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THERMODYNAMICS OF ASSOCIATED SOLUTIONS. VAPOUR–LIQUID EQUILIBRIUM FOR THE SYSTEMS ACETIC ACID–WATER AND ACETIC ACID–2-BUTANONE WITH ASSOCIATION IN BOTH PHASES

ISAMU NAGATA * and TSUTOMU SATOH

Department of Chemical Engineering, Division of Physical Sciences, Kanazawa University, Kodatsuno 2, Kanazawa 920 (Japan)

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ABSTRACT

A model using a concentration-dependent liquid-phase association constant for acetic acid was employed to correlate isothermal vapour–liquid equilibrium data for binary solutions of acetic acid with water and 2-butanone. Results of data reduction show that cross-dimerization between acetic acid and water is required to represent satisfactorily two sets of literature data.

LIST OF SYMBOLS

A, B	acetic acid and water or 2-butanone
a_{ij}	binary interaction parameter
F	objective function as defined by eqn. (14)
G_{ij}	coefficient as defined by $\exp(-\alpha_{ij}\tau_{ij})$
h_{AB}	enthalpy of complex formation
K	thermodynamic liquid-phase association constant
K_{AB}	liquid-phase mole fraction solvation constant as defined by $x_{AB}/x_{A_1}x_{B_1}$
K_x	liquid-phase mole fraction association constant as defined by $x_{A_2}/x_{A_1}^2$
K_γ	activity coefficient ratio as defined by $\gamma_{A_2}/\gamma_{A_1}^2$
P	total pressure
P_i^s	saturated vapour pressure of pure component i
R	universal gas constant
T	absolute temperature
v_i^L	molar liquid volume of pure component i
x_i	liquid-phase mole fraction of component i or species i
y_i	vapour-phase mole fraction of component i

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* Author to whom correspondence should be addressed.

Greek letters

α_{ij}	non-randomness parameter
γ_i	activity coefficient of component i
σ_P, σ_T	standard deviations in pressure and temperature
σ_x, σ_y	standard deviations in liquid-phase and vapour-phase mole fraction
τ_{ij}	coefficient as defined by a_{ij}/T
ϕ_i	vapour-phase fugacity coefficient of component i at T and P
ϕ_i^s	vapour-phase fugacity coefficient of pure component i at T and P_i^s

Subscripts

A_1, A_2	monomer and dimer of acetic acid
AB	1 : 1 complex of acetic acid and water
B_1	monomer of water or 2-butanone
i, j, k	components

Superscripts

$\hat{}$	calculated property
$\star$	pure-liquid reference state

INTRODUCTION

In a previous paper [1] a new model was presented to correlate binary isothermal vapour–liquid equilibrium data for solutions of acetic acid with benzene, n-heptane, toluene and tetrachloromethane, and to predict the ternary isothermal vapour–liquid equilibrium for acetic acid–toluene–n-heptane from binary parameters alone. The model uses the liquid-phase dimerization constant for pure acetic acid to derive a concentration-dependent association constant defined in terms of the thermodynamic association, and involves the NRTL equation [2] to describe molecular interactions between the chemical species present. Since the thermodynamic association constant is defined in terms of the activities of acetic acid monomer and dimer and is independent of concentration, it relates the activity coefficients of acetic acid monomer and dimer at a specific concentration to their values in pure acetic acid.

In this paper the model is extended to mixtures of acetic acid with water and 2-butanone.

SOLUTION MODEL

In the liquid phase the model assumes the existence of monomers (A_1) and dimers (A_2) of acetic acid and further that molecules of acetic acid and water (B) interact strongly to form complex AB according to $A_1 + B_1 = AB$. The thermodynamic dimerization constant for acetic acid K and the solvation constant K_{AB} in the liquid phase are defined as

$$K = \frac{x^\star_{A_2}\gamma^\star_{A_2}}{\left(x^\star_{A_1}\gamma^\star_{A_1}\right)^2} = \frac{x_{A_2}\gamma_{A_2}}{\left(x_{A_1}\gamma_{A_1}\right)^2} = K_x K_\gamma \tag{1}$$

$$K_{AB} = \frac{x_{AB}}{x_{A_1}x_{B_1}} \tag{2}$$

where x_{A_1}, x_{A_2}, x_{AB} and x_{B_1} are the true mole fractions of the monomer and dimer of acetic acid, the heterodimer of acetic acid and water and the monomer of water respectively, γ_{A_1} and γ_{A_2} are the activity coefficients of the acetic acid monomer and dimer, K_x is the liquid-phase mole fraction dimerization constant as defined by $x_{A_2}/x_{A_1}{}^2$, K_γ is the activity coefficient ratio expressed by $\gamma_{A_2}/\gamma_{A_1}{}^2$ and the superscript * refers to pure acetic acid state.

The activity coefficient of any i of the chemical species A_1, A_2, AB and B_1 is given by the NRTL equation [2]

$$\ln \gamma_i = \frac{\sum_i \tau_{ji} G_{ji} x_j}{\sum_k G_{ki} x_k} + \sum_j \frac{x_j G_{ij}}{\sum_k G_{kj} x_k}\left(\tau_{ij} - \frac{\sum_r x_r \tau_{rj} G_{rj}}{\sum_k G_{kj} x_k}\right) \tag{3}$$

where

$$\tau_{ji} = a_{ji}/T \tag{4}$$

$$G_{ji} = \exp(-\alpha_{ji}\tau_{ji}) \tag{5}$$

and the energy parameter a_{ji} and the non-randomness parameter α_{ji} are assigned as follows. In principle, we must take into account an interaction for each pair of all the chemical species present. The total number of such pairs is six. For each pair three parameters (two energy parameters and an α_{ji}) could be used. Then, the number of resulting parameters is 18, which is too many. We confine ourselves to use a minimum number of three as adjustable parameters in fitting the model to experimental results. We study four cases to test the suitability of the model. In all cases we assume that the interaction energy parameter between the monomer and dimer of acetic acid in the mixture is the same as that in pure acetic acid, namely $a_{A_1A_2} = a_{A_2A_1} = -100$ K and $\alpha_{A_1A_2} = \alpha_{A_2A_1} = 0.3$ [1]:

(I) $a_{A_1B_1} = 2a_{A_2B_1}$, $a_{B_1A_1} = 2a_{B_1A_2}$, $a_{A_2B_1} = a_{A_2AB} = a_{A_1AB} = a_{ABB_1}$, $a_{B_1A_2} = a_{ABA_2} = a_{ABA_1} = a_{B_1AB}$. In this case $a_{A_1B_1}$, $a_{B_1A_1}$ and α are parameters;

(II) $a_{A_1B_1} = 2a_{A_2B_1}$, $a_{B_1A_1} = 2a_{B_1A_2}$, $a_{A_1AB} = 2a_{A_2AB}$, $a_{ABA_1} = 2a_{ABA_2}$, $a_{B_1AB} = a_{ABB_1}$, $a_{A_1AB} = a_{ABA_1} = a_{B_1AB}$ and all α are taken as 0.3. The adjustable parameters are $a_{A_1B_1}$, a_{A_1AB} and $a_{B_1A_1}$;

(III) $a_{A_1B_1} = 2a_{A_2B_1} = a_{B_1A_1} = 2a_{B_1A_2}$, $a_{A_1AB} = 2a_{A_2AB}$, $a_{ABA_1} = 2a_{ABA_2}$, $a_{B_1AB} = a_{ABB_1}$, $a_{A_1AB} = a_{ABA_1}$ and all α are taken as 0.3. Here three parameters are $a_{A_1B_1}$, a_{A_1AB} and a_{B_1AB};

(IV) the parameters are the same as those used in case (I) and the solvation constant is zero.

The liquid-phase mole fraction dimerization constant for pure acetic acid changes with temperature [3] as expressed by

$$\ln K_x^\star = \frac{3131}{T} - 6.5197 \tag{6}$$

Christensen et al. [4] correlated the excess molar enthalpy data for acetic acid–n-heptane [5] and acetic acid–water [6] using the Redlich–Kister equation. We obtained the molar enthalpies of infinite dilution of acetic acid in these solvents from the same equation: 4.3 kJ mol^{-1} for acetic acid–n-heptane; -1.4 kJ mol^{-1} for acetic acid–water. The difference between these values provides the molar enthalpy of hydrogen bond formation between acetic acid and water, $h_{AB} = -5.7$ kJ mol^{-1}. This value fixes the temperature dependence of K_{AB} for acetic acid–water according to

$$\frac{\mathrm{d} \ln K_{AB}}{\mathrm{d}(1/T)} = -\frac{h_{AB}}{R} \tag{7}$$

At 20 °C we set $K_{AB} = 4$ for case I and $K_{AB} = 1$ for cases II and III.

The stoichiometric mole fractions of both components are given in terms of the equilibrium constants and the monomer mole fractions of the same components

$$x_A = \frac{x_{A_1} + 2K_x x_{A_1}{}^2 + K_{AB} x_{A_1} x_{B_1}}{x_{A_1} + 2K_x x_{A_1}{}^2 + 2K_{AB} x_{A_1} x_{B_1} + x_{B_1}} \tag{8}$$

$$x_B = \frac{x_{B_1} + K_{AB} x_{A_1} x_{B_1}}{x_{A_1} + 2K_x x_{A1}{}^2 + 2K_{AB} x_{A_1} x_{B_1} + x_{B_1}} \tag{9}$$

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

$$x_{A_1} + x_{A_2} + x_{AB} + x_{B_1} = x_{A_1} + K_x x_{A_1}{}^2 + K_{AB} x_{A_1} x_{B_1} + x_{B_1} = 1 \tag{10}$$

According to a theorem discussed by Prigogine and Defay [7], the following equations relate the apparent activity coefficients to the true quantities

$$x_A \gamma_A = \frac{x_{A_1} \gamma_{A_1}}{x_{A_1}^\star \gamma_{A_1}^\star} \tag{11}$$

$$x_B \gamma_B = x_{B_1} \gamma_{B_1} \tag{12}$$

For given values of K, $a_{A_1A_2} = 100$ K, $\alpha_{A_1A_2} = 0.3$, K_{AB} and the three adjustable parameters of the NRTL equation, the true compositions and true activity coefficients at any apparent composition are obtained by simultaneous solution of the pertinent equations described above. The equations are straightforwardly solved by iterations as described previously [1].

CALCULATED RESULTS

We reduced the available literature data for the vapour–liquid equilibrium for acetic acid–water and acetic acid–2-butanone with our equations using the thermodynamic relation given by

$$y_i \phi_i P = \gamma_i x_i \phi_i^s P_i^s \exp\left[\frac{v_i^L(P - P^s)}{RT}\right] \tag{13}$$

where y_i and x_i are the apparent vapour and liquid mole fraction of component i, P is the total pressure, P_i^s is the pure-component vapour pressure taken from the original vapour–liquid equilibrium data set, ϕ_i is the vapour-phase fugacity coefficient of component i at P and T, ϕ_i^s is that of pure component i at P_i^s and T, and v_i^L is the pure-liquid molar volume calcaluted from the modified Rackett equation [8]. In systems containing

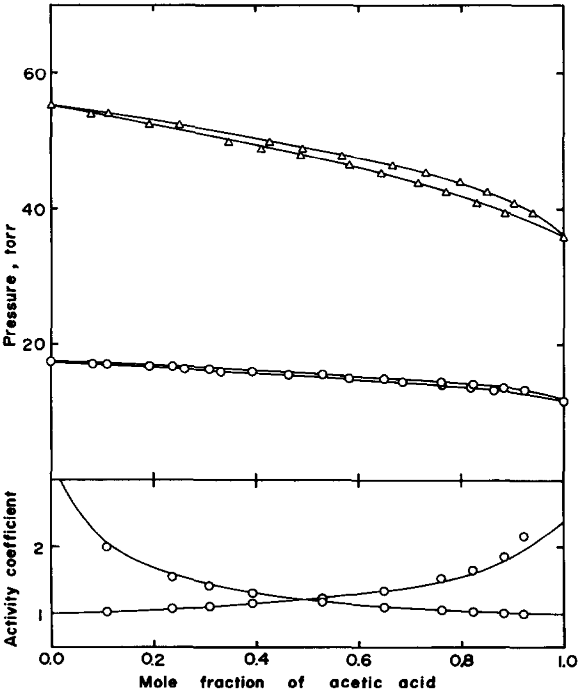

Fig. 1. Vapour–liquid equilibria for acetic acid–water. Calculated (———). Experimental: (○) 20 ° C, (△) 40 ° C, data of Lazeeva and Markuzin [11].

TABLE 1

Calculated results for acetic acid–water and acetic acid–2-butanone

System (A–B)	Temp. (°C)	Number of data points	Case [a]	Root-mean-square deviations				Parameters (K)			Variance of fit [b]	Ref.
				δP (Torr)	δT (K)	δx ($\times 10^3$)	δy ($\times 10^3$)	PA(1)	PA(2)	PA(3)		
Acetic acid–water	20	10	I	0.21	0.00	0.0	4.8	331.42	105.78	2.1436 [c]	3.78	11
			II	0.27	0.00	0.0	6.3	451.44	−285.30	−523.45	6.37	
			III	0.39	0.00	0.0	11.3	2232.60	32.42	448.31	20.47	
			IV	0.39	0.00	0.0	5.5	702.15	−194.25	0.9578 [c]	5.05	
	40	11	I	0.31	0.00	0.0	6.9	295.24	121.31	1.7488	7.45	11
			II	0.47	0.00	0.0	7.4	465.09	−300.64	−357.35	8.68	
			III	0.86	0.00	0.0	12.8	2564.95	21.01	840.94	26.21	
			IV	0.55	0.00	0.0	2.8	1012.87	−579.20	0.3061	1.66	
	69.7	11	I	1.95	0.00	0.2	6.4	410.53	305.22	1.8376	11.46	13
			II	0.75	0.00	0.1	6.1	33.35	74.65	−599.12	6.50	
			III	0.80	0.00	0.4	5.9	−588.59	53.04	−591.56	6.39	
			IV	1.63	0.00	0.0	19.7	117.31	−111.98	1.0629	62.89	
	79.9	11	I	0.24	0.00	0.0	7.2	279.47	264.62	1.6120	7.93	13

			II	0.55	0.00	0.1	5.4	139.47	−33.09	−510.43	4.92	
			III	0.50	0.00	0.0	8.1	−880.88	62.36	−632.85	10.30	
			IV	0.93	0.00	0.0	14.0	250.74	−92.24	3.8157	31.11	
	80	10	I	1.15	0.00	0.2	9.7	350.87	256.13	1.6683	16.88	11
			II	1.76	0.00	0.0	6.8	416.76	−262.50	−126.32	11.74	
			III	1.68	0.00	0.3	8.6	−1134.50	72.41	−772.75	15.84	
			IV	1.67	0.00	0.1	5.7	494.51	−224.22	1.1013	9.12	
	89.9	11	I	0.91	0.00	0.3	7.0	285.83	298.31	1.5250	8.81	13
			II	0.92	0.00	0.2	5.7	32.16	94.19	−528.40	6.26	
			III	0.99	0.00	0.1	6.2	−783.98	72.64	−657.31	7.32	
			IV	1.83	0.00	0.3	15.8	−20.15	−14.73	4.3462	42.96	
Acetic acid–2-butanone	68.51	8 [d]	IV	2.14	0.00	0.6	5.6	−1551.04	2447.52	0.1154	10.57	15
	78	9	IV	2.29	0.00	0.9	2.8	−574.97	1206.24	0.4908	9.27	

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[a] I, PA(1) = $a_{A_1B_1}$, PA(2) = $a_{B_1A_1}$ and PA(3) = α_{AB}; II, PA(1) = $a_{A_1B_1}$, PA(2) = $a_{B_1A_1}$ and PA(3) = a_{A_1AB}; III, PA(1) = $a_{A_1B_1}$, PA(2) = a_{A_1AB} and PA(3) = a_{B_1AB}; IV, PA(1) = $a_{A_1B_1}$, PA(2) = $a_{B_1A_1}$, PA(3) = α_{AB} and K_{AB} = 0.

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

[c] Value of non-randomness parameter is dimensionless.

[d] One erroneous experimental point was rejected.

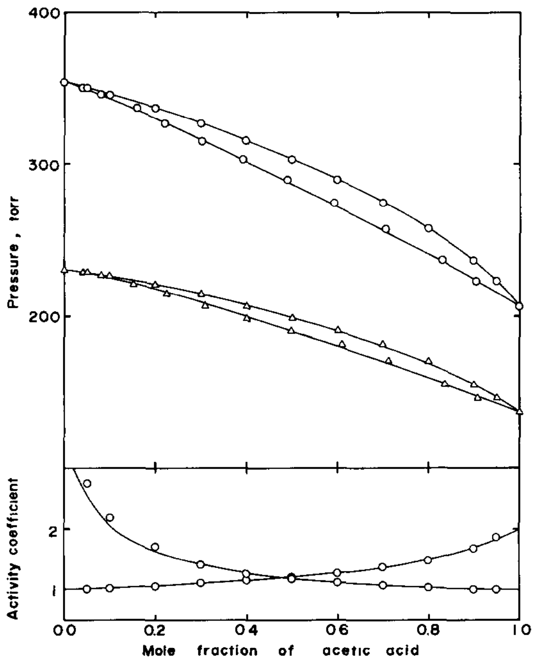

Fig. 2. Vapour–liquid equilibria for acetic acid–water. Calculated (———). Experimental: (△) 69.7 ° C, (○) 79.9 ° C, data of Arich and Tagliavini [13].

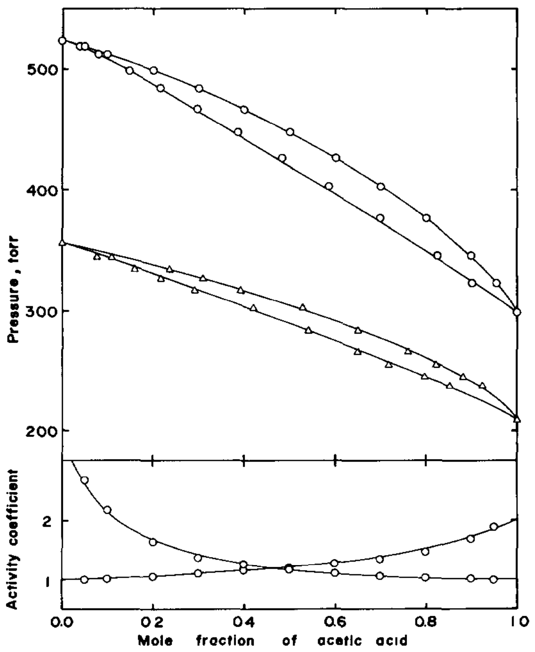

Fig. 3. Vapour–liquid equilibria for acetic acid–water. Calculated (———). Experimental: (△) data of Lazeeva and Markuzin at 80 ° C [11]; (○) data of Arich and Tagliavini at 89.9 ° C [13].

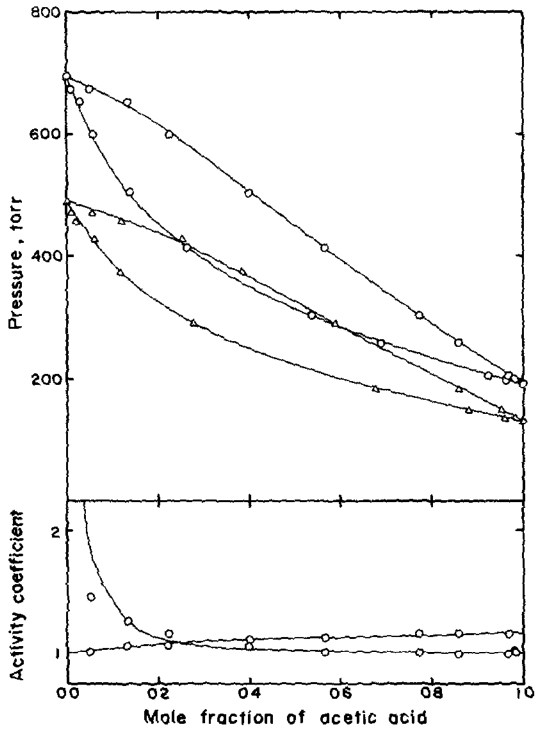

Fig. 4. Vapour–liquid equilibria for acetic acid–2-butanone. Calculated (———). Experimental: (△) 68.51° C, (○) 78° C, data of Rasmussen et al. [15].

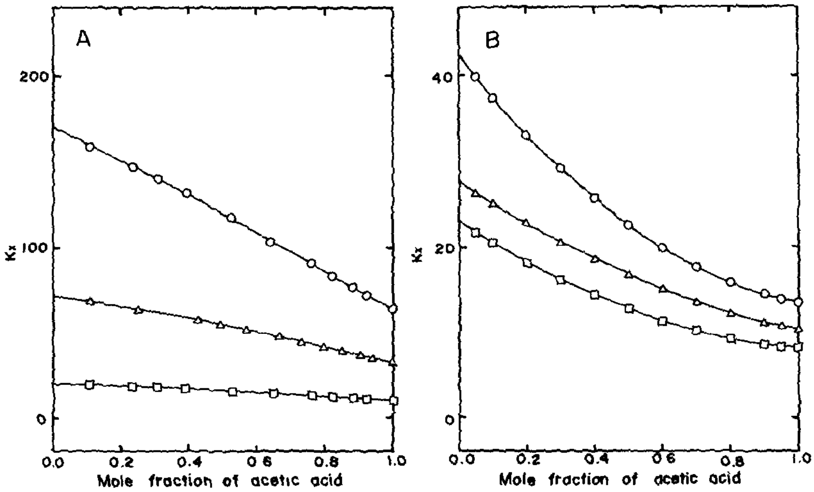

Fig. 5. Variation in liquid-phase mole fraction association constant with composition for acetic acid–water: A (○) 20° C, (△) 40° C, (□) 80° C, data of Lazeeva and Markuzin [11]; B (○) 69.7° C, (△) 79.9° C, (□) 89.9° C, data of Arich and Tagliavini [13].

one or more carboxylic acids, the fugacity coefficients ϕ_i and ϕ_i^S are calculated on the basis of chemical theory whose expressions for fugacity coefficients are derived from the thermodynamics of chemical equilibrium [9, 10].

The computer program used to obtain optimum parameters, based on the maximum-likelihood principle, was similar to that given by Prausnitz et al. [10]. The optimum parameters were obtained by minimizing the objective function

$$F = \sum_{i=1}^{N} \left[\frac{(P_i - \hat{P}_i)^2}{\sigma_P^{\ 2}} + \frac{(T_i - \hat{T}_i)^2}{\sigma_T^{\ 2}} + \frac{(x_{1i} - \hat{x}_{1i})^2}{\sigma_x^{\ 2}} + \frac{(y_{1i} - \hat{y}_{1i})^2}{\sigma_y^{\ 2}} \right] \tag{14}$$

where a circumflex indicates the calculated true value corresponding to each measured variable, and the standard deviations were assumed for the measured variables: $\sigma_P = 1$ Torr for pressure; $\sigma_T = 0.05$ K for temperature; $\sigma_x = 0.001$ for liquid mole fraction; $\sigma_y = 0.003$ for vapour mole fraction.

The experimental vapour–liquid equilibrium data of Lazeeva and Markuzin [11] for acetic acid–water are available from Gmehling and Onken [12] and those of Arich and Tagliavini [13] from Gmehling et al. [14]. The binary results of vapour–liquid equilibrium data reduction are given in Table 1. In case IV where the solvation constant is not included, our model reproduces well the data Laveeva and Markuzin [11], but does not represent satisfactorily those of Arich and Tagliavini [13]. A survey of the results obtained in cases I–IV indicates that case II provides the best correlation. For acetic acid–2-butanone we did not assume complex formation between

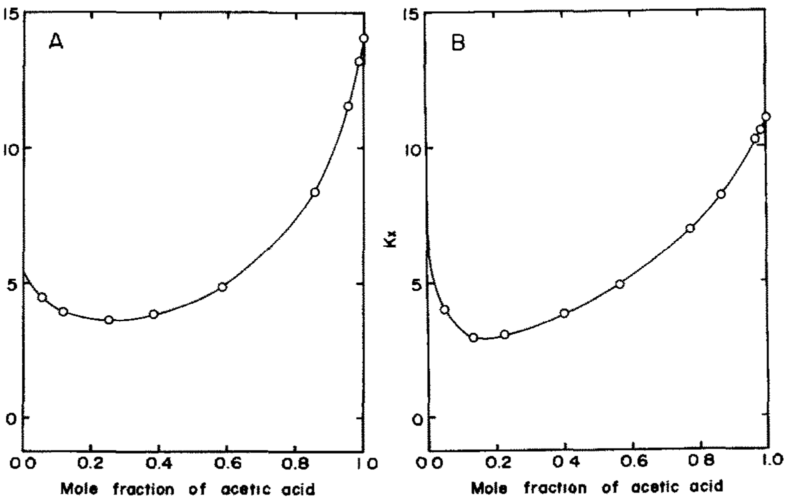

Fig. 6. Variation in liquid-phase mole fraction association constant with composition for acetic acid–2-butanone: A (o) 68.5 °C; B (o) 78 °C, data of Rasmussen et al. [15].

acetic acid and 2-butanone. Figures 1–4 compare the experimental vapour–liquid equilibrium results with the calculated values, where those for acetic acid–water is based on case II. The liquid-phase mole fraction association constant K_x versus liquid composition is plotted in Figs. 5 and 6. The relation for acetic acid–2-butanone is markedly different from that for acetic acid–water. The concentration of the acetic acid monomer in 2-butanone is higher than the corresponding value in water.

In conclusion, the new model is able to correlate accurately the isothermal experimental vapour–liquid equilibrium results of the acetic acid–water and acetic acid–2-butanone systems.

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