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THERMODYNAMICS OF ASSOCIATED SOLUTIONS. VAPOUR–LIQUID EQUILIBRIUM AND EXCESS ENTHALPY FOR ACETIC ACID–POLAR UNASSOCIATED COMPONENT MIXTURES

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ABSTRACT

Isothermal vapour–liquid equilibrium and excess enthalpy data for binary mixtures of acetic acid with 2-butanone, ethyl acetate and water are analysed using an association model, which employs the dimerisation constant of acetic acid and the solvation constant of 1 : 1 complex formation between acetic acid and an active unassociated component with allowance for a physical contribution given by the NRTL equation. Calculated results agree well with experimental values.

INTRODUCTION

The thermodynamic properties of liquid mixtures containing self-associating and/or solvating components have been studied using useful models with a combination of chemical and physical interactions. Strong chemical interactions result in the formation of chemical species between like and unlike molecules. Many association models have employed separate chemical and physical contribution terms.

The isothermal vapour–liquid equilibrium and excess enthalpy data of binary solutions containing acetic acid and a non-polar component have been successfully analysed using an association model which assumes only the dimerisation equilibrium of acid molecules with physical interactions between chemical species [1]. In this work, an extended form of the previous approach is presented to correlate vapour–liquid equilibrium and excess enthalpy data for mixtures of acetic acid with 2-butanone, ethyl acetate and water under the assumptions of the dimerisation of acetic acid molecules as well as the 1 : 1 solvation of an acetic acid molecule and an active unassociating component molecule.

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SOLUTION MODEL

In a binary mixture of acetic acid (A) and a solvating component (B) there exist four chemical species A_1, A_2, AB and B_1 according to two chemical reactions ($A_1 + A_1 \rightarrow A_2$ and $A_1 + B_1 \rightarrow AB$) [2]. The thermodynamic dimerisation constant for the acid K_T and the solvation constant K_{AB} are defined by

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

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

where x_{A_1}, x_{A_2}, x_{AB} and x_{B_1} are the true mole fractions of the monomer and dimer of the acid, the heterodimer of the acid and a solvating component and the monomer of a solvating component respectively, γ_{A_1} and γ_{A_2} are the activity coefficients of the monomer and dimer of the acid, K_x is the liquid-phase mole fraction dimerisation constant as defined by $x_{A_2}/x^2_{A_1}$, K_γ is the activity coefficient ratio given by $\gamma_{A_2}/\gamma^2_{A_1}$, and the superscript $\star$ indicates a pure acid state.

The NRTL equation [3] is used to express the activity coefficient of any chemical species i:

$$\ln \gamma_i = \frac{\sum\limits_{j} \tau_{ji} G_{ji} x_j}{\sum\limits_{k} G_{ki} x_k} + \sum_j \left[\frac{x_j G_{ij}}{\sum\limits_{k} G_{kj} x_k} \left(\tau_{ij} - \frac{\sum\limits_{r} x_r \tau_{rj} G_{rj}}{\sum\limits_{k} G_{kj} x_j} \right) \right] \tag{3}$$

where the coefficients τ_{ji} and G_{ji} are expressed in terms of the energy parameter a_{ji}:

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

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

In the determination of the energy parameters a_{ji} and the non-randomness parameters α_{ji}, there are four options and the following assignment for a_{ji} is selected as described previously [2]: $a_{A_1B_1} = 2a_{A_2B_1}$, $a_{B_1A_1} = 2a_{B_1A_2}$, $a_{A_1AB} = a_{ABA_1} = a_{B_1AB} = a_{ABB_1} = 2a_{A_2AB} = 2a_{ABA_2}$ and all α_{ji} are taken as 0.3. The three remaining parameters $a_{A_1B_1}$, $a_{B_1A_1}$ and a_{A_1AB} are obtained from fitting the model to experimental vapour–liquid equilibrium data. For acetic acid we take the value of $a_{A_1A_2} = a_{A_2A_1} = -100$ K [2] and the liquid-phase mole fraction dimerisation constant and the enthalpy of hydrogen bond formation are $K^{\star}_x = 62$ at 20 °C and $h_A = -26$ kJ mol^{-1} as given by Freedman [4]. The temperature-dependence of the dimerisation constant is given by an integrated form of the van't Hoff equation:

$$K^{*}_x = K^{*}_x(20\,°C)\exp[(h_A/R)(1/293.15 - 1/T)] \tag{6}$$

Values of the solvation constant and the enthalpy of complex formation are as follows: $K_{AB} = 0.7$ at 65 °C and $h_{AB} = -12.8$ kJ mol^{-1} for acetic acid–2-butanone; $K_{AB} = 0.6$ at 65 °C and $h_{AB} = -11.2$ kJ mol^{-1} for acetic acid–ethyl acetate; $K_{AB} = 2.0$ at 20 °C and $h_{AB} = -14.1$ kJ mol^{-1} for acetic acid–water. The new values of K_{AB} and h_{AB} for acetic acid–water are different from previous values [2]. Values of h_{AB} were approximately estimated as $h_{AB} = h_A/2 - h^E_{x_A \to 0}$, where $h^E_{x_A \to 0}$ is the molar enthalpy of infinite dilution of acetic acid in each binary mixture and was calculated from the Redlich–Kister equation [5–7]. The value of $h^E_{x_A \to 0}$ for acetic acid–ethyl acetate was that for acetic acid–methyl acetate at 35 °C [5].

The monomer mole fractions of the chemical species present satisfy the following equations:

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

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

$$x_{A_1} + x_{A_2} + x_{AB} + x_{B_1} = x_{A_1} + K_x x_{A_1}^2 + K_{AB} x_{A1} x_{B_1} + x_{B_1} = 1 \tag{9}$$

According to Prigogine and Defay [8] the activity of the nominal component is equal to the corresponding monomer activity:

$$x_A \gamma_A = \frac{x_{A_1} \gamma_{A_1}}{x_{A_1}^\star \gamma_{A_1}^\star} \tag{10}$$

$$x_B \gamma_B = x_{B_1} \gamma_{B_1} \tag{11}$$

Equations (10) and (11) are used to reduce vapour–liquid equilibrium data.

The excess enthalpy of the mixture h^E is expressed as the sum of chemical and physical contribution terms:

$$h^E = \frac{h_A K_x x_{A_1}^2 + h_{AB} K_{AB} x_{A_1} x_{B_1}}{x_{A_1} + 2K_x x_{A_1}^2 + 2K_{AB} x_{A_1} x_{B_1} + x_{B_1}} - \frac{x_A h_A K_x^\star x_{A1}^{\star 2}}{x_{A_1}^\star + 2K_A^\star x_{A_1}^{\star 2}}$$
$$+ R \sum_I x_I \left\{ \frac{\sum_J x_J [\partial(\tau_{JI} G_{JI})/\partial(1/T)]}{\sum_K G_{KI} x_I} \right.$$
$$\left. - \frac{\sum_J \tau_{JI} G_{JI} x_J \sum_K x_K [\partial(G_{KI})/\partial(1/T)]}{\left(\sum_K G_{KI} x_K\right)^2} \right\} \tag{12}$$

The linear temperature-dependences of the three energy parameters are assumed to be

$$a_{A_1B_1} = C_{A_1B_1} + D_{A_1B_1}(T - 273.15)$$

$$a_{B_1A_1} = C_{B_1A_1} + D_{B_1A_1}(T - 273.15)$$

$$a_{A_1AB} = C_{A_1AB} + D_{A_1AB}(T - 273.15) \tag{13}$$

CALCULATION PROCEDURE AND RESULTS

In this work, the vapour–liquid equilibrium and excess enthalpy data of binary mixtures containing acetic acid were separately correlated with the association model, because a simultaneous correlation of both data usually gives larger deviations between calculated and experimental results than a separated correlation. First we try to fit the model to experimental vapour–liquid equilibrium data in order to obtain an optimum set of the parameters. Secondly, using the obtained binary parameters and other pertinent pure-component properties, we can calculate the monomer mole fractions of the chemical species present for each value of the nominal compositions of the excess enthalpy data [1].

Vapour–liquid equilibrium data reduction was performed on the basis of the following thermodynamic relation:

$$P\phi_i y_i = \gamma_i x_i P_i^s \phi_i^s \exp\left[\frac{v_i(P - P_i^s)}{RT}\right] \tag{14}$$

where P is the total pressure, y the nominal vapour-phase mole fraction, P^s the pure-component vapour pressure and v^L the pure-liquid molar volume calculated from a modified Rackett equation [9]. The fugacity coefficients ϕ were calculated using the chemical theory of vapour-phase imperfections [10,11]:

$$\ln \phi_i = \frac{z_i}{y_i} \exp\left(\frac{B_i^F P}{RT}\right) \tag{15}$$

where z is the true vapour-phase mole fraction and B_i^F the free contribution to the second virial coefficient. The true vapour-phase mole fractions and the fugacity coefficients were calculated as described by Prausnitz et al. [12].

A set of optimum binary parameters were sought using a computer program which minimises the objective function [12]

$$F_1 = \sum_{i=1}^{N} \left[\frac{(P_i - \hat{P}_i)^2}{\sigma_P^2} + \frac{(T_i - \hat{T}_i)^2}{\sigma_T^2} + \frac{(x_{1i} - \hat{x}_{1i})^2}{\sigma_x^2} + \frac{(y_{1i} - \hat{y}_{1i})^2}{\sigma_y^2} \right] \tag{16}$$

TABLE 1

Calculated results of vapour–liquid equilibrium data reduction for binary acetic acid–solvating component mixtures

System (A–B)	Temperature (°C)	Number of data points	Root-mean-square deviations				Parameters				Variance of fit [a]		Reference
			δP (Torr)	δT (K)	δx ($\times 10^3$)	δy ($\times 10^3$)	$a_{A_1A_2}$ (K)	$a_{A_1B_1}$ (K)	$a_{B_1A_1}$ (K)	a_{A_1AB} (K)	I [b]	II [c]	
Acetic acid– 2-butanone	68.5	8 [d]	2.05	0.00	1.0	2.9	−100	−568.28	548.91	2400.84		9.79	[13]
	78	8 [d]	3.37	0.00	1.5	4.0	−100	−708.99	1342.04	−242.17		24.64	[13]
Acetic acid– ethyl acetate	65	11	1.65	0.00	1.4	10.7	−100	−613.43	757.43	844.65		24.62	[14]
Acetic acid– water	20	10	0.10	0.00	0.2	2.1	−100	756.99	−383.97	−121.49	6.37	0.79	[15]
	40	11	0.39	0.00	0.2	1.8	−100	835.45	−436.33	85.06	8.68	0.73	[15]
	69.7	11	0.91	0.00	0.6	5.6	−100	84.73	38.53	−481.61	6.50	6.42	[16]
	79.9	11	0.50	0.00	0.5	5.2	−100	88.35	52.81	−382.28	4.92	4.74	[16]
	80	10	1.75	0.00	0.7	4.6	−100	260.15	−77.54	24.36	11.74	8.42	[15]
	89.9	11	0.71	0.00	0.5	5.0	−100	26.63	101.78	−462.85	6.26	4.93	[16]

[a] Variance of fit = (sum of squared, weighted residuals)/(number of degrees of freedom) = F_1/(number of data points − number of parameters).

[b] Reference 2.

[c] This work.

[d] One erroneous experimental point rejected.

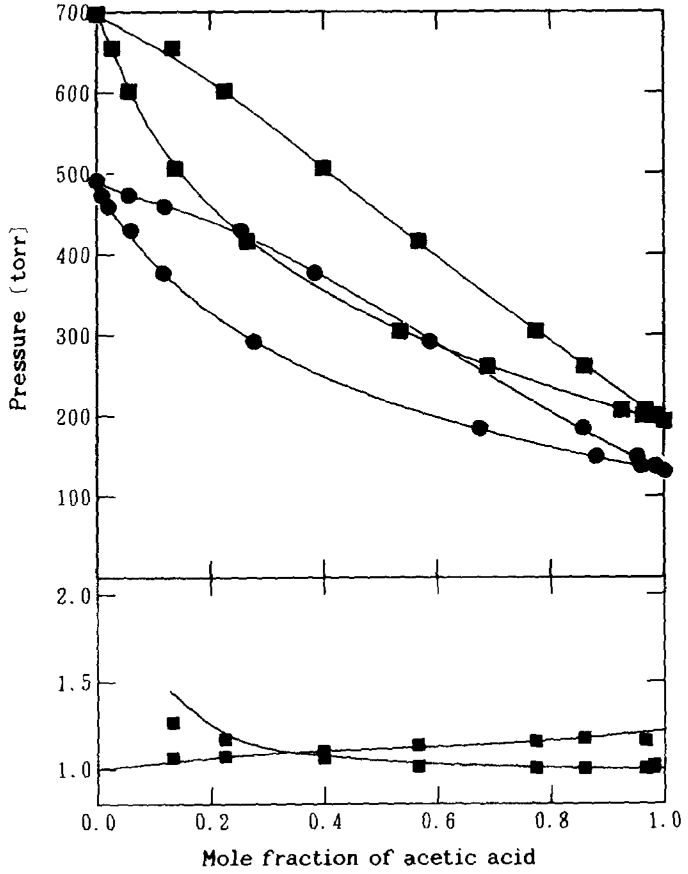

Fig. 1. Vapour–liquid equilibria for acetic acid–2-butanone: calculated (———) and experimental (●, 68.5° C; ■, 78° C; data of Rasmussen et al. [13]).

where a circumflex indicates the most probable calculated value corresponding to each experimental variable and the standard deviations in the observed variables were set as $\sigma_P = 1$ Torr, $\sigma_T = 0.05$ K, $\sigma_x = 0.001$ and $\sigma_y = 0.003$ [12].

The pure-component vapour pressures were taken from original references for vapour–liquid equilibrium data. Table 1 gives detailed results of vapour–liquid equilibrium data reduction for three systems. Figures 1 and 2 compare the experimental and calculated results for acetic acid–2-butanone and acetic acid–ethyl acetate. Figures 3 and 4 show how the liquid-phase mole fraction dimerisation constant K_x changes with liquid composition in these two systems. A new set of solvation parameters for acetic acid–water gives smaller values of the variance of fit than a previous set [2].

In the correlation of excess enthalpy data, the binary parameters given in Table 1 were used to obtain the true mole fractions of all chemical species for any value of the acid nominal mole fraction x_A at a specified tempera-

TABLE 2

Calculated results of excess enthalpy data for binary acetic acid–solvating component mixtures

System (A–B)	Temperature (°C)	Number of data points	Parameters						Absolute arithmetic mean deviation (J mol^{-1})	Reference
			$C_{A_1B_1}$ (J mol^{-1})	$D_{A_1B_1}$ (J mol^{-1} K^{-1})	$C_{B_1A_1}$ (J mol^{-1})	$D_{B_1A_1}$ (J mol^{-1} K^{-1})	C_{A_1AB} (J mol^{-1})	D_{A_1AB} (J mol^{-1} K^{-1})		
Acetic acid–2-butanone	20	17 [a]	10018.1	39.8512	8964.55	16.9584	−7306.78	−20.9735	1.0	[6]
Acetic acid–ethyl acetate	22.5 [b]	8 [c]	−9532.90	−29.4374	−1196.19	−3.3938	3999.20	15.9257	1.7	[18]
Acetic acid–water	20	9	−4563.83	−45.6347	30539.1	57.2914	−3574.11	7.7532	5.5	[7]
	40	9	6578.55	5.8813	8985.65	−48.8419	102.91	64.6142	2.0	[7]

[a] Two experimental points which deviate greatly rejected.

[b] Original experimental data points ranged from 19 to 26 °C.

[c] One experimental point which deviates greatly rejected.

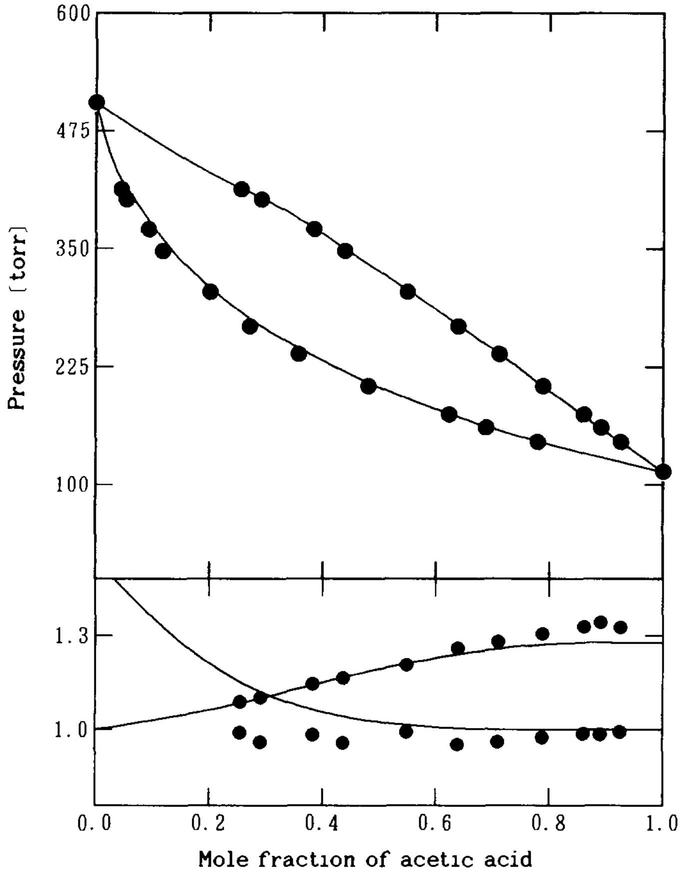

Fig. 2. Vapour–liquid equilibrium for acetic acid–ethyl acetate at 65 °C: calculated (———) and experimental (●; data of Macedo and Rasmussen [14]).

ture for the excess enthalpy data as described previously [1]. The six constants of eqn. (13) were obtained using the simplex method [17], which minimises the sum of squares of deviation in excess enthalpy for all data points:

$$F_2 = \sum_{i=1}^{N} \left(h_i^{\mathrm{E}} - \hat{h}_i^{\mathrm{E}}\right)^2 \qquad (17)$$

Table 2 shows calculated results for excess enthalpy and the calculated values are satisfactorily compared with the experimental results in Figs. 5 and 6.

We may conclude that the proposed model is able to reproduce the vapour–liquid equilibrium and excess enthalpy data of the acetic acid–solvating component systems studied with good accuracy.

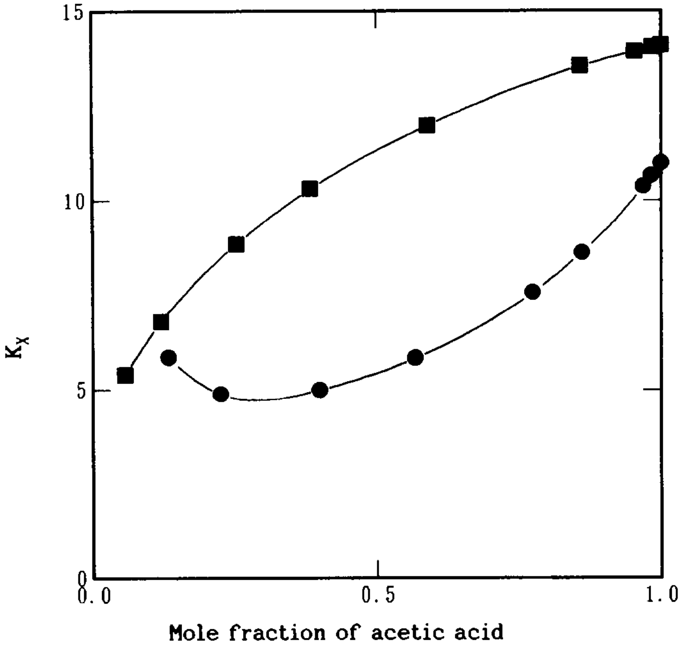

Fig. 3. Variation in liquid-phase mole fraction dimerisation constant with composition for acetic acid–2-butanone: ●, 68.5 °C; ■, 78 °C; data of Rasmussen et al. [13].

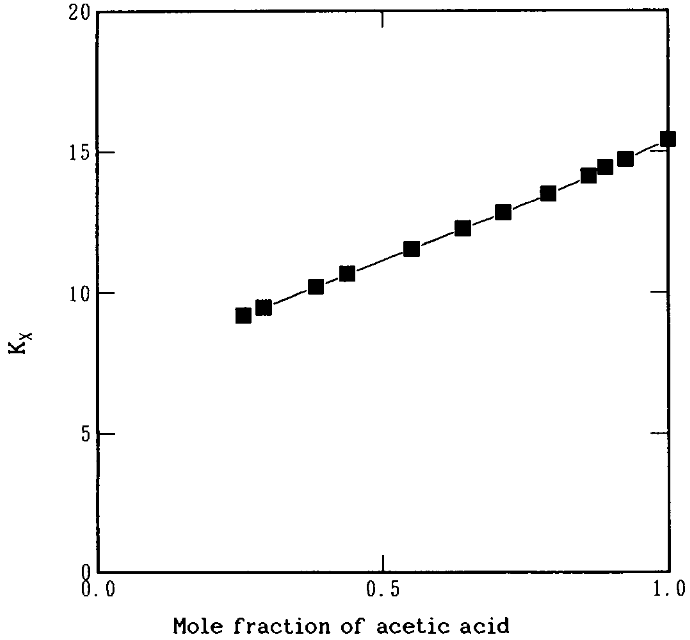

Fig. 4. Variation in liquid-phase mole fraction dimerisation constant with composition for acetic acid–ethyl acetate at 65 °C; ■, data of Macedo and Rasmussen [14].

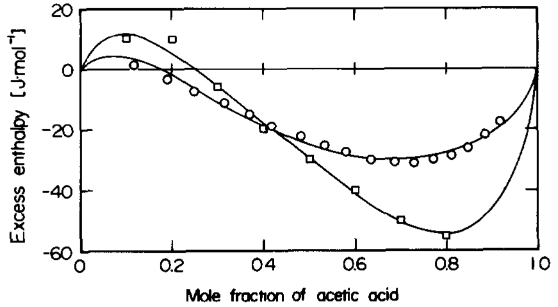

Fig. 5. Excess enthalpies for acetic acid–2-butanone and acetic acid–ethyl acetate; calculated (———) and experimental (○, acetic acid–2-butanone at 20 °C [6]; □, acetic acid–ethyl acetate at 22.5 °C; data of Lontin [18]).

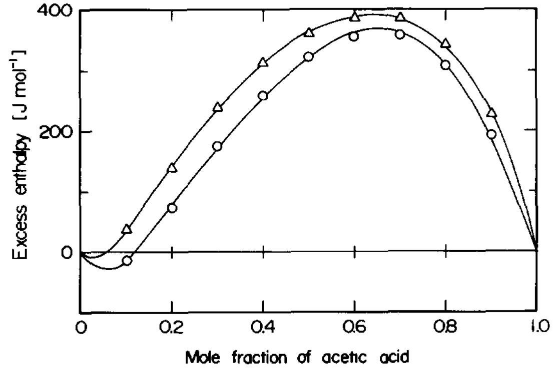

Fig. 6. Excess enthalpies for acetic acid–water: calculated (———) and experimental (○, 20 °C; △, 40 °C; data from Hasse et al. [7]).

LIST OF SYMBOLS

A, B	acetic acid and solvating component
a_{ji}	binary interaction parameter related to π_{ji}
B_i^F	free contribution to the second virial coefficient of component i
$C_{A_1B_1}$, $D_{A_1B_1}$, $C_{B_1A_1}$, $D_{B_1A_1}$, C_{A_1AB}, D_{A_1AB}	constants of eqn. (13)
F_1, F_2	objective functions as defined by eqns. (16) and (17)
G_{ji}	coefficient as defined by $\exp(-\alpha_{ji}\tau_{ji})$
h_A	molar enthalpy of hydrogen bond formation
h_{AB}	molar enthalpy of complex formation
h^E	molar excess enthalpy
K_{AB}	liquid-phase solvation constant
K_T	liquid-phase thermodynamic dimerisation constant for acetic acid

K_x	liquid-phase mole fraction dimerisation constant as defined by $x_{A2}/x_{A_1}^2$
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 molecular species i
y_i	nominal vapour-phase mole fraction of component i
z_i	true vapour-phase mole fraction of molecular species i at equilibrium

Greek letters

α_{ji}	non-randomness parameter for the j–i pair
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_{ji}	coefficient as defined by a_{ji}/T
ϕ_i	vapour-phase fugacity coefficient of component i at T and P
ϕ_i	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 a solvating component
B_1	monomer of a solvating component
i, j, k, r, I, J, K	chemical molecular species or components

Superscripts

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

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