters by minimizing the object function.

$$F = \sum_{i=1}^{N}\left[\frac{(P_i - \hat{P}_i)^2}{\sigma_P^2} + \frac{(T_i - \hat{T}_i)^2}{\sigma_T^2} + \frac{(x_{1_i} - \hat{x}_{1_i})^2}{\sigma_x^2} + \frac{(y_{1_i} - \hat{y}_{1_i})^2}{\sigma_y^2}\right] \tag{22}$$

where a circumflex denotes the most probable calculated value corresponding to each measured variable and the standard deviations of the measured values are: for pressure, $\sigma_P = 1$ Torr; for temperature, $\sigma_T = 0.05$ K; for liquid-phase mole fraction, $\sigma_x = 0.001$; for vapour-phase mole fraction, $\sigma_y = 0.003$. Table 3 indicates the results of vapour–liquid equilibrium calculations and Figs. 1–4 compare the calculated results with the experimental values for some typical examples.

Table 4 lists the binary results of excess molar enthalpies. The coefficients, C_{JI} and D_{JI}, were obtained by minimizing the sum of the squares of the deviations between the experimental and calculated values.

TABLE 3

Calculated results of binary vapour–liquid equilibrium data

System (A + B)	Temp./°C	No. of data points	Root-mean square deviations				Parameters/K		Reference
			δp/Torr	$\delta T/K$	$\delta x \times 10^3$	$\delta y \times 10^3$	a_{AB}	a_{BA}	
Acetic acid + water	20	10	0.13	0.00	0.2	2.2	515.81	−244.68	9
	25	8	0.60	0.05	2.2	17.1	−29.06	72.47	9
	25	11	0.36	0.00	1.1	15.0	81.05	−62.13	10
	40	11	0.35	0.00	0.4	3.3	534.39	−262.06	9
	60	10	1.59	0.03	0.7	5.5	603.90	−300.70	11
	69.7	11	2.35	0.00	1.2	9.3	572.49	−294.46	11
	70	12	1.74	0.00	2.5	12.5	518.58	−282.59	10
	79.9	11	1.84	0.00	1.0	9.9	559.72	−300.32	11
	80	10	1.32	0.00	0.6	5.5	585.80	−307.80	9
	80.09	7	1.57	0.00	0.9	8.0	550.78	−291.86	9
	89.9	11	2.26	0.00	1.1	9.4	540.29	−300.79	11
Acetic acid + 2-butanone	68.51	8 [a]	2.25	0.00	1.2	6.5	−301.63	664.25	12
	78	9	5.47	0.01	2.7	5.2	−307.84	621.32	12
Acetic acid + ethyl acetate	65.01 ≈65.18	11	1.20	0.04	1.7	13.7	−245.14	451.27	13
	72.94 ≈73.08	11	1.77	0.07	3.1	22.2	−262.46	507.45	13
Water + benzene	25	MS [b]					546.62	1075.3	14
Water + 2-butanone	25	MS					21.44	379.69	14
Water + cyclohexane	25	MS					767.01	1490.5	14
Water + tetrachloromethane	25	MS					690.90	1453.4	14
Water + tolune	25	MS					539.46	1166.3	14
Water + ethyl acetate	30	MS					130.90	423.95	14

[a] One erroneous point rejected. [b] Mutual solubilities.

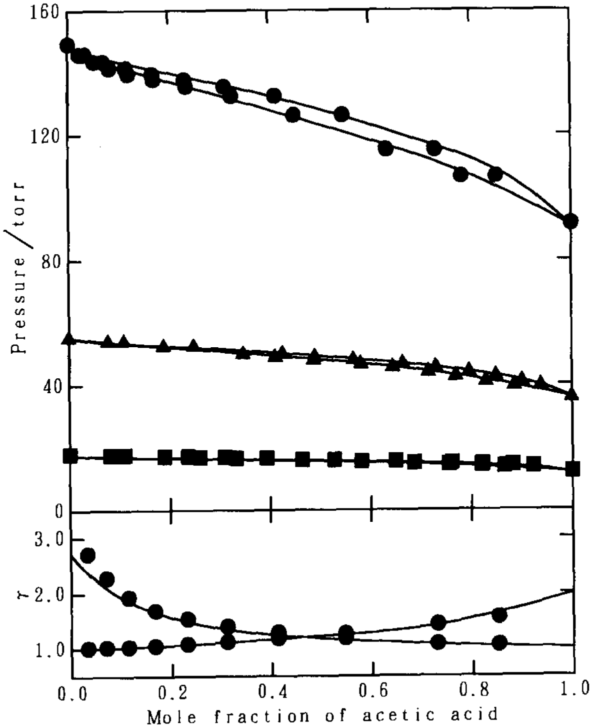

Fig. 1. Vapour–liquid equilibria for the acetic acid + water system. Calculated: —. Experimental: ■, 20°C [9]; ▲, 40°C [9]; ●, 60°C [11].

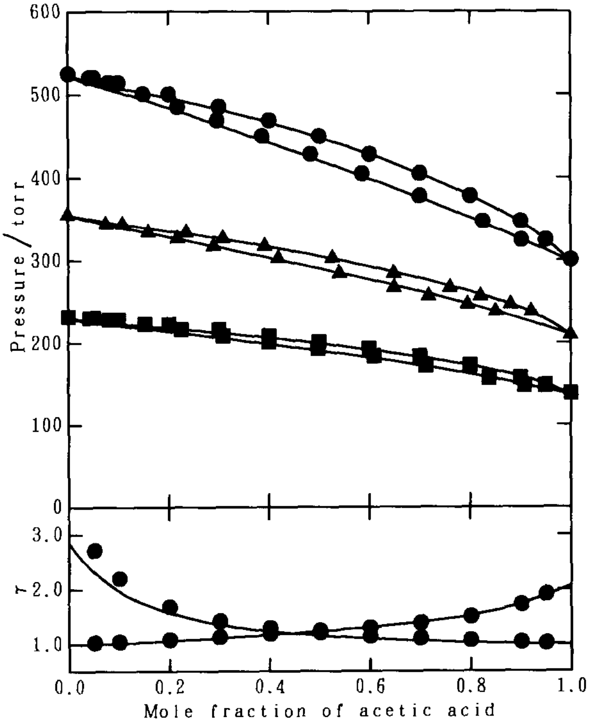

Fig. 2. Vapour–liquid equilibria for the acetic acid + water system. Calculated: —. Experimental: ■, 69.7°C [11]; ▲, 80°C [9]; ●, 89.9°C [11].

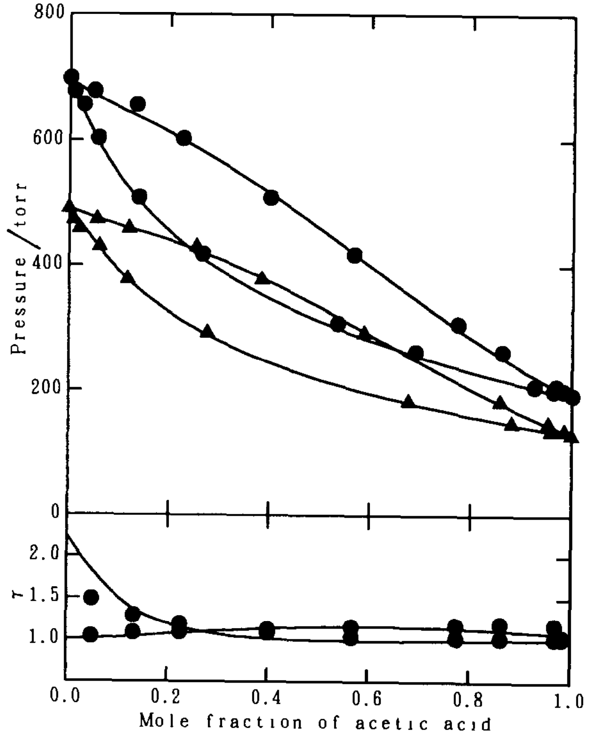

Fig. 3. Vapour–liquid equilibria for the acetic acid + 2-butanone system. Calculated: —. Experimental: ▲, 68.51°C [12]; ●, 78°C [12].

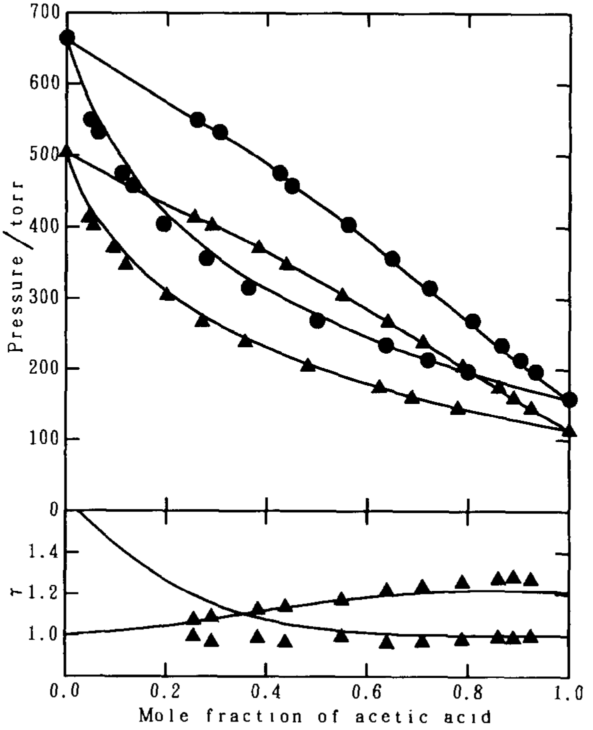

Fig. 4. Vapour–liquid equilibria for the acetic acid + ethyl acetate system. Calculated: —. Experimental: ▲, 65.01–65.18°C [13]; ●, 72.94–73.08°C [13].

TABLE 4

Calculated results of binary excess enthalpy data

System (A + B)	Temp./°C	No. of data points	Parameters				Abs. arith. mean dev.	Reference
			C_{BA}/K	D_{BA}	C_{AB}/K	D_{AB}		
Acetic acid + water	20	11	530.18	2.4578	253.33	−0.0934	2.83	15
Acetic acid + water	40	10	838.07	3.3492	327.43	0.1085	9.00	15
Acetic acid + 2-butanone	20	19	259.02	1.0128	457.27	1.7561	1.61	16
Acetic acid + ethyl acetate	19–26	9	352.40	1.6383	339.67	1.4212	1.48	15
Acetic acid + methyl acetate	35	13	124.53	0.6595	449.07	1.7307	3.07	15

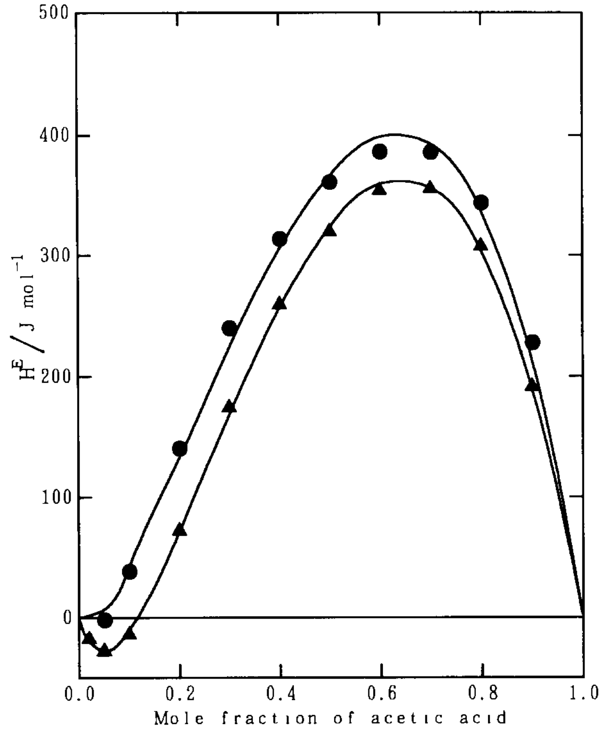

Fig. 5. Excess molar enthalpies for the acetic acid + water system. Calculated: —. Experimental: ▲, 20°C [15]; ●, 40°C [15].

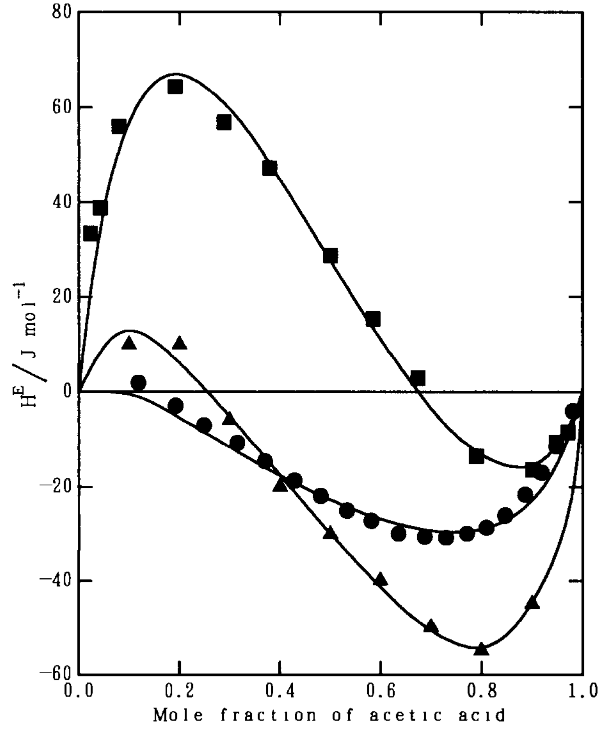

Fig. 6. Excess molar enthalpies for three acetic acid + organic compound systems. Calculated: —. Experimental: ●, acetic acid + 2-butanone at 20°C [16]; ▲ acetic acid + ethyl acetate at 19–26°C [15]; ■, acetic acid + methyl acetate at 35°C [15].

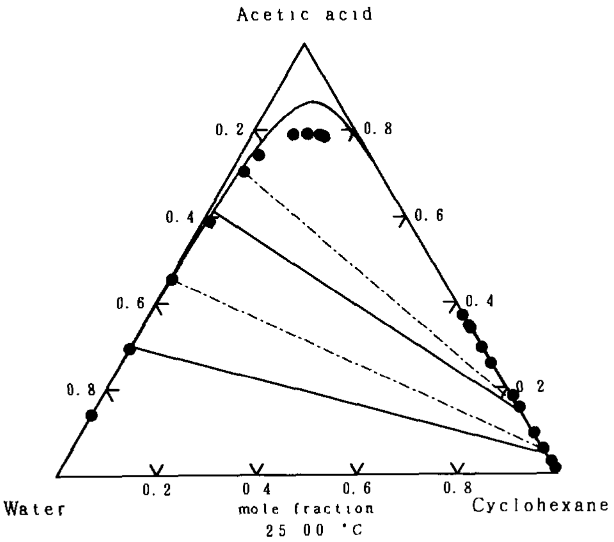

Fig. 7. Ternary liquid–liquid equilibria for the acetic acid + water + cyclohexane system at 25°C. Calculated: —. Experimental tie line [18]: ●– – –●.

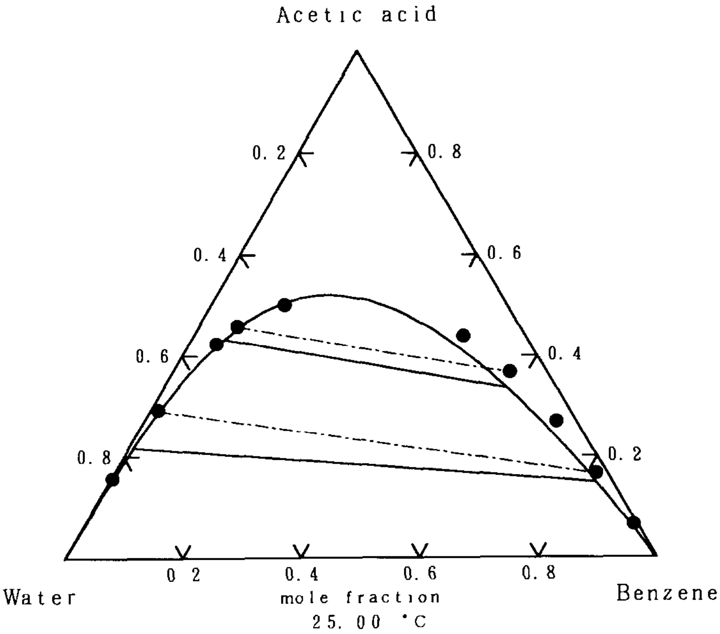

Fig. 8. Ternary liquid–liquid equilibria for the acetic acid + water + benzene system at 25°C. Calculated: —. Experimental tie line [18]: ●– – –●.

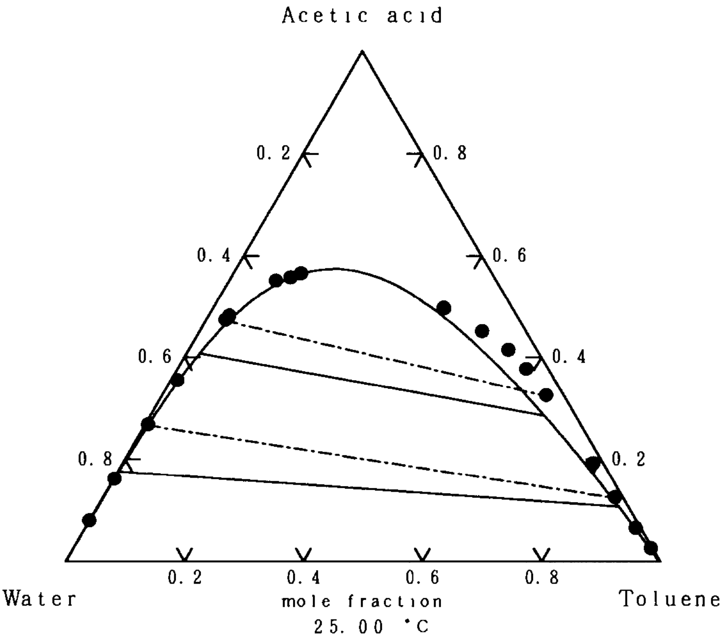

Fig. 9. Ternary liquid–liquid equilibria for the acetic acid + water + toluene system at 25°C. Calculated: —. Experimental tie line [18]: ●– – –●.

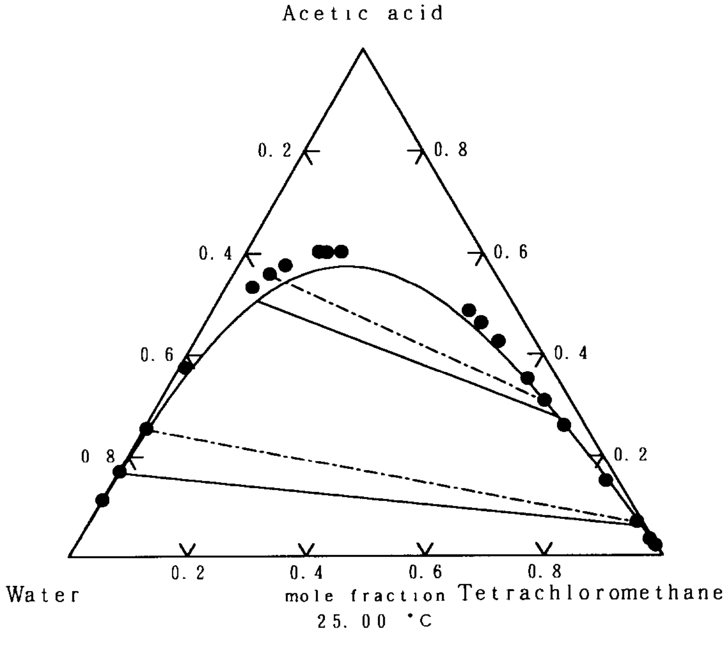

Fig. 10. Ternary liquid–liquid equilibria for the acetic acid + water + tetrachloromethane system at 25°C. Calculated: —. Experimental tie line [18]: ●– – –●.

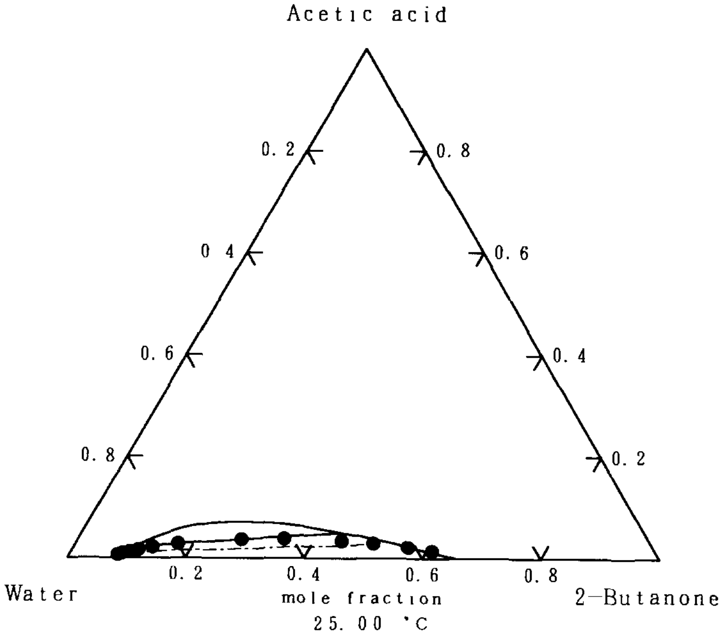

Fig. 11. Ternary liquid–liquid equilibria of the acetic acid + water + 2-butanone system at 25°C. Calculated: —. Experimental tie line [18]: ●- - -●.

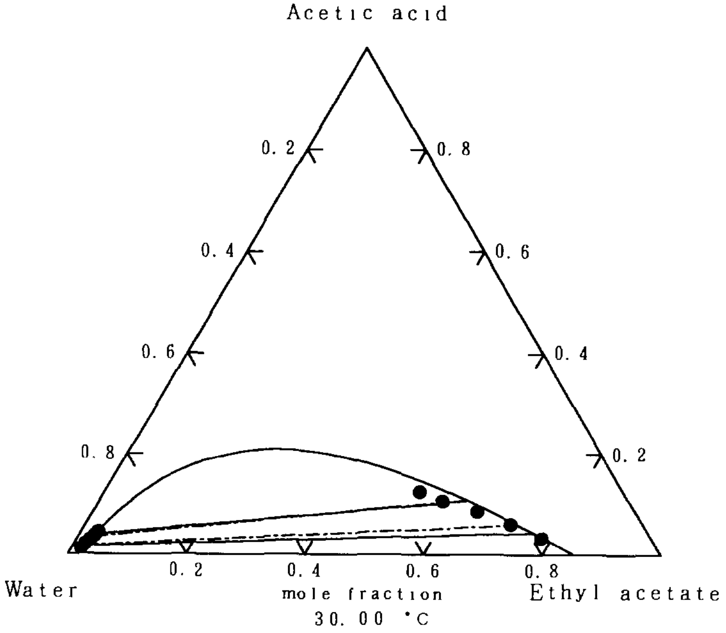

Fig. 12. Ternary liquid–liquid equilibria for the acetic acid + water + ethyl acetate at 30°C. Calculated: —. Experimental tie line [18]: ●- - -●.

The simplex method of Nelder and Mead [17] was used for this purpose. Figures 5 and 6 present the calculated and observed values of solutions of acetic acid with 2-butanone, ethyl acetate, methyl acetate and water.

Ternary prediction of liquid–liquid equilibrium was performed for six systems: acetic acid + water + cyclohexane, acetic acid + water + benzene, acetic acid + water + toluene, acetic acid + water + tetrachloromethane, acetic acid + water + 2-butanone and acetic acid + water + ethyl acetate. Figures 7–12 show that agreement is good.

We may conclude that the UNIQUAC associated-solution model is good in the correlation of vapour–liquid equilibrium and excess molar enthalpy data of binary acetic acid + active non-associating mixtures and could be used for the prediction of ternary liquid–liquid equilibrium data of solutions including acetic acid, water and one non-associated component.

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