Thermochimica Acta, 143 (1989) 253–264
Elsevier Science Publishers B.V., Amsterdam – Printed in The Netherlands

THERMODYNAMICS OF ASSOCIATED SOLUTIONS: VAPOUR–LIQUID EQUILIBRIUM FOR THE ACETIC ACID–PROPANOIC ACID AND PROPANOIC ACID–WATER SYSTEMS WITH ASSOCIATION IN BOTH PHASES

ISAMU NAGATA * and TOSHIHIRO YAMAMOTO

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

(Received 16 August 1988)

ABSTRACT

The isothermal vapour–liquid equilibria of the acetic acid–propanoic acid and propanoic acid–water systems have been modelled by a new association model which incorporates the association constant between like molecules and the solvation constant between unlike molecules using the NRTL equation for molecular interactions between chemical species.

INTRODUCTION

Carboxylic acids are known to self-associate in both the vapour and liquid phases [1–6]. Large negative deviations from vapour ideality at normal or even low pressures can be described by means of expressions for fugacity coefficients based on the thermodynamics of chemical equilibrium [3,7,8]. Marek [7] applied vapour–liquid equilibrium relationships, including the effect of the association of one component in both phases, to binary mixtures of acetic acid with water, benzene and *p*-xylene. Jenkins and Gibson-Robinson [9] presented an extension of the work of Marek and Standart [2] by incorporating a concentration-dependent liquid phase association constant to correlate the vapour–liquid equilibria of the acetic acid–toluene system.

A new association model has been presented from this laboratory to give a good representation of the vapour–liquid equilibria of binary solutions containing a carboxylic acid; the model can be extended in a straightforward manner to multicomponent mixtures [10–12]. The new model uses the thermodynamic liquid phase dimerization constant of carboxylic acid, which allows the liquid phase mole fraction dimerization constant to change with

---

* Author to whom all correspondence should be addressed.

composition, with an allowance for molecular interactions expressed by the NRTL equation [13].

In this work we apply the new model to binary acetic acid–propanoic acid and propanoic acid–water mixtures.

SOLUTION MODEL

In the liquid phase, acetic acid (A) and propanoic acid (B) partly dimerize to form homodimers A_2 and B_2 and heterodimers AB according to three chemical reactions, $A_1 + A_1 = A_2$, $B_1 + B_1 = B_2$ and $A_1 + B_1 = AB$. All the equilibrium constants for these reactions are defined by

$$K_{AA}^{L} = \frac{x_{A_2}^{*}\gamma_{A_2}^{*}}{(x_{A_1}^{*}\gamma_{A}^{*})^2} = \frac{x_{A_2}\gamma_{A_2}}{(x_{A_1}\gamma_{A_1})^2} = K_{Ax}K_{A\gamma} \tag{1}$$

$$K_{BB}^{L} = \frac{x_{B_2}^{*}\gamma_{B_2}^{*}}{(x_{B_1}^{*}\gamma_{B_1}^{*})^2} = \frac{x_{B_2}\gamma_{B_2}}{(x_{B_1}\gamma_{B_1})^2} = K_{Bx}K_{B\gamma} \tag{2}$$

$$K_{AB}^{L} = \frac{x_{AB}\gamma_{AB}}{x_{A_1}\gamma_{A_1}x_{B_1}\gamma_{B_1}} = K_{ABx}K_{AB\gamma} \tag{3}$$

where the superscript * denotes pure liquid acid and

$$K_{Ax} = \frac{x_{A_2}}{x_{A_1}^2}, \quad K_{A\gamma} = \frac{\gamma_{A_2}}{\gamma_{A_1}^2} \tag{4}$$

$$K_{Bx} = \frac{x_{B_2}}{x_{B_1}^2}, \quad K_{B\gamma} = \frac{\gamma_{B_2}}{\gamma_{B_1}^2} \tag{5}$$

$$K_{ABx} = \frac{x_{AB}}{x_{A_1}x_{B_1}}, \quad K_{AB\gamma} = \frac{\gamma_{AB}}{\gamma_{A_1}\gamma_{B_1}} \tag{6}$$

We can take $K_{AB}^{L} = 2(K_{AA}^{L}K_{BB}^{L})^{1/2}$ as a consequence of the similar chemical nature of both acids [6].

The NRTL equation [13] is used to express molecular interactions between five molecular species, A_1, A_2, B_1, B_2 and AB. The activity coefficient of any molecular species i is given by

$$\ln \gamma_i = \frac{\sum_j \tau_{ji}G_{ji}x_j}{\sum_k G_{ki}x_k} + \sum_j \frac{x_j G_{ij}}{\sum_k G_{kj}x_k}\left(\tau_{ij} - \frac{\sum_l x_l \tau_{lj} G_{lj}}{\sum_k G_{kj}x_k}\right) \tag{7}$$

with

$$G_{ij} = \exp(-\alpha_{ij}\tau_{ij}) \tag{8}$$

$$\tau_{ij} = a_{ij}/T \tag{9}$$

We use two adjustable interaction parameters a_{AB} and a_{BA} with the assumptions that $a_{A_1B_1} = 2a_{A_2B_1} = 2a_{A_1B_2} = 4a_{A_2B_2} = a_{AB}$, $a_{B_1A_1} = 2a_{B_2A_1} = 2a_{B_1A_2} = 4a_{B_2A_2} = a_{BA}$, and one value for the non-randomness parameters α_{ij} of all binary pairs. As described in previous papers (10–12), $a_{A_1A_2} = a_{A_2A_1} = -100\ K$ and $a_{B_1B_2} = a_{B_2B_1} = -80\ K$.

As the chemical potential of the nominal associating component should be equal to that of the monomer of the same component [1], the following relations can be derived

$$x_A\gamma_A = \frac{x_{A_1}\gamma_{A_1}}{(x_{A_1}^*\gamma_{A_1}^*)} \tag{10}$$

$$x_B\gamma_B = \frac{x_{B_1}\gamma_{B_1}}{(x_{B_1}^*\gamma_{B_1}^*)} \tag{11}$$

The monomer mole fractions are related to the stoichiometric mole fractions by

$$x_A = \frac{x_{A_1} + 2K_{Ax}x_{A_1}^2 + K_{ABx}x_{A_1}x_{B_1}}{x_{A_1} + 2K_{Ax}x_{A_1}^2 + 2K_{ABx}x_{A_1}x_{B_1} + 2K_{Bx}x_{B_1}^2 + x_{B_1}} \tag{12}$$

$$x_B = \frac{x_{B_1} + 2K_{Bx}x_{B_1}^2 + K_{ABx}x_{A_1}x_{B_1}}{x_{A_1} + 2K_{Ax}x_{A_1}^2 + 2K_{ABx}x_{A_1}x_{B_1} + 2K_{Bx}x_{B_1}^2 + x_{B_1}} \tag{13}$$

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

$$x_{A_1} + K_{Ax}x_{A_1}^2 + K_{ABx}x_{A_1}x_{B_1} + K_{Bx}x_{B_1}^2 + x_{B_1} = 1 \tag{14}$$

CALCULATION PROCEDURE

The compositions of the vapour and liquid phases are related by a set of the thermodynamic relations, one for each component i.

$$P\phi_i y_i = \gamma_i x_i P_i^s \phi_i^s \exp\left[\frac{v_i^L(P - P_i^s)}{RT}\right] \tag{15}$$

where P is the total pressure, y is the vapour phase mole fraction, P^s is the pure component saturated vapour pressure and v^L is the pure liquid molar volume calculated from the modified Rackett equation [14].

According to a chemical theory of vapour phase imperfections [3,8], deviations from the ideal gas law are attributed to dimerization, to association of like molecules and to solvation of unlike molecules. The three equilibrium constants are defined by

$$K_{\mathrm{AA}}^{\mathrm{V}}=\frac{f_{\mathrm{A}_2}}{f_{\mathrm{A}_1}^2}=\frac{z_{\mathrm{A}_2}}{z_{\mathrm{A}_1}^2}\,\frac{\phi_{\mathrm{A}_2}^{\ominus}}{\phi_{\mathrm{A}_1}^{\ominus 2}P} \tag{16}$$

$$K_{\mathrm{BB}}^{\mathrm{V}}=\frac{f_{\mathrm{B}_2}}{f_{\mathrm{B}_1}^2}=\frac{z_{\mathrm{B}_2}}{z_{\mathrm{B}_1}^2}\,\frac{\phi_{\mathrm{B}_2}^{\ominus}}{\phi_{\mathrm{B}_1}^{\ominus 2}P} \tag{17}$$

$$K_{\mathrm{AB}}^{\mathrm{v}}=\frac{f_{\mathrm{AB}}}{f_{\mathrm{A}_1}f_{\mathrm{B}_1}}=\frac{z_{\mathrm{AB}}}{z_{\mathrm{A}_1}z_{\mathrm{B}_1}}\,\frac{\phi_{\mathrm{AB}}^{\ominus}}{\phi_{\mathrm{A}_1}^{\ominus}\phi_{\mathrm{B}_1}^{\ominus}P} \tag{18}$$

where f is the fugacity of the true, chemical species and the true mole fraction z is not identical to y which is the stoichiometric mole fraction. It is assumed that the Lewis fugacity rule is used for calculating the fugacity coefficients of the true species and the second virial coefficients for monomer i and homodimer i_2 are given by $B_{\mathrm{A}_1}^{\mathrm{F}}=B_{\mathrm{A}_2}^{\mathrm{F}}$ and $B_{\mathrm{B}_1}^{\mathrm{F}}=B_{\mathrm{B}_2}^{\mathrm{F}}$. B_i^{F} is the free contribution to the second virial coefficient of species i [15]. Then the fugacity coefficients of the true species are given by

$$\phi_{\mathrm{A}_1}^{\ominus}=\exp\frac{B_{\mathrm{A}_1}^{\mathrm{F}}P}{RT}=\phi_{\mathrm{A}_2}^{\ominus} \tag{19}$$

$$\phi_{\mathrm{B}_1}^{\ominus}=\exp\frac{B_{\mathrm{B}_1}^{\mathrm{F}}P}{RT}=\phi_{\mathrm{B}_2}^{\ominus} \tag{20}$$

$$\phi_{\mathrm{AB}}^{\ominus}=\exp\frac{B_{\mathrm{AB}}^{\mathrm{F}}P}{RT} \tag{21}$$

The mass balance equations are

$$n_{\mathrm{A}}=n_{\mathrm{A}_1}+2n_{\mathrm{A}_2}+n_{\mathrm{AB}} \tag{22}$$

$$n_{\mathrm{B}}=n_{\mathrm{B}_1}+2n_{\mathrm{B}_2}+n_{\mathrm{AB}} \tag{23}$$

The true mole fractions of the species are found from eqns. (16)–(23).

Prigogine and Defay [1] proved that in a mixture of both associating components A and B, the fugacity of component A is equal to the fugacity of monomer A_1 and that of component B is equal to the fugacity of monomer B_1. Thus,

$$\phi_{\mathrm{A}}=\left(\frac{z_{\mathrm{A}_1}}{y_{\mathrm{A}}}\right)\exp\frac{B_{\mathrm{A}_1}^{\mathrm{F}}P}{RT} \tag{24}$$

and

$$\phi_{\mathrm{B}}=\left(\frac{z_{\mathrm{B}_1}}{y_{\mathrm{B}}}\right)\exp\frac{B_{\mathrm{B}_1}^{\mathrm{F}}P}{RT} \tag{25}$$

The chemical equilibrium constant K_{ij}^{V} is calculated from the relation

$$K_{ij}^{V} = \frac{-B_{ij}^{D}(2-\delta_{ij})}{RT} \tag{26}$$

where $\delta_{ij} = 0$ when $i \neq j$, and $\delta_{ij} = 1$ when $i = j$, and B_{ij}^{D} is the dimerization contribution to the second virial coefficient [15]. More details of the calculations described above are shown elsewhere [8].

The temperature variation of the liquid phase mole fraction dimerization constants for pure acetic and propanoic acids was given by Barton and Hsu [5], who correlated Freedman's calculated results of the mole fraction equilibrium constant derived from an equation for the excess acoustic absorption of pure acetic and propanoic acids [4]

$$\ln K_{Ax}^{*} = \frac{3131}{T} - 6.5197 \tag{27}$$

$$\ln K_{Bx}^{*} = \frac{4930}{T} - 8.6632 \tag{28}$$

Isothermal experimental vapour–liquid equilibrium data for the acetic acid–propanoic acid system are available graphically at 20 °C. Equations (27) and (28) provide values of K_{Ax}^{*} and K_{Bx}^{*} at 20 °C. From these K_{Ax}^{*} and K_{Bx}^{*}, the monomer and dimer mole fractions of pure acetic acid are solved from $x_{A_1}^{*} + K_{Ax}^{*} x_{A_1}^{*2} = 1$ and similarly those of propanoic acid are obtained. Then the activity coefficients of the monomer and dimer at two pure liquid reference states are calculated by using the NRTL equation with $a_{A_1A_2} = a_{A_2A_1} = -100$ K, $a_{B_1B_2} = a_{B_2B_1} = -80$ K and $\alpha_{A_1A_2} = \alpha_{A_2A_1} = \alpha_{B_1B_2} = \alpha_{B_2B_1} = 0.3$. Hence we can obtain the values of K_{AA}^{L} and K_{BB}^{L} from eqns. (1) and (2), and K_{AB}^{L} from the relation $K_{AB}^{L} = 2\sqrt{K_{AA}^{L} K_{BB}^{L}}$.

For a set of starting values of $a_{AB} = -100$ K and $a_{BA} = -100$ K, an iterative method is used to obtain the true compositions and the activity coefficients of all the chemical species present at the first nominal composition of x_A by simultaneous solution of eqns. (1)–(7), (12) and (14). Similarly, computations advance gradually to the last data point. Then the parameters are readjusted to give a better fitting of the model to the experimental data. The computer program used in this work was similar to that described by Prausnitz et al. [8].

For the propanoic acid–water system where complex formation between unlike molecules is assumed in the same manner as the acetic acid–water system [3], $a_{A_1B_1}$, $a_{B_1A_1}$ and a_{A_1AB} are sought, on the assumptions that $a_{A_1B_1} = 2a_{A_2B_1}$, $2a_{B_1A_2} = a_{B_1A_1}$, $a_{A_1AB} = 2a_{A_2AB} = a_{ABA_1} = a_{B_1AB} = a_{ABB_1}$ and all α_{ij} are set as 0.3. The three parameters were obtained by minimizing the following objective function

$$F = \sum_{i}^{N} \left[\frac{(P_i - \hat{P}_i)^2}{\sigma_P^2} + \frac{(T_i - \hat{T}_i)^2}{\sigma_T^2} + \frac{(x_{1i} - \hat{x}_{1i})^2}{\sigma_x^2} + \frac{(y_{1i} - \hat{y}_{1i})^2}{\sigma_y^2} \right] \tag{29}$$

where a circumflex indicates a calculated value corresponding to each experimental point and σ is the estimated standard deviation for each of the measured variables: $\sigma_P = 1$ Torr for pressure, $\sigma_T = 0.05\,^\circ C$ for temperature, $\sigma_x = 0.001$ for the liquid phase mole fraction and $\sigma_y = 0.003$ for the vapour phase mole fraction.

CALCULATED RESULTS

Figure 1 shows experimental and calculated vapour–liquid equilibrium for the acetic acid–propanoic acid system. Both components self-associate strongly and solvate with each other. The data are well represented by the model. The fugacity coefficients are appreciably far from unity and the activity coefficients deviate only slightly from ideal solution behaviour. Figure 2 plots the variation of the liquid phase mole fraction equilibrium constants as a function of composition.

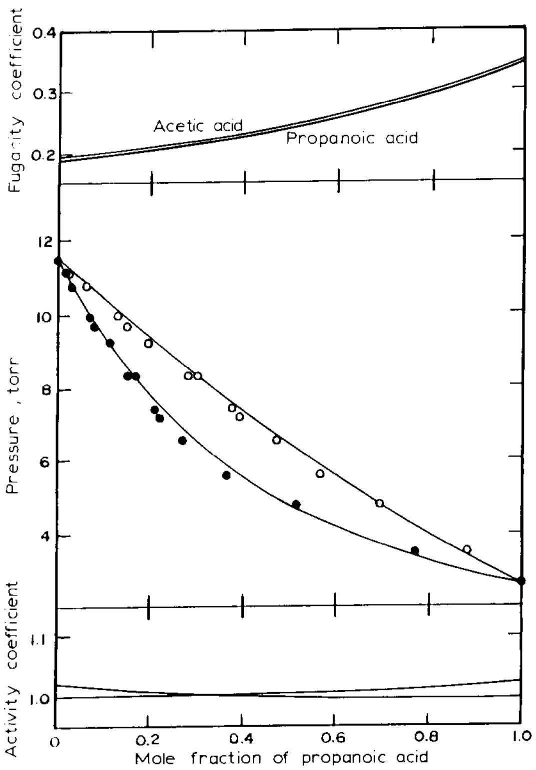

Fig. 1. Vapour–liquid equilibrium for acetic acid–propanoic acid at 20 ° C. Experimental data of Christian [16] (●); calculated with $a_{AB} = 280.51$ K, $a_{BA} = -279.33$ K and $\alpha_{AB} = \alpha_{BA} = 0.3528$ (———).

TABLE 1

Calculated results for binary systems with solvation

System (A–B)	Temp. (°C)	Number of data points	Root mean square deviations				Parameters				Variance of fit [a]	Ref.
			δP (Torr)	δT (K)	δx ($\times 10^3$)	δy ($\times 10^3$)	$a_{A_1B_1}$ (K)	$a_{B_1A_1}$ (K)	a_{A_1AB} (K)	α_{AB}		
Propanoic acid–water	40	8	1.14	0.00	0.0	6.4	−56.67	972.28	−1968.05	0.3	8.44	17
	50	8	1.46	0.00	0.0	7.4	−66.82	1042.83	−1938.16	0.3	13.04	17
	60	8	2.31	0.00	0.0	6.7	−180.83	1066.58	−1449.54	0.3	16.43	17
	60 [b]	17	2.62	0.00	0.0	16.7	273.84	657.65	−1569.64	0.3	45.78	18
	80 [b]	18	2.35	0.02	0.4	9.5	−86.02	945.20	−1685.11	0.3	18.92	18
	90 [b]	17	1.93	0.01	0.2	8.9	−168.95	1030.16	−1537.26	0.3	15.32	18

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

[b] Pure component vapour pressures were calculated from the Antoine equation whose constants were taken from the literature: propanoic acid [19]; water [20].

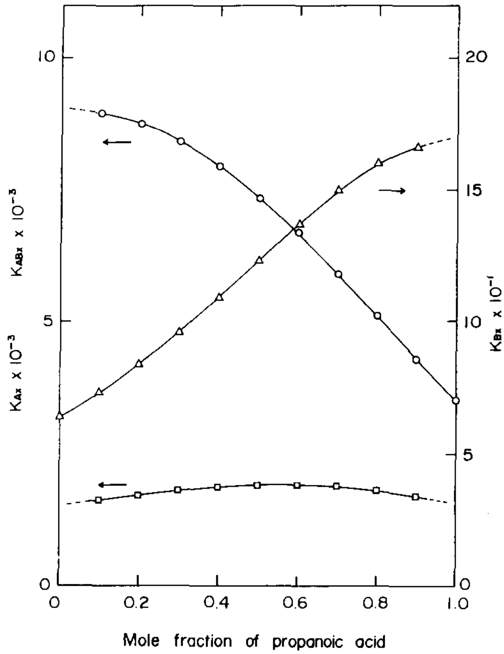

Fig. 2. Variation of liquid phase mole fraction equilibrium constants with composition: K_{Ax} (○——○); K_{ABx} (□——□); and K_{Bx} (△——△).

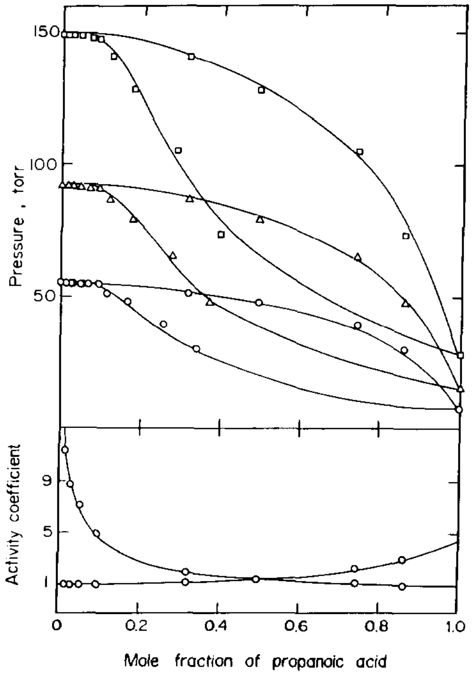

Fig. 3. Vapour–liquid equilibria for propanoic acid–water. Experimental data of Brazusskene [17] at (○) 40 °C, (△) 50 °C and (□) 60 °C; calculated (———).

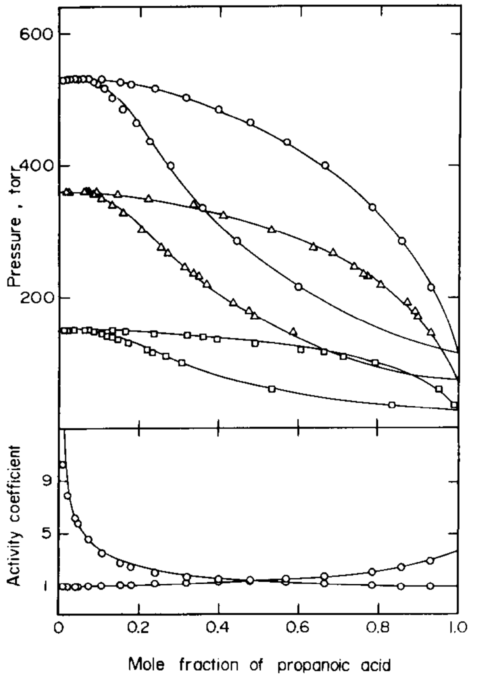

Fig. 4. Vapour–liquid equilibria for propanoic acid–water. Experimental data of Rafflenbeul and Hartmann [18] at (□) 60 °C, (△) 80 °C and (○) 90 °C: calculated (———).

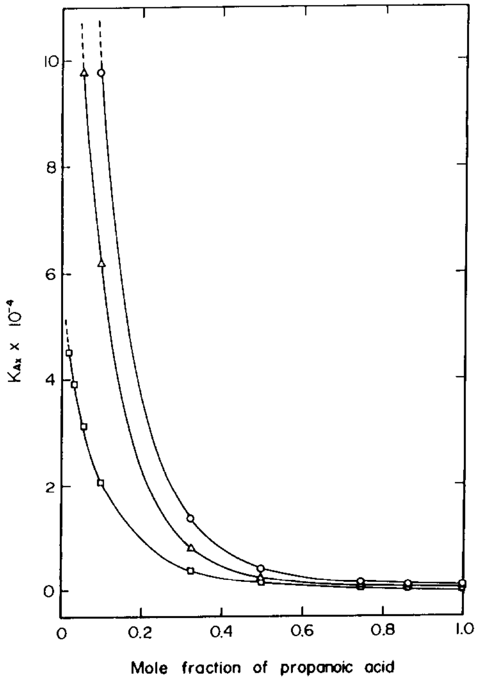

Fig. 5. Variation of liquid phase mole fraction association constant with composition. Propanoic acid–water at (○———○) 40 °C, (△———△) 50 °C and (□———□) 60 °C.

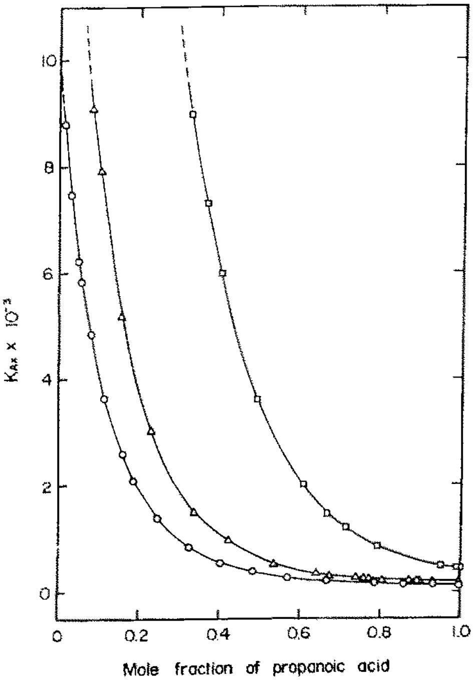

Fig. 6. Variation of liquid phase mole fraction association constant with composition. Propanoic acid–water at (□——□) 60 °C, (△——△) 80 °C and (○——○) 90 °C.

For the propanoic acid–water system, water was assumed not to self-associate. The liquid phase mole fraction solvation constant K_{ABx} is 0.8 at 25 °C and the enthalpy of complex formation h_{AB} is -5.7 kJ mol^{-1}, which is the same as that for the acetic acid–water system [11]. h_{AB} was assumed to be temperature independent and fixes the temperature dependence of K_{ABx} by the van't Hoff relation. Table 1 shows calculated results for the propanoic acid–water system and a graphical comparison between the calculated and experimental results is given in Figs. 3 and 4, showing that the model works well for this system. The liquid phase mole fraction dimerization constant varies with composition as shown by Figs. 5 and 6.

LIST OF SYMBOLS

A, B	acetic acid and propanoic acid or propanoic acid and water
a_{ij}	NRTL binary interaction parameter related to τ_{ij} for i–j
B_{ij}^{D}	dimerization contribution to the second virial coefficient for i–j interaction
B_{ij}^{F}	free contribution to the second virial coefficient for i–j interaction

F	objective function as defined by eq. (29)
f	fugacity
G_{ij}	coefficient as defined by $\exp(-\alpha_{ij}\tau_{ij})$
h_{AB}	enthalpy of complex formation for propanoic acid–water
K_{AA}^{L}, K_{BB}^{L}	liquid phase thermodynamic association constants for acetic acid and propanoic acid
K_{AB}^{L}	liquid phase thermodynamic solvation constant between acetic acid and propanoic acid
K_{Ax}, K_{Bx}	liquid phase mole fraction association constants for acetic acid and propanoic acid
K_{ABx}	liquid phase mole fraction solvation constant for acetic acid and propanoic acid or propanoic acid and water
$K_{A\gamma}$, $K_{B\gamma}$, $K_{AB\gamma}$	activity coefficient ratios
K_{ij}^{V}	vapour phase equilibrium dimerization constant for i–j pair
n	number of moles
P	total pressure
P_i^s	saturated vapour pressure of pure component i
R	universal gas constant
T	absolute temperature
v_i^L	pure liquid molar volume of component i
x_i	liquid phase mole fraction of component i or molecular species i
y_i	vapour phase mole fraction of component i
z_i	true vapour phase mole fraction of molecular species i

Greek letters

α_{ij}	NRTL non-randomness parameter for i–j pair
γ_i	activity coefficient of component i or molecular species i
δ_{ij}	Kronecker δ, $\delta_{ij}=0$ for $i \neq j$ and $\delta_{ij}=1$ for $i=j$
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}	NRTL binary parameter as defined by a_{ij}/T for i–j interaction
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
$\phi_i^{\ominus}$	vapour phase fugacity coefficient of true molecular species i

Subscripts

A_1, A_2	monomer and dimer of acetic acid or propanoic acid
AB	1 : 1 complex of acetic acid and propanoic acid or propanoic acid and water

B_1, B_2	monomer and dimer of propanoic acid or monomer of water
i, j, k, l	chemical molecular species or components

Superscripts

*	pure liquid state
L	liquid
V	vapour

REFERENCES

1 I. Prigogine and I. Defay, Chemical Thermodynamics, Longmans Green, London, 1954, Chapter 26.

2 J. Marek and G. Standart, Collect. Czech. Chem. Commun., 19 (1954) 1074.

3 K.H. Nothnagel, D.S. Abrams and J.M. Prausnitz, Ind. Eng. Chem. Process Des. Dev., 12 (1973) 25.

4 E. Freedman, J. Chem. Phys., 21 (1953) 1784.

5 J.R. Barton and C.C. Hsu, Chem. Eng. Sci., 27 (1972) 1315.

6 J.M. Prausnitz, R.N. Lichtenthaler and E. Azvedo, Molecular Thermodynamics of Fluid Phase Equilibria, 2nd edn., Prentice–Hall, Englewood Cliffs, NJ, 1986, p. 186.

7 J. Marek, Collect. Czech. Chem. Commun., 20 (1955) 1490.

8 J.M. Prausnitz, T.F. Anderson, C.A. Eckert, R. Hsieh and J.P. O'Connell, Computer Calculations of Multicomponent Vapor–Liquid and Liquid–Liquid Equilibria, Prentice–Hall, Englewood Cliffs, NJ, 1980, Chapters 3, 4, 6 and Appendices A, C and D.

9 J.D. Jenkins and M. Gibson-Robinson, Chem. Eng. Sci., 32 (1977) 931.

10 I. Nagata and T. Satoh, Thermochim. Acta, 132 (1988) 53.

11 I. Nagata and T. Satoh, Thermochim. Acta, 138 (1989) 207.

12 I. Nagata, Thermochim. Acta, 142 (1989) 351.

13 H. Renon and J.M. Prausnitz, AIChE. J., 14 (1968) 135.

14 C.F. Spencer and R.P. Danner, J. Chem. Eng. Data, 17 (1972) 236.

15 J.G. Hayden and J.P. O'Connell, Ind. Eng. Chem. Process Des. Dev., 14 (1975) 209.

16 S.D. Christian, J. Phys. Chem., 61 (1957) 1441.

17 D.J. Brazusskene, Liet. Zemes Ukio Akad. Moksliniai Darb., 6 (1965) 141.

18 L. Rafflenbeul and H. Hartmann, Chem. Techn., 7 (1978) 145.

19 T. Boublik, V. Fried and E. Hála, The Vapour Pressures of Pure Substances, 2nd edn., Elsevier, Amsterdam, 1984, p. 186.

20 J.A. Riddick, N.B. Bunger and T.K. Sakano, Organic Solvents, 4th edn., Wiley-Interscience, New York, 1986, p. 73.