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THERMODYNAMICS OF ASSOCIATED SOLUTIONS. VAPOUR–LIQUID EQUILIBRIUM FOR SOLUTIONS OF ACETIC ACID AND NON-POLAR COMPONENTS WITH ASSOCIATION IN BOTH PHASES

ISAMU NAGATA * and TSUTOMU SATOH

Department of Chemical Engineering, Kanazawa University, Kanazawa 920 (Japan)

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ABSTRACT

An association model is presented to calculate successfully the isothermal vapour–liquid equilibria of binary solutions of acetic acid with benzene, n-heptane, toluene and tetrachloromethane. The model introduces a concentration-dependent liquid-phase association constant and assumes that acetic acid self-associates to form dimers. The physical interaction terms between each binary of three chemical species, the monomers and dimers of acetic acid and a non-polar component, are expressed by the NRTL equation. The model is easily extended to multicomponent mixtures as shown by good predicted vapour–liquid equilibrium results for acetic acid–toluene–n-heptane derived from binary parameters alone.

LIST OF SYMBOLS

A, B	acetic acid and a non-polar component
A, B, C	constants of the Antoine equation
a_{ij}	NRTL binary interaction parameter
F	objective function as defined by eqn. (11)
G_{ij}	coefficient as defined by $\exp(-\alpha_{ij}\tau_{ij})$
K	thermodynamic liquid-phase association constant
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	non-randomness parameter
γ_i	activity coefficient of component i or species i
σ_P, σ_T	standard deviations in pressure and temperature
σ_x, σ_y	standard deviations in liquid-phase and vapour-phase mole fractions
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
B_1	monomer of a non-polar component
i, j, k, r	chemical molecular species or components

Superscripts

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

INTRODUCTION

In the correlation of the vapour–liquid equilibria of binary systems containing acetic acid using suitable solution models, it is very often necessary to take into account vapour-phase non-ideality and to use some models for activity coefficients in order to express liquid-phase non-ideality without an allowance for liquid-phase association [1].

Some researchers [2–5] have taken into consideration association in both liquid and vapour phases to derive approaches. Marek and Standart [2] presented equilibrium relationships for mixtures containing a substance which partly associates to dimers in both phases. Kohler [3] used the association constant given in terms of activities and the Margules equation as an activity coefficient expression to correlate the total pressures of mixtures of acetic acid with tetrachloromethane and benzene, postulating a strong attractive interaction between monomers and dimers. Jenkins and Gibson-Robinson [4] developed an extension of the work of Marek and Standart [2] by incorporating a concentration-dependent liquid-phase dimerization constant. This model gave a good fit for both pressure and composition for the isothermal vapour–liquid equilibria of the system acetic acid–toluene. Grenzheuser and Gmehling [5] combined the perturbed hard-chain theory with the chemical theory. Their thermodynamic model reproduced well binary vapour–liquid equilibria for carboxylic acids either with associating or with polar or non-polar components, and provided successful calculations for multicomponent systems from binary information.

In this paper we present a new method which follows the approach suggested by Kohler [3] for the liquid phase and which uses the NRTL equation [6] to calculate the activity coefficients of components. The method proposed here is shown to represent very well the vapour–liquid equilibria of binary mixtures including acetic acid and a non-polar component. It also predicts satisfactorily the ternary vapour–liquid equilibria of acetic acid–toluene–n-heptane from binary parameters only.

SOLUTION MODEL

In a binary liquid mixture of acetic acid (A) and a non-polar component (B), acetic acid is assumed to form cyclic dimers only according to the chemical reaction represented by $A_1 + A_1 = A_2$. The thermodynamic equilibrium constant for dimerization in the liquid phase is given by

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

where x_{A_1} and x_{A_2} are the true mole fractions of the monomer and dimer of acetic acid, γ_{A_1} and γ_{A_2} are the activity coefficients of the monomer and dimer, the liquid-phase mole fraction dimerization constant K_x is defined by $x_{A_2}/x^2_{A_1}$, the activity coefficient ratio K_γ is given by $\gamma_{A_2}/\gamma^2_{A_1}$ and the superscript * denotes pure-liquid reference state. K is independent of composition and K_x is dependent on composition.

The activity coefficient of any species i of the three molecular species A_1, A_2 and B_1 in the mixture is expressed by the NRTL equation

$$\ln \gamma_i = \frac{\sum\limits_i \tau_{ji} G_{ji} x_j}{\sum\limits_k G_{ki} x_k} + \sum_j \frac{x_j G_{ij}}{\sum\limits_k G_{kj} x_k}\left(\tau_{ij} - \frac{\sum\limits_r x_r \tau_{rj} G_{rj}}{\sum\limits_k G_{kj} x_k}\right) \tag{2}$$

where

$$\tau_{ji} = a_{ji}/T \tag{3}$$

$$G_{ji} = \exp(-\alpha_{ji}\tau_{ji}) \tag{4}$$

and the subscripts i, j, k and r range over the three species. Generally the NRTL equation involves three adjustable parameters for each binary system and nine parameters could be used for the present pseudo-ternary mixture. However, the use of nine parameters is never justified in binary data reduction and therefore the number of parameters must be reduced. First, we assumed that an interaction between the monomers and dimers in pure acetic acid is expressed by only one energy parameter $a_{A_1A_2} = a_{A_2A_1}$ and the non-randomness parameter $\alpha_{A_1A_2}$ $(= \alpha_{A_2A_1})$ is set as 0.3. Secondly, in the mixture, in addition to the interaction between the monomers and dimers, physical terms signifying the interaction between monomeric acetic acid and a non-polar component and that between dimeric acetic acid and a non-polar component must be included. Three additional parameters are assigned as follows: $a_{A_1B} = 2a_{A_2B} = a_{AB}$, $a_{BA_1} = 2a_{BA_2} = a_{BA}$, $\alpha_{A_1B} = \alpha_{BA_1} = \alpha_{A_2B} = \alpha_{BA_2} = \alpha_{AB}$. Once a specific value of $a_{A_1A_2}$ is fixed, then the assigned value of $a_{A_1A_2}$ is used for all mixtures studied in this work. The three parameters, a_{AB}, a_{BA} and α_{AB}, are obtained in fitting the model to experimental results.

The chemical potential of the stoichiometric associating component is equal to that of its monomer [7]. This equality leads to the exact relations

$$x_A\gamma_A = x_{A_1}\gamma_{A_1}/(x^{\star}_{A_1}\gamma^{\star}_{A_1}) \tag{5}$$

and

$$x_B\gamma_B = x_{B_1}\gamma_{B_1} \tag{6}$$

since $x^{\star}_{B_1}\gamma^{\star}_{B_1} = 1$.

The monomer mole fractions are related to the stoichiometric mole fractions

$$x_A = \frac{x_{A_1} + 2K_x x^2_{A_1}}{x_{A_1} + 2K_x x^2_{A_1} + x_{B_1}} \tag{7}$$

$$x_B = \frac{x_{B_1}}{x_{A_1} + 2K_x x^2_{A_1} + x_{B_1}} \tag{8}$$

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

$$x_{A_1} + K_x x^2_{A_1} + x_{B_1} = 1 \tag{9}$$

COMPUTATIONAL PROCEDURE

Vapour–liquid equilibrium calculations are based on the following thermodynamic relation [1]

$$P\phi_i y_i = \gamma_i x_i P^s_i \phi^s_i \exp[v^L_i(P - P^s_i)/RT] \tag{10}$$

where P is the total pressure, y is the vapour-phase mole fraction, ϕ is the fugacity coefficient, P^s is the pure-component vapour pressure calculated from the Antoine equation and v^L is the pure-liquid molar volume estimated by the modified Rackett equation [8]. The chemical theory of vapour imperfections [9] is used to calculate ϕ when one or more carboxylic acid is in the vapour phase. Details are also given by Prausnitz et al. [1].

The computer program used for parameter estimation was similar to that described by Prausnitz et al. [1], based on the maximum-likelihood principle.

TABLE 1

Antoine constants for pure components [a]

Component	A	B	C	Ref.
Acetic acid	7.38782	1533.313	222.309	10
Benzene	6.90565	1211.033	220.790	11
n-Heptane	6.90240	1268.115	216.900	11
Tetrachloromethane	6.89406	1219.580	227.160	11
Toluene	6.95464	1344.800	219.482	11

[a] The Antoine equation is given by $\log_{10} P^s$ (torr) $= A - B/[C + t\ (°\mathrm{C})]$.

The optimal model parameters were sought by minimizing the objective function

$$F = \sum_{i=1}^{N} \left[\frac{(P_i - \hat{P}_i)^2}{\sigma_P^2} + \frac{(T_i - \hat{T}_i)^2}{\sigma_T^2} + \frac{(x_{1i} - \hat{x}_{1i})^2}{\sigma_x^2} + \frac{(y_{1i} - \hat{y}_{1i})^2}{\sigma_y^2} \right] \tag{11}$$

where a circumflex denotes the estimated true value corresponding to each measured variable. The standard deviations in the measured variables were assigned as $\sigma_P = 1$ Torr, $\sigma_T = 0.05$ K, $\sigma_x = 0.001$ and $\sigma_y = 0.003$ [1].

The vapour pressures of the pure components were calculated from the Antoine equation whose constants are given in Table 1 [10,11].

Freedman [12] calculated the values of the mole fraction liquid-phase equilibrium constant $K_x^\star$ by using an equation for the excess acoustic absorption of pure acetic acid. Barton and Hsu [13] correlated Freedman's calculated results as follows

$$\ln K_x^\star = 3131/T - 6.5197 \tag{12}$$

Values of $a_{\mathrm{A_1A_2}}$ ranging from -20 to -150 K gave similar results of binary data reduction and, as shown later, considerably improved ternary calculated results were obtained using $a_{\mathrm{A_1A_2}} = -100$ K. So, in this work, we fix the value of $a_{\mathrm{A_1A_2}}$ equal to -100 K. At a specified temperature where experimental vapour–liquid equilibrium data are available, the mole fractions $x_{\mathrm{A_1}}^\star$, $x_{\mathrm{A_2}}^\star$ of the monomer and dimer in pure acetic acid are easily obtained using $K_x^\star$ calculated from eqn. (12). Substituting these values of $x_{\mathrm{A_1}}^\star$, $x_{\mathrm{A_2}}^\star$, $a_{\mathrm{A_1A_2}} = -100$ K and $\alpha_{\mathrm{A_1A_2}} = 0.3$ into eqn. (2) gives the activity coefficients $\gamma_{\mathrm{A_1}}^\star$ and $\gamma_{\mathrm{A_2}}^\star$ of the monomer and dimer and the activity coefficient ratio $K_\gamma^\star$. Then, the thermodynamic equilibrium constant K is derived from eqn. (1) as a product of $K_x^\star$ and $K_\gamma^\star$. Assuming a set of starting values of $a_{\mathrm{AB}} = a_{\mathrm{BA}} = 300$ K and $\alpha_{\mathrm{AB}} = 0.4$, we may proceed to calculations of $x_{\mathrm{A_1}}$, $x_{\mathrm{A_2}}$ and $x_{\mathrm{B_1}}$ from the high concentration range of acetic acid to the low concentration range as follows. For given values of K, x_{A} and x_{B}, we use $K_x^\star$ as the first approximate value of K_x in order to obtain $x_{\mathrm{A_1}}$, $x_{\mathrm{A_2}}$ and $x_{\mathrm{B_1}}$ from eqns. (1), (7) and (9). Then these first approximate values of $x_{\mathrm{A_1}}$, $x_{\mathrm{A_2}}$ and $x_{\mathrm{B_1}}$ are substituted into eqn. (2) to obtain $\gamma_{\mathrm{A_1}}$, $\gamma_{\mathrm{A_2}}$

and K_γ. Dividing K by K_γ gives K_x. The resulting mole fraction dimerization constant K_x is used for the next iteration to solve the second approximate value of x_{A_1}, x_{A_2} and x_{B_1}. The convergence is usually obtained within ten iterations. After final values of x_{A_1}, x_{A_2} and x_{B_1} are obtained, the nominal activity coefficients of the components are given immediately by eqns. (5) and (6). The derived value of K_x for the first data point can be used as an initial value of K_x for the next data point.

EXPERIMENTAL DATA SETS EXAMINED

Some isothermal experimental vapour–liquid equilibrium data sets are available from the compilation of Gmehling et al. [14]; for acetic acid–benzene at 20 °C [15], 25 °C [16] and 49.99 °C [17]; for acetic acid–n-heptane at 20 °C [15,18] and 30 and 40 °C [18]; for acetic acid–toluene at 30 °C [18] and 69.94 and 80.05 °C [17]; for acetic acid–tetrachloromethane at 20 °C [19,20], 32.38 °C [19] and 35 °C [21]; for toluene–n-heptane at 30 °C [18]; for acetic acid–toluene–n-heptane at 30 °C [22].

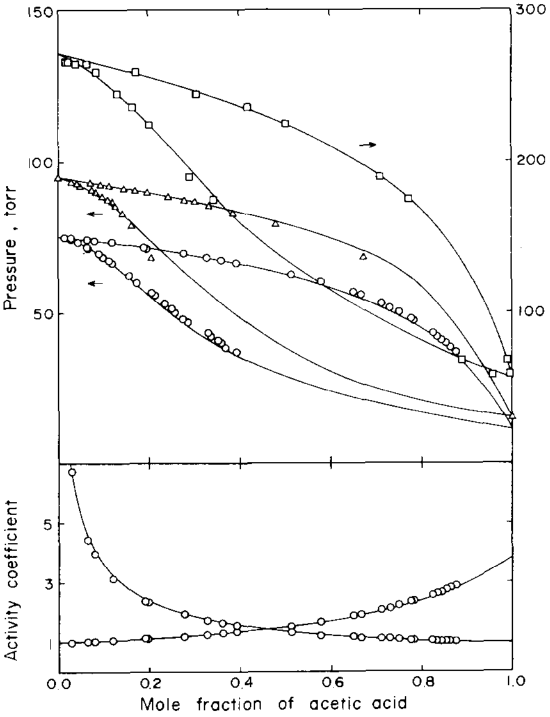

Fig. 1. Vapour–liquid equilibria for acetic acid–benzene. Calculated (———). Experimental: (○) data of Werner [15] at 20 °C; (△) data of Hovorka and Dreisbach [16] at 25 °C; (□) data of Zawidzki [17] at 49.99 °C.

TABLE 2

Calculated results for binary systems

System (A–B)	Temp. (°C)	Number of data points	Root-mean-square deviations				Parameters				Ref.
			δP (Torr)	δT (K)	δx ($\times 10^3$)	δy ($\times 10^3$)	$a_{A_1A_2}$ (K)	a_{AB} (K)	a_{BA} (K)	α_{AB}	
Acetic acid–benzene	20	26	1.01	0.00	0.0	3.0	−100	240.52	464.98	1.0301	15
	25	13	1.18	0.00	0.0	6.3	−100	120.42	491.61	0.3800	16
	49.99	10	1.88	0.01	0.1	5.0	−100	224.54	259.93	0.5513	17
Acetic acid–n-heptane	20	22	0.55	0.00	0.0	14.9	−100	779.94	803.59	0.3590	15
		12	0.70	0.00	0.0	5.1	−100	945.22	750.73	0.3959	18
	30	15	0.77	0.00	0.0	2.5	−20	978.63	804.21	0.4172	18
			0.84	0.00	0.0	2.8	−100	1008.29	827.48	0.4438	
			0.35	0.00	0.0	6.6	−150	1023.39	878.71	0.4517	
	40	14	1.04	0.00	0.0	11.6	−100	984.36	822.24	0.4391	18
Acetic acid–toluene	30	15	0.30	0.00	0.0	4.1	−20	368.42	464.15	0.9192	18
			0.27	0.00	0.0	4.0	−100	387.66	441.96	0.9602	
			0.28	0.00	0.0	4.1	−150	372.38	417.67	0.9645	
	69.94	15	1.36	0.02	0.2	4.3	−100	281.11	277.44	0.4470	17
	80.05	15	0.87	0.01	0.2	6.1	−100	254.73	343.12	0.4035	17
Acetic acid–tetrachloromethane	20	18	0.42	0.00	0.0		−100	372.06	655.86	0.8974	19
		9	1.70	0.00	0.0	8.8	−100	94.10	695.35	0.6261	20
	32.38	18	0.43	0.00	0.0		−100	355.85	599.23	0.8553	19
	35	10	3.31	0.00	0.3	14.1	−100	617.21	543.97	0.9807	21
Toluene–n-heptane	30	10	0.37	0.00	0.0	3.8		63.47	73.04	0.3	18

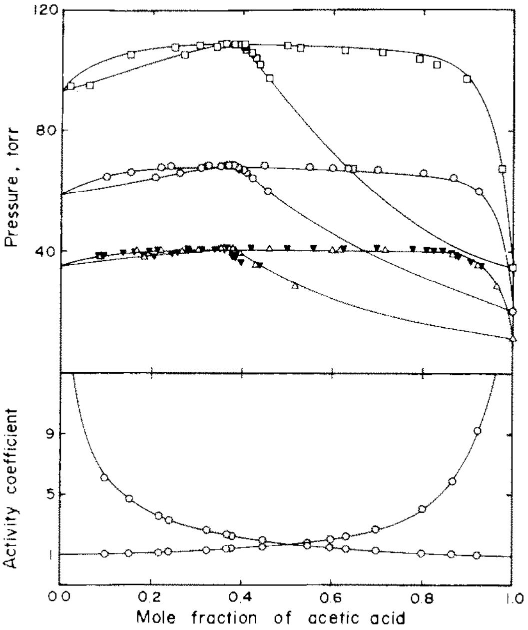

Fig. 2. Vapour–liquid equilibria for acetic acid–n-heptane. Calculated (———). Experimental: (▼) data of Werner [15] at 20 °C; data of Markuzin and Pavlova [18] at (△) 20 °C, (○) 30 °C, (□) 40 °C.

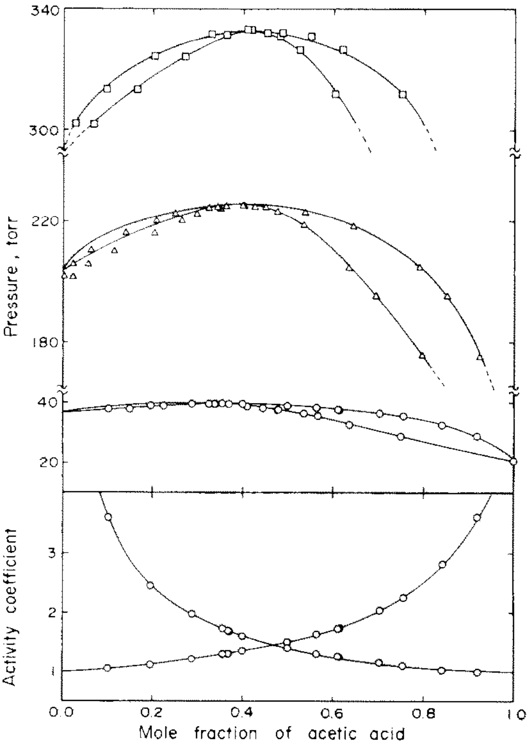

Fig. 3. Vapour–liquid equilibria for acetic acid–toluene. Calculated (———). Experimental: data of Zawidzki [17] at (△) 69.94 °C, (□) 80.05 °C; (○) data of Markuzin and Pavlova [18] at 30 °C.

CALCULATED RESULTS

Table 2 shows the binary parameters and the root-mean-square deviations between the estimated true and experimental values of measured variables obtained in fitting the model to the experimental results. As shown for acetic acid–n-heptane and acetic acid–toluene at 30 °C the values of $a_{A_1A_2}$ ranging from -20 to -150 K give similar results. Figures 1–5 show comparisons between the experimental results and the calculated values for binary systems, indicating that the model represents the vapour–liquid equilibria of the systems with good accuracy. Figure 6 illustrates plots of the liquid-phase mole fraction dimerization constant K_x as a function of mole fraction for some systems.

Only one set of isothermal ternary vapour–liquid equilibrium data is available for the acetic acid–toluene–n-heptane system at 30 °C [22]. Table 3 summarizes predicted ternary results obtained from the binary parameters alone. For the interaction parameter between the monomer and dimer of

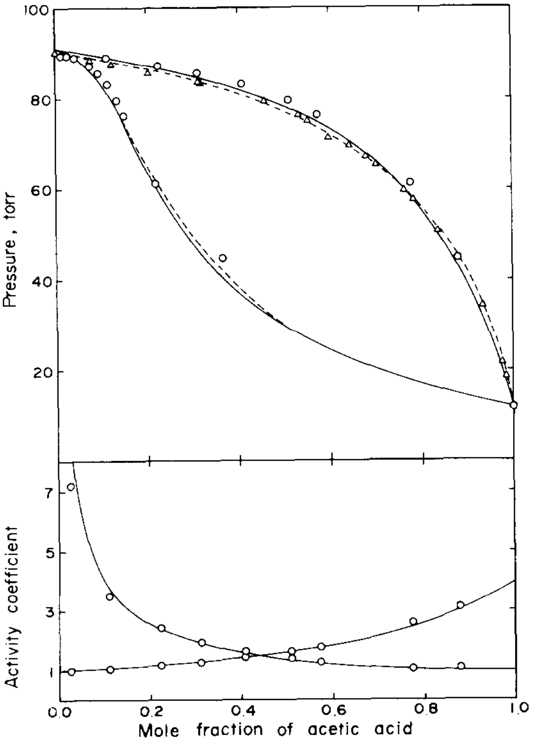

Fig. 4. Vapour–liquid equilibria for acetic–tetrachloromethane at 20 ° C. Calculated: (- - - - - -) fitted to data of Miksch et al. [19]; (———) fitted to data of Plekhotkin and Markuzin [20]. Experimental: (△) data of Miksch et al. [19]; (○) data of Plekhotkin and Markuzin [20].

TABLE 3

Predicted ternary results based on three different values of $a_{A_1A_2}$

System	Temp. (° C)	Number of data points	$a_{A_1A_2}$ (K)	Absolute arithmetic mean deviations				
				Δy_1 ($\times 10^3$)	Δy_2 ($\times 10^3$)	Δy_3 ($\times 10^3$)	ΔP (torr)	$\Delta P/P$ (%)
Acetic acid(1)			−20	9.0	7.2	11.4	1.55	2.90
-toluene(2)	30	47	−100	8.5	6.8	10.5	1.62	3.00
-n-heptane(3)			−150	9.4	7.8	11.8	1.36	2.58

acetic acid the use of $a_{A_1A_2} = -100$ K instead of -20 or -150 K gives improved predicted results. Table 4 shows detailed calculated results based on $a_{A_1A_2} = -100$ K.

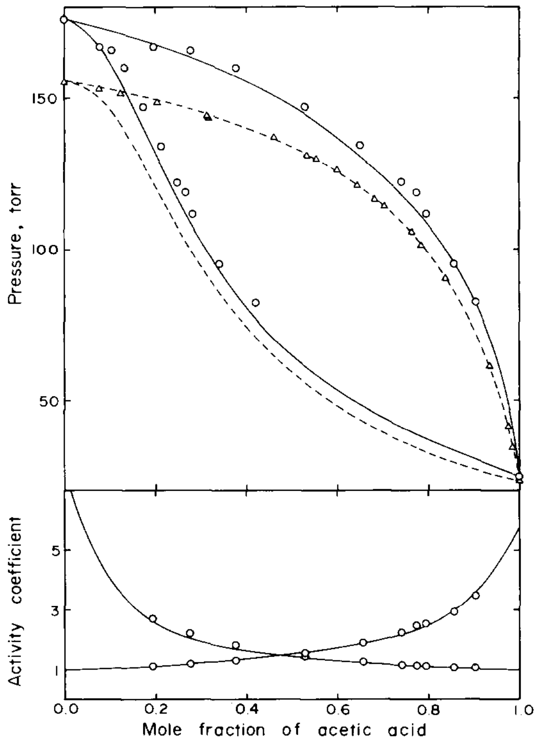

Fig. 5. Vapour–liquid equilibria for acetic acid–tetrachloromethane. Calculated: (- - - - - -) fitted to data of Miksch et al. [19]; (———) fitted to data of Tamir et al. [21]. Experimental: (△) data of Miksch et al. [19] at 32.38° C; (○) data of Tamir et al. [21] at 35° C.

TABLE 4

Comparison of calculated and experimental vapour–liquid equilibrium data for acetic acid(1)–toluene(2)–n-heptane(3) at 30 ° C

Experimental					Deviations [a]			
x_1	x_2	y_1	y_2	P (torr)	Δy_1 ($\times 10^3$)	Δy_2 ($\times 10^3$)	Δy_3 ($\times 10^3$)	ΔP (torr)
0.0998	0.8102	0.1190	0.7010	45.6	−20.0	20.3	−0.3	1.89
0.1999	0.7199	0.2030	0.6270	47.1	−16.0	18.2	−2.2	2.57
0.3000	0.6307	0.2760	0.5610	47.5	−2.1	5.1	−3.0	2.71
0.3971	0.5429	0.3270	0.5110	47.0	1.6	0.8	−2.4	2.21
0.5003	0.4497	0.3830	0.4620	46.5	10.1	−1.9	−8.2	2.04
0.5999	0.3601	0.4250	0.4210	45.4	6.2	1.4	−7.6	1.72
0.6989	0.2713	0.4780	0.3740	44.2	6.4	2.9	−9.3	1.94
0.8002	0.1798	0.5380	0.3180	41.5	−0.8	8.7	−7.9	1.65
0.9300	0.0630	0.6930	0.1890	33.3	−8.5	5.8	2.7	0.93
0.9700	0.0270	0.7870	0.1120	28.2	−33.7	6.6	27.1	1.13
0.0997	0.6305	0.1240	0.4730	52.2	−15.0	9.9	5.1	0.98
0.2001	0.5599	0.2140	0.4080	54.0	−3.2	−0.1	3.3	1.67
0.2998	0.4902	0.2780	0.3720	54.7	9.4	3.5	−12.9	1.84
0.4000	0.4200	0.3080	0.3480	54.8	0.0	13.0	−13.0	1.74
0.5000	0.3501	0.3520	0.3040	55.1	8.0	0.7	−8.7	2.16
0.6000	0.2800	0.3840	0.2760	54.7	5.0	4.7	−9.7	2.25
0.6999	0.2100	0.4310	0.2370	53.9	13.9	0.0	−13.9	2.55
0.7996	0.1404	0.4710	0.2030	52.5	4.4	5.5	−9.9	3.45
0.9000	0.0699	0.5470	0.1490	45.2	−6.7	6.4	0.3	1.70
0.1000	0.4500	0.1510	0.3260	57.7	−2.2	11.2	−9.0	1.21
0.2000	0.4001	0.2300	0.2930	58.9	0.9	18.3	−19.2	1.11
0.3004	0.3496	0.2820	0.2570	59.9	4.9	11.9	−16.8	1.48
0.4000	0.3000	0.3170	0.2280	60.2	5.5	7.1	−12.6	1.53
0.5003	0.2501	0.3570	0.2000	60.4	16.3	1.9	−18.2	1.76
0.6000	0.2001	0.3820	0.1780	59.8	14.8	2.6	−17.4	1.47
0.6998	0.1501	0.4190	0.1500	59.1	23.0	−1.1	−21.9	1.58
0.7998	0.1005	0.4470	0.1270	58.2	15.5	2.4	−17.9	2.60
0.9300	0.0350	0.5380	0.0800	47.6	−5.7	5.4	0.3	1.22
0.9700	0.0150	0.6680	0.0310	36.6	−5.1	−15.7	20.8	0.16
0.0999	0.2699	0.1680	0.1960	61.5	−2.9	4.0	−1.1	1.08
0.1999	0.2398	0.2470	0.1720	63.5	−2.6	7.4	−4.8	1.55
0.2999	0.2100	0.3040	0.1560	64.2	7.7	10.8	−18.5	1.62
0.4003	0.1804	0.3390	0.1370	64.2	12.2	7.4	−19.6	1.44
0.4999	0.1502	0.3620	0.1160	64.0	12.5	1.1	−13.6	1.28
0.6001	0.1201	0.3780	0.1060	63.7	8.7	5.5	−14.2	1.25
0.7001	0.0899	0.3950	0.0910	63.3	5.6	5.8	−11.4	1.47
0.8002	0.0600	0.4220	0.0700	62.5	7.2	1.5	−8.7	2.11
0.9003	0.0299	0.4450	0.0450	56.5	−19.7	−3.1	22.8	0.91
0.1002	0.0898	0.1870	0.0810	63.5	−7.2	12.6	−5.4	0.10
0.2000	0.0800	0.2590	0.0720	66.1	−18.4	14.4	4.0	0.82
0.3000	0.0702	0.3160	0.0610	67.7	−7.0	10.9	−3.9	1.78
0.4999	0.0503	0.3640	0.0400	67.8	−3.0	1.3	1.7	1.97
0.6001	0.0401	0.3830	0.0330	67.4	2.2	−0.2	−2.0	1.91

(continued)

TABLE 4 (continued)

Experimental					Deviations [a]			
x_1	x_2	y_1	y_2	P (torr)	Δy_1 ($\times 10^3$)	Δy_2 ($\times 10^3$)	Δy_3 ($\times 10^3$)	ΔP (torr)
0.6999	0.0302	0.3970	0.0280	66.7	3.8	0.2	−4.0	1.77
0.8001	0.0198	0.4090	0.0290	65.7	1.0	7.5	−8.5	1.83
0.9006	0.0100	0.4440	0.0310	60.5	0.4	16.1	−16.5	0.67
0.9300	0.0070	0.4880	0.0300	57.4	13.7	17.7	−31.4	1.20
Root-mean-square deviation					11.0	8.9	13.0	1.73

[a] Deviation = experimental value–calculated value.

CONCLUSION

The proposed model makes use of the thermodynamic equilibrium constant for the dimerization reaction of acetic acid in the liquid phase and reproduces the isothermal vapour–liquid equilibrium data of systems of

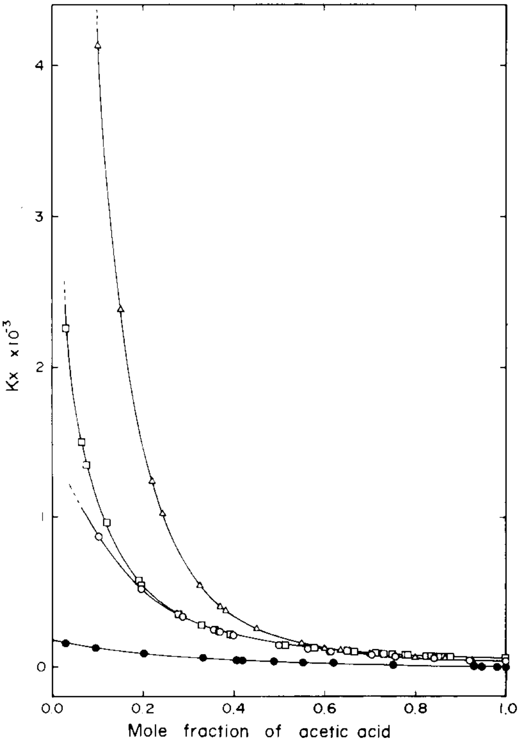

Fig. 6. Variation of liquid-phase mole fraction association constant with composition for acetic acid–benzene at 20 ° C (□), acetic acid–n-heptane at 30 ° C (△) and acetic acid–toluene at 30 ° C (○) and 80.05 ° C (●).

acetic acid with benzene, n-heptane, toluene and tetrachloromethane with good accuracy. Moreover, the model is able to predict well the isothermal vapour–liquid equilibrium of the acetic acid–toluene–n-heptane system from binary information only.

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