Thermochimica Acta, 108 (1986) 305–323
Elsevier Science Publishers B.V., Amsterdam – Printed in The Netherlands

THERMODYNAMICS OF ASSOCIATED SOLUTIONS. EXCESS THERMODYNAMIC PROPERTIES OF LIQUID MIXTURES OF SOME ORGANIC COMPOUNDS WITH AMINES

ISAMU NAGATA

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

(Received 13 May 1986)

ABSTRACT

The UNIQUAC associated-solution model reproduces successfully the vapor pressure isotherms of binary aliphatic amine-saturated hydrocarbon mixtures by use of smaller values of the association constant for aliphatic amines than those given by Brandani. In the correlation of vapor–liquid equilibrium and excess enthalpy data for amine–alcohol mixtures, two cases are studied for solvation equilibria between these two self-associating components (A, B). In vapor–liquid equilibrium data reduction, for aliphatic amine–alcohol mixtures, a single solvation model forming A_iB_j complexes gives better results than a multisolvation model forming copolymers such as $(A_iB_j)_k$, $(A_iB_j)_kA_l$, $A_i(B_jA_k)_lB_m$, etc., and for aniline–alcohol mixtures the latter is better than the former. In excess enthalpy data reduction, both models give very similar results.

INTRODUCTION

Vapor–liquid equilibrium data for binary aliphatic amine–saturated hydrocarbon mixtures had been correlated by means of the UNIQUAC associated-solution model using the pure-liquid association parameters determined by Brandani's method [1], and the UNIQUAC associated-solution model failed unless a solvation effect is considered empirically [2]. The UNIQUAC associated-solution model correlates well the phase equilibrium and excess enthalpy data for binary and ternary mixtures of aniline with hydrocarbons by use of a smaller value of the association constant for aniline than that estimated by Brandani [3]. This paper shows that the UNIQUAC associated solution model accurately reproduces vapor–liquid equilibrium and excess molar enthalpy data for solutions containing one amine and one non-associating component or an aliphatic alcohol.

THEORY

Binary mixtures containing one associating and one active component

Let A stand for the self-associating component and B the active non-associating component. The self-associating component in solution forms linear

0040-6031/86/$03.50

polymers according to successive reactions expressed by

$$A_1 + A_i = A_{i+1} \tag{1}$$

and the equilibrium association constant for the above reaction is defined as

$$K_A = \frac{\Phi_{A_{i+1}}}{\Phi_{A_i}\Phi_{A_1}}\left(\frac{i}{i+1}\right) \tag{2}$$

K_A is independent of the degree of association. The temperature dependence of the association constant is fixed by the van't Hoff relation

$$\frac{\partial \ln K_A}{\partial(1/T)} = -\frac{h_A}{R} \tag{3}$$

where h_A is the enthalpy of hydrogen-bond formation and is assumed to be independent of the degree of association and of temperature. The active component forms chemical species A_iB according to the solvation reaction

$$A_i + B = A_iB \tag{4}$$

and the solvation constant K_{AB} is defined as

$$K_{AB} = \frac{\Phi_{A_iB}}{\Phi_{A_i}\Phi_{B_1}}\left(\frac{i}{ir_A + r_B}\right) \tag{5}$$

The structural parameters of the species A_iB are assumed to be expressed in terms of those for the monomer.

$$r_{A_iB} = ir_A + r_B$$

$$q_{A_iB} = iq_A + q_B \tag{6}$$

The activity coefficients for the self-associating component A and the active nonassociating component B [2,3] are expressed by

$$\ln \gamma_A = \ln\left(\frac{\Phi_{A_1}}{\Phi^0_{A_1}x_A}\right) + \frac{r_A}{V^0_A} - \frac{r_A}{V} - \left(\frac{Z}{2}\right)q_A\left[\ln\left(\frac{\Phi_A}{\theta_A}\right) + 1 - \frac{\Phi_A}{\theta_A}\right]$$
$$+ q_A\left[-\ln(\theta_A + \theta_B\tau_{BA}) + \theta_B\left(\frac{\tau_{BA}}{\theta_A + \theta_B\tau_{BA}} - \frac{\tau_{AB}}{\theta_B + \theta_A\tau_{AB}}\right)\right] \tag{7}$$

$$\ln \gamma_B = \ln\left(\frac{\Phi_{B_1}}{x_B}\right) + 1 - \frac{r_B}{V} - \left(\frac{Z}{2}\right)q_B\left[\ln\left(\frac{\Phi_B}{\theta_B}\right) + 1 - \frac{\Phi_B}{\theta_B}\right]$$
$$+ q_B\left[-\ln(\theta_B + \theta_A\tau_{AB}) + \theta_A\left(\frac{\tau_{AB}}{\theta_B + \theta_A\tau_{AB}} - \frac{\tau_{BA}}{\theta_A + \theta_B\tau_{BA}}\right)\right] \tag{8}$$

where

$$\tau_{BA} = \exp(-a_{BA}/T)$$

$$\tau_{AB} = \exp(-a_{AB}/T) \tag{9}$$

with

$$\Phi_A = x_A r_A/(x_A r_A + x_B r_B)$$
$$\Phi_B = x_B r_B/(x_A r_A + x_B r_B) \tag{10}$$
$$\theta_A = x_A q_A/(x_A q_A + x_B q_B)$$
$$\theta_B = x_B q_B/(x_A q_A + x_B q_B) \tag{11}$$

The true molar volume of the mixture V, the value of V in the pure self-associating component V_A^0, and the segment fraction of the monomer A at the pure-liquid state of the self-associating component $\Phi_{A_1}^0$ are expressed as

$$\frac{1}{V} = \frac{\Phi_{A_1}}{r_A(1 - K_A\Phi_{A_1})} + \frac{\Phi_{B_1}}{r_B}\left[1 + \frac{K_{AB} r_B \Phi_{A_1}}{(1 - K_A\Phi_{A_1})}\right] \tag{12}$$

$$1/V_A^0 = (1 - K_A\Phi_{A_1}^0)/r_A \tag{13}$$

$$\Phi_{A_1}^0 = \left[(2K_A + 1) - (1 + 4K_A)^{1/2}\right]/2K_A^2 \tag{14}$$

The segment fractions of the monomers, Φ_{A_1} and Φ_{B_1}, are numerically solved from the mass balance equations

$$\Phi_A = \frac{\Phi_{A_1}}{(1 - K_A\Phi_{A_1})^2}\left[1 + r_A K_{AB}\Phi_{B_1}\right] \tag{15}$$

$$\Phi_B = \Phi_{B_1}\left[1 + \frac{r_B K_{AB}\Phi_{A_1}}{(1 - K_A\Phi_{A_1})}\right] \tag{16}$$

Binary mixtures containing two associating components

Let A and B stand for the self-associating components. There are many stoichiometric possibilities for the solvation of the two self-associating components. In this paper, two solvation models are considered: (a) single solvation model [4,5]; (b) multisolvation model [6,7].

Single solvation model

In this case, together with species A_i and B_i, species A_iB_j are formed by the solvation reaction

$$A_i + B_j = A_iB_j \tag{17}$$

where the suffixes i and j range from unity to infinity. The solvation constant for the above reaction is defined as

$$K_{AB} = \frac{\Phi_{A_iB_j}}{\Phi_{A_i}\Phi_{B_j}}\left(\frac{ij}{ir_A + jr_B}\right) \tag{18}$$

The activity coefficient of the self-associating component B is given by

$$\ln \gamma_B = \ln\left(\frac{\Phi_{B_1}}{\Phi^0_{B_1} x_B}\right) + \frac{r_B}{V^0_B} - \frac{r_B}{V} - \left(\frac{Z}{2}\right) q_B \left[\ln\left(\frac{\Phi_B}{\theta_B}\right) + 1 - \frac{\Phi_B}{\theta_B}\right]$$
$$+ q_B \left[-\ln(\theta_B + \theta_A \tau_{AB}) + \theta_A \left(\frac{\tau_{AB}}{\theta_B + \theta_A \tau_{AB}} - \frac{\tau_{BA}}{\theta_A + \theta_B \tau_{BA}}\right)\right] \tag{19}$$

where $1/V$, $1/V^0_B$ and $\Phi^0_{B_1}$ are expressed by

$$\frac{1}{V} = \frac{\Phi_{A_1}}{r_A(1 - K_A \Phi_{A_1})} + \frac{K_{AB} \Phi_{A_1} \Phi_{B_1}}{(1 - K_A \Phi_{A_1})(1 - K_B \Phi_{B_1})} + \frac{\Phi_{B_1}}{r_B(1 - K_B \Phi_{B_1})} \tag{20}$$

$$1/V^0_B = \left(1 - K_B \Phi^0_{B_1}\right)/r_B \tag{21}$$

$$\Phi^0_{B_1} = \left[2K_B + 1 - (1 + 4K_B)^{1/2}\right]/2K^2_B \tag{22}$$

Φ_{A_1} and Φ_{B_1} are solved from the mass balance equations for both associating components given by

$$\Phi_A = \frac{\Phi_{A_1}}{(1 - K_A \Phi_{A_1})^2}\left[1 + \frac{r_A K_{AB} \Phi_{B_1}}{(1 - K_B \Phi_{B_1})}\right] \tag{23}$$

$$\Phi_B = \frac{\Phi_{B_1}}{(1 - K_B \Phi_{B_1})^2}\left[1 + \frac{r_B K_{AB} \Phi_{A_1}}{(1 - K_A \Phi_{A_1})}\right] \tag{24}$$

The excess molar enthalpy of the mixture [5] is

$$H^E = \frac{h_A x_A K_A (\Phi_{A_1})^2}{\Phi_A (1 - K_A \Phi_{A_1})^2}\left\{1 + K_{AB} r_A \Phi_{B_1}\left[1 + \frac{K_B \Phi_{B_1}}{(1 - K_B \Phi_{B_1})}\right]\right\}$$
$$+ \frac{h_B x_B K_B (\Phi_{B_1})^2}{\Phi_B (1 - K_B \Phi_{B_1})^2}\left\{1 + K_{AB} r_B \Phi_{A_1}\left[1 + \frac{K_A \Phi_{A_1}}{(1 - K_A \Phi_{A_1})}\right]\right\}$$
$$- \frac{h_A x_A K_A \left(\Phi^0_{A_1}\right)^2}{\left(1 - K_A \Phi^0_{A_1}\right)^2} - \frac{h_B x_B K_B \left(\Phi^0_{B_1}\right)^2}{\left(1 - K_B \Phi^0_{B_1}\right)^2}$$
$$- R\left[\frac{q_A x_A \theta_B}{(\theta_A + \theta_B \tau_{BA})} \frac{\partial \tau_{BA}}{\partial(1/T)} + \frac{q_B x_B \theta_A}{(\theta_B + \theta_A \tau_{AB})} \frac{\partial \tau_{AB}}{\partial(1/T)}\right] \tag{25}$$

In excess enthalpy data reduction, the linear temperature dependence of the energy parameters is assumed as follows

$$a_{BA} = C_A + D_A(T - 273.15)$$
$$a_{AB} = C_B + D_B(T - 273.15) \tag{26}$$

Multisolvation model

The pure *i*-mers of both associating components can solvate step by step to form linear copolymers according to the solvation reactions of the form

$$\begin{array}{ll}
\mathrm{A}_i + \mathrm{B}_j = \mathrm{A}_i\mathrm{B}_j & \mathrm{B}_i + \mathrm{A}_j = \mathrm{B}_i\mathrm{A}_j \\
\mathrm{A}_i\mathrm{B}_j + \mathrm{A}_k = \mathrm{A}_i\mathrm{B}_j\mathrm{A}_k & \mathrm{B}_i\mathrm{A}_j + \mathrm{B}_k = \mathrm{B}_i\mathrm{A}_j\mathrm{B}_k \\
\qquad\vdots & \qquad\vdots \\
(\mathrm{A}_i\mathrm{B}_j)_k + \mathrm{A}_l = (\mathrm{A}_i\mathrm{B}_j)_k\mathrm{A}_l & (\mathrm{B}_i\mathrm{A}_j)_k + \mathrm{B}_l = (\mathrm{B}_i\mathrm{A}_j)_k\mathrm{B}_l \\
\mathrm{A}_i(\mathrm{B}_j\mathrm{A}_k)_l + \mathrm{B}_m = \mathrm{A}_i(\mathrm{B}_j\mathrm{A}_k)_l\mathrm{B}_m & \mathrm{B}_i(\mathrm{A}_j\mathrm{B}_k)_l + \mathrm{A}_m = \mathrm{B}_i(\mathrm{A}_j\mathrm{B}_k)_l\mathrm{A}_m
\end{array} \quad (27)$$

where the suffixes i, j, k, l and m range from unity to infinity. It is assumed that one solvation constant K_{AB} holds for all these solvation reactions.

The following mass balance equations [6,7] are simultaneously solved to obtain the monomeric segment fractions of the self-associating components.

$$\Phi_{\mathrm{A}} = \bar{S}_{\mathrm{A}} + \left[2 + r_{\mathrm{B}}K_{\mathrm{AB}}S_{\mathrm{A}}(2 - r_{\mathrm{A}}r_{\mathrm{B}}K_{\mathrm{AB}}^2S_{\mathrm{A}}S_{\mathrm{B}}) + r_{\mathrm{A}}K_{\mathrm{AB}}S_{\mathrm{B}}\right] \times \left[\frac{r_{\mathrm{A}}K_{\mathrm{AB}}\bar{S}_{\mathrm{A}}S_{\mathrm{B}}}{(1 - r_{\mathrm{A}}r_{\mathrm{B}}K_{\mathrm{AB}}^2S_{\mathrm{A}}S_{\mathrm{B}})^2}\right] \quad (28)$$

$$\Phi_{\mathrm{B}} = \bar{S}_{\mathrm{B}} + \left[2 + r_{\mathrm{A}}K_{\mathrm{AB}}S_{\mathrm{B}}(2 - r_{\mathrm{A}}r_{\mathrm{B}}K_{\mathrm{AB}}^2S_{\mathrm{A}}S_{\mathrm{B}}) + r_{\mathrm{B}}K_{\mathrm{AB}}S_{\mathrm{A}}\right] \times \left[\frac{r_{\mathrm{B}}K_{\mathrm{AB}}S_{\mathrm{A}}\bar{S}_{\mathrm{B}}}{(1 - r_{\mathrm{A}}r_{\mathrm{B}}K_{\mathrm{AB}}^2S_{\mathrm{A}}S_{\mathrm{B}})^2}\right] \quad (29)$$

where the sums $\bar{S}_{\mathrm{A}}$, $\bar{S}_{\mathrm{B}}$, S_{A} and S_{B} are defined by

$$\bar{S}_{\mathrm{A}} = \Phi_{\mathrm{A}_1}/(1 - K_{\mathrm{A}}\Phi_{\mathrm{A}_1})^2 \quad (30)$$

$$\bar{S}_{\mathrm{B}} = \Phi_{\mathrm{B}_1}/(1 - K_{\mathrm{B}}\Phi_{\mathrm{B}_1})^2 \quad (31)$$

$$S_{\mathrm{A}} = \Phi_{\mathrm{A}_1}/(1 - K_{\mathrm{A}}\Phi_{\mathrm{A}_1}) \quad (32)$$

$$S_{\mathrm{B}} = \Phi_{\mathrm{B}_1}/(1 - K_{\mathrm{B}}\Phi_{\mathrm{B}_1}) \quad (33)$$

V is expressed as

$$\frac{1}{V} = \frac{S_{\mathrm{A}}}{r_{\mathrm{A}}} + \frac{S_{\mathrm{B}}}{r_{\mathrm{B}}} + \left(\frac{2}{r_{\mathrm{A}}r_{\mathrm{B}}K_{\mathrm{AB}}} + \frac{S_{\mathrm{A}}}{r_{\mathrm{A}}} + \frac{S_{\mathrm{B}}}{r_{\mathrm{B}}}\right)\frac{r_{\mathrm{A}}r_{\mathrm{B}}K_{\mathrm{AB}}^2S_{\mathrm{A}}S_{\mathrm{B}}}{(1 - r_{\mathrm{A}}r_{\mathrm{B}}K_{\mathrm{AB}}^2S_{\mathrm{A}}S_{\mathrm{B}})} \quad (34)$$

The excess molar enthalpy of the mixture is described as

$$\begin{aligned}
H^{\mathrm{E}} = {} & h_{\mathrm{A}} x_{\mathrm{A}} \left(\frac{\overline{U}_{\mathrm{A}} \Phi_{\mathrm{A}_1}}{\Phi_{\mathrm{A}}} - \overline{U}_{\mathrm{A}}^{0} \Phi_{\mathrm{A}_1}^{0} \right) + h_{\mathrm{B}} x_{\mathrm{B}} \left(\frac{\overline{U}_{\mathrm{B}} \Phi_{\mathrm{B}_1}}{\Phi_{\mathrm{B}}} - \overline{U}_{\mathrm{B}}^{0} \Phi_{\mathrm{B}_1}^{0} \right) \\
& + \left\{ h_{\mathrm{A}} \left[\frac{\overline{U}_{\mathrm{A}}}{K_{\mathrm{AB}} U_{\mathrm{A}}} \left(\frac{x_{\mathrm{B}}}{r_{\mathrm{A}} \Phi_{\mathrm{B}}} + \frac{x_{\mathrm{A}}}{r_{\mathrm{B}} \Phi_{\mathrm{A}}} \right) + \frac{\overline{U}_{\mathrm{A}} x_{\mathrm{A}} \Phi_{\mathrm{A}_1}}{\Phi_{\mathrm{A}}} \right. \right. \\
& \left. \times \left(2 - r_{\mathrm{A}} r_{\mathrm{B}} K_{\mathrm{AB}}^{2} \Phi_{\mathrm{A}_1} \Phi_{\mathrm{B}_1} U_{\mathrm{A}} U_{\mathrm{B}} \right) + \frac{\overline{U}_{\mathrm{A}} U_{\mathrm{B}} x_{\mathrm{B}} \Phi_{\mathrm{B}_1}}{U_{\mathrm{A}} \Phi_{\mathrm{B}}} \right] \\
& + h_{\mathrm{B}} \left[\frac{\overline{U}_{\mathrm{B}}}{K_{\mathrm{AB}} U_{\mathrm{B}}} \left(\frac{x_{\mathrm{B}}}{r_{\mathrm{A}} \Phi_{\mathrm{B}}} + \frac{x_{\mathrm{A}}}{r_{\mathrm{B}} \Phi_{\mathrm{A}}} \right) + \frac{\overline{U}_{\mathrm{B}} x_{\mathrm{B}} \Phi_{\mathrm{B}_1}}{\Phi_{\mathrm{B}}} \right. \\
& \left. \times \left(2 - r_{\mathrm{A}} r_{\mathrm{B}} K_{\mathrm{AB}}^{2} \Phi_{\mathrm{A}_1} \Phi_{\mathrm{B}_1} U_{\mathrm{A}} U_{\mathrm{B}} \right) + \frac{U_{\mathrm{A}} \overline{U}_{\mathrm{B}} x_{\mathrm{A}} \Phi_{\mathrm{A}_1}}{U_{\mathrm{B}} \Phi_{\mathrm{A}}} \right] \\
& + h_{\mathrm{AB}} \left[\left(\frac{x_{\mathrm{B}}}{r_{\mathrm{A}} \Phi_{\mathrm{B}}} + \frac{x_{\mathrm{A}}}{r_{\mathrm{B}} \Phi_{\mathrm{A}}} \right) \frac{\left(1 + r_{\mathrm{A}} r_{\mathrm{B}} K_{\mathrm{AB}}^{2} \Phi_{\mathrm{A}_1} \Phi_{\mathrm{B}_1} U_{\mathrm{A}} U_{\mathrm{B}} \right)}{K_{\mathrm{AB}}} \right. \\
& \left. \left. + 2 \left(\frac{U_{\mathrm{A}} x_{\mathrm{A}} \Phi_{\mathrm{A}_1}}{\Phi_{\mathrm{A}}} + \frac{U_{\mathrm{B}} x_{\mathrm{B}} \Phi_{\mathrm{B}_1}}{\Phi_{\mathrm{B}}} \right) \right] \right\} \frac{r_{\mathrm{A}} r_{\mathrm{B}} K_{\mathrm{AB}}^{2} \Phi_{\mathrm{A}_1} \Phi_{\mathrm{B}_1} U_{\mathrm{A}} U_{\mathrm{B}}}{\left(1 - r_{\mathrm{A}} r_{\mathrm{B}} K_{\mathrm{AB}}^{2} \Phi_{\mathrm{A}_1} \Phi_{\mathrm{B}_1} U_{\mathrm{A}} U_{\mathrm{B}} \right)^{2}} \\
& - R \left[\frac{q_{\mathrm{A}} x_{\mathrm{A}} \theta_{\mathrm{B}}}{(\theta_{\mathrm{A}} + \theta_{\mathrm{B}} \tau_{\mathrm{BA}})} \frac{\partial \tau_{\mathrm{BA}}}{\partial (1/T)} + \frac{q_{\mathrm{B}} x_{\mathrm{B}} \theta_{\mathrm{A}}}{(\theta_{\mathrm{B}} + \theta_{\mathrm{A}} \tau_{\mathrm{AB}})} \frac{\partial \tau_{\mathrm{AB}}}{\partial (1/T)} \right] \qquad (35)
\end{aligned}$$

where

$$\overline{U}_{\mathrm{A}} = K_{\mathrm{A}} \Phi_{\mathrm{A}_1} / \left(1 - K_{\mathrm{A}} \Phi_{\mathrm{A}_1} \right)^{2} \qquad (36)$$

$$\overline{U}_{\mathrm{B}} = K_{\mathrm{B}} \Phi_{\mathrm{B}_1} / \left(1 - K_{\mathrm{B}} \Phi_{\mathrm{B}_1} \right)^{2} \qquad (37)$$

$$U_{\mathrm{A}} = 1 / \left(1 - K_{\mathrm{A}} \Phi_{\mathrm{A}_1} \right) \qquad (38)$$

$$U_{\mathrm{B}} = 1 / \left(1 - K_{\mathrm{B}} \Phi_{\mathrm{B}_1} \right) \qquad (39)$$

DATA REDUCTION

Experimental vapor–liquid equilibrium data taken from the literature were reduced using the thermodynamic equation

$$\phi_I y_I P = \gamma_I x_I P_I^{\mathrm{s}} \phi_I^{\mathrm{s}} \exp\left[v_I^{\mathrm{L}} \left(P - P_I^{\mathrm{s}} \right) / RT \right] \qquad (40)$$

where y is the vapor-phase mole fraction, P is the total pressure, P^{s} is the vapor pressure of pure component and R is the universal gas constant. The fugacity coefficients, ϕ_I and ϕ_I^s, were calculated by use of the equation

$$\ln \phi_I = \left(2\sum_J y_J B_{IJ} - \sum_I \sum_J y_I y_J B_{IJ}\right)\frac{P}{RT} \tag{41}$$

and the second virial coefficients B_{IJ} were estimated from the method of Hayden and O'Connell [8]. v^L is the pure-liquid molar volume calculated by means of the modified Rackett equation [9]. The parameter estimation program used was similar to that described by Prausnitz et al. [10], based on the maximum likelihood principle. The optimum parameters were obtained by minimizing the objective function

$$F = \sum_{i=1}^{N}\left[\frac{(P_i-\hat{P}_i)^2}{\sigma_P^2} + \frac{(T_i-\hat{T}_i)^2}{\sigma_T^2} + \frac{(x_i-\hat{x}_i)^2}{\sigma_x^2} + \frac{(y_i-\hat{y}_i)^2}{\sigma_y^2}\right] \tag{42}$$

where a circumflex indicates an estimated true value corresponding to each measured variable. The standard deviations in the measured variables were set as $\sigma_P = 1.0$ Torr, $\sigma_T = 0.05$ K, $\sigma_x = 0.001$ and $\sigma_y = 0.003$. The vapor pressures of the pure components were calculated from the Antoine equation whose constants are presented in Table 1 [11–13], together with the

TABLE 1

Antoine parameters and molecular structural parameters for pure components

Component	Antoine constants [a]			Structural constants		Ref.
	A	B	C	r	q	
Methylamine	7.33690	1011.532	233.286	1.28	1.22	11
Ethylamine	7.38605	1137.300	235.850	1.82	1.66	11
Dimethylamine	7.08212	960.242	221.667	1.87	1.70	11
n-Propylamine	6.92651	1044.051	210.836	2.36	2.09	11
n-Butylamine	7.21300	1308.400	224.190	2.90	2.52	11
Diethylamine	5.80159	583.279	144.145	2.95	2.56	11
n-Hexylamine	7.17000	1486.100	213.800	3.98	3.39	11
Dipropylamine	7.20663	1415.400	218.000	4.03	3.43	11
Diisopropylamine	7.80430	1758.500	273.150	4.03	3.43	11
Aniline	7.46441	1840.790	216.923	2.98	2.38	11
Tetrachloromethane	6.89406	1219.583	227.160	2.71	2.37	12
n-Butane	6.82485	943.453	239.711	2.53	2.22	13
n-Hexane	6.87776	1171.530	224.366	3.61	3.09	12
n-Heptane	6.90240	1268.115	216.900	4.15	3.52	12
n-Nonane	6.93513	1428.811	201.619	5.23	4.38	12
Methanol	7.89750	1474.080	229.130	1.15	1.12	12
Ethanol	8.32109	1718.100	237.520	1.69	1.55	12
1-Propanol	7.84767	1499.210	204.640	2.23	1.98	12
1-Butanol	7.47680	1362.390	178.770	2.77	2.42	12

[a] $\log_{10} P^s(\text{Torr}) = A - B/[C + t(°\text{C})]$.

TABLE 2

Values of association constant and enthalpy of hydrogen-bond formation for pure self-associating components

Component	K_A (temp. °C)	$-h_A$ (kJ mol^{-1})
Methylamine	6.0 (20)	9.0
Ethylamine	4.0 (20)	9.0
Dimethylamine	2.0 (20)	9.0
n-Propylamine	2.0 (20)	8.0
n-Butylamine	2.0 (60)	9.0
Diethylamine	1.2 (60)	9.0
n-Hexylamine	1.5 (60)	9.0
Dipropylamine	1.2 (60)	
Diisopropylamine	1.2 (60)	
Aniline	15.0 (50)	15.4
Methanol	125.1 (50)	23.6
Ethanol	103.2 (50)	23.6
1-Propanol	89.9 (50)	23.6
1-Butanol	83.0 (50)	23.3

molecular structural parameters estimated by the method of Vera et al. [14]. These structural parameters were also used in the original UNIQUAC model.

The simplex method [15] was used to obtain the coefficients of eqn. (26), C_l and D_l, by minimizing the sum-of-squares of deviation in excess molar enthalpy for all data points.

CALCULATED RESULTS AND DISCUSSION

The values of the association constant and the enthalpy of hydrogen-bond formation for each of the self-associating components used in this work are

TABLE 3

Solvation constants and enthalpies of complex formation

Mixture (A–B)	K_{AB} (temp. °C)	$-h_{AB}$ (kJ mol^{-1})
Methylamine–tetrachloromethane	1.5 (20)	7
Dimethylamine–tetrachloromethane	1.5 (20)	7
Diethylamine–tetrachloromethane	1.2 (20)	7
n-Butylamine–methanol	15 (50)	27
n-Butylamine–ethanol	13 (40)	27
n-Butylamine–1-propanol	12 (40)	
n-Butylamine–1-butanol	10 (40)	
Aniline–methanol	20 (50)	27
Aniline–ethanol	12 (50) [a]	27
	20 (50) [b]	27

[a] Single solvation model.

[b] Multisolvation model.

TABLE 4

Calculated results obtained in vapor–liquid equilibrium data reduction for mixtures containing one aliphatic amine and one saturated hydrocarbon

Mixture (A–B)	Temp. (°C)	No. of data points	Type of model	Root-mean-square deviations				Parameters (K)		Ref.
				δP (Torr)	δT (°C)	δx ($\times 10^3$)	δy ($\times 10^3$)	a_{AB}	a_{BA}	
Methylamine–n-butane	−55	21	I [a]	0.75	0.01	0.1		62.66	60.52	18
			II [b]	0.96	0.01	0.3		76.58	431.15	
	−20	21	I	0.69	0.04	0.7		74.86	33.31	18
			II	1.07	0.07	1.1		63.89	389.82	
	15	21	I	0.52	0.09	1.4		158.06	−59.29	18
			II	0.49	0.09	0.9		50.47	335.58	
Methylamine–n-hexane	−55	21	I	0.95	0.01	0.1		−43.39	184.25	19
			II	1.09	0.01	0.2		42.08	513.59	
	−20	21	I	1.23	0.05	0.5		−7.74	115.65	19
			II	2.08	0.09	1.2		41.72	433.69	
	20	21	I	0.45	0.05	1.7		23.99	46.53	19
			II	0.48	0.07	1.2		26.24	372.49	
Methylamine–n-nonane	−40	20	I	1.62	0.03	0.3		−78.03	235.23	18
			II	1.76	0.03	0.4		31.39	518.46	
	−20	20	I	1.48	0.06	0.6		−58.21	189.70	18
			II	2.08	0.09	1.0		32.77	470.14	
	0	20	I	0.69	0.05	1.0		−50.58	162.26	18
			II	1.16	0.10	1.2		27.57	435.49	
	20	20	I	0.44	0.05	1.6		−41.45	131.36	18
			II	0.55	0.08	1.2		20.24	405.42	
Ethylamine–n-butane	−55	24	I	0.28	0.00	0.0		79.79	−9.73	18
			II	0.54	0.00	0.0		12.31	264.40	
	−20	24	I	1.02	0.04	0.3		145.74	−68.29	18

TABLE 4 (continued)

Calculated results obtained in vapor–liquid equilibrium data reduction for mixtures containing one aliphatic amine and one saturated hydrocarbon

Mixture (A–B)	Temp. (°C)	No. of data points	Type of model	Root-mean-square deviations				Parameters (K)		Ref.
				δP (Torr)	δT (°C)	δx ($\times 10^3$)	δy ($\times 10^3$)	a_{AB}	a_{BA}	
			II [b]	1.01	0.04	0.4		11.10	235.90	
	20	24	I [a]	1.17	0.16	1.2		266.64	−157.18	18
			II	0.28	0.03	0.5		9.39	195.29	
Ethylamine–n-hexane	−40	24	I	0.42	0.00	0.0		−48.59	109.72	18
			II	0.60	0.00	0.0		−37.21	332.56	
	−20	24	I	0.63	0.01	0.2		66.31	−16.79	18
			II	0.97	0.01	0.2		−21.99	283.87	
Ethylamine–n-hexane	0	24	I	1.06	0.03	0.7		146.20	−83.28	18
			II	1.41	0.05	0.5		−19.04	256.43	
	20	24	I	1.20	0.06	1.6		188.05	−120.90	18
			II	0.78	0.05	0.7		−24.32	239.13	
Dimethylamine–n-hexane	−50	10	I	0.11	0.00	0.0		−62.11	124.86	20
			II	0.22	0.00	0.0		−39.66	283.30	
	−20	10	I	0.53	0.01	0.1		−8.29	43.82	20
			II	0.98	0.02	0.3		−34.85	237.44	
	20	10	I	0.93	0.05	1.2		−39.52	55.91	20
			II	0.94	0.06	1.2		−54.31	217.63	
n-Propylamine–n-hexane	−20	22	I	0.18	0.00	0.0		−1.20	51.49	18
			II	0.26	0.00	0.0		−31.35	214.00	
	0	22	I	0.13	0.00	0.0		17.41	20.90	18
			II	0.24	0.00	0.0		−32.92	194.63	
	20	22	I	0.49	0.01	0.1		26.36	3.44	18
			II	0.42	0.01	0.1		−37.87	184.64	

n-Butylamine–n-hexane	60	7	I	1.41	0.07	1.0	8.2	283.96	−186.18	21
			II	1.65	0.08	1.0	11.5	−27.64	138.27	
n-Butylamine–n-heptane	55	17	I	1.29	0.04	1.8	8.6	411.84	−241.52	22
			II	1.51	0.04	1.0	8.5	28.47	63.70	
	75	18	I	1.07	0.05	1.5	6.4	406.54	−250.14	22
			II	1.39	0.08	0.8	8.6	29.20	55.40	
Diethylamine–n-hexane	60	7	I	1.58	0.09	0.7	3.6	441.93	−278.52	21
			II	0.58	0.04	0.4	3.4	57.11	−18.17	
Diethylamine–n-heptane	35	24	I	1.54	0.04	1.6	5.7	475.15	−271.76	22
			II	1.18	0.03	0.5	6.0	132.24	−69.44	
	55	21	I	1.60	0.06	2.1	4.6	427.73	−269.48	22
			II	0.89	0.04	0.7	4.3	74.58	−30.89	
n-Hexylamine–n-hexane	25	7	I	0.72	0.01	0.2	3.2	293.11	−182.96	23
			II	0.99	0.01	0.1	4.0	−45.55	127.74	
	50	15	I	0.96	0.02	0.4	3.9	396.85	−223.65	23
			II	1.06	0.03	0.4	7.9	46.93	21.11	
	60	7	I	1.89	0.05	1.4	10.0	238.53	−169.94	21
			II	1.64	0.03	1.0	10.1	−21.09	85.56	
Dipropylamine–n-hexane	60	7	I	1.69	0.06	0.7	18.7	420.33	−265.52	21
			II	0.61	0.01	0.3	19.8	121.92	−78.87	
Diisopropylamine–n-hexane	60	7	I	1.56	0.07	0.3	11.8	517.88	−297.64	21
			II	1.30	0.05	0.4	15.3	261.81	−168.27	

---

[a] UNIQUAC associated-solution model.

[b] Original UNIQUAC model.

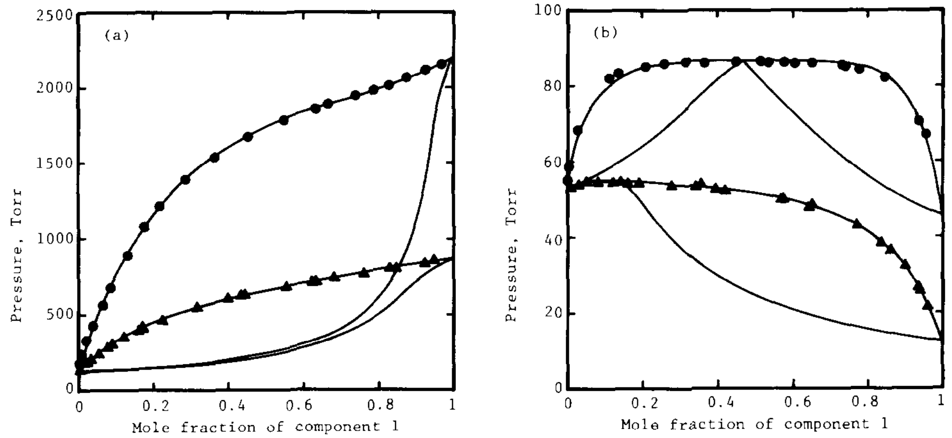

Fig. 1. Vapor–liquid equilibria for aliphatic amine–saturated hydrocarbon mixtures. Experimental: (a) methylamine (1)–n-hexane (2) at 20°C (●) [19], ethylamine (1)–n-hexane (2) at 20°C (▲) [18]; (b) methylamine (1)–n-butane (2) at −55°C (●) [18]; ethylamine (1)–n-butane (2) at −55°C (▲) [18]. Calculated (———).

shown in Table 2. Those values for aniline and alcohols were taken from previous papers [3,16], the values of h_A for aliphatic amines are identical to those obtained previously [17] and the values of K_A for aliphatic amines were derived from binary vapor–liquid equilibrium data reduction. Table 3

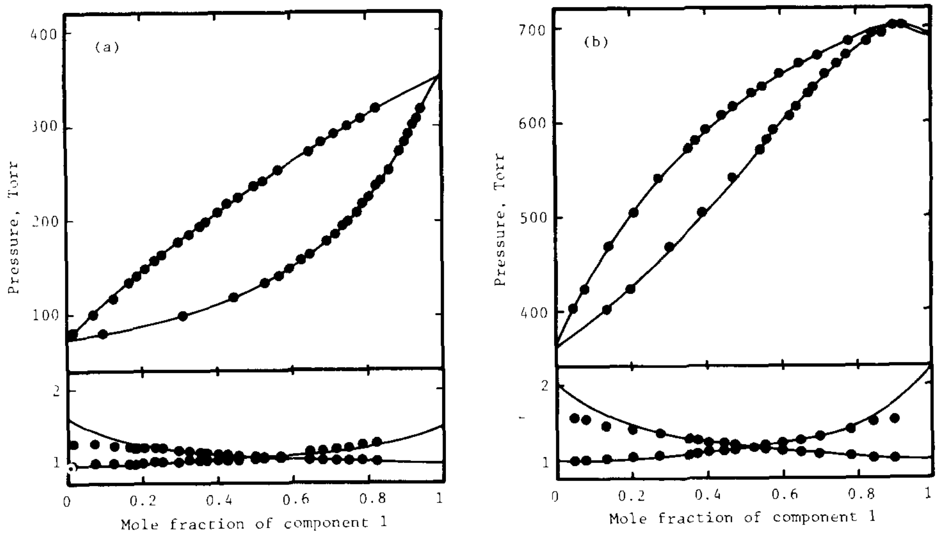

Fig. 2. Vapor–liquid equilibria for aliphatic amine–saturated hydrocarbon mixtures. Experimental (●): (a) diethylamine (1)–n-heptane (2) at 35°C [22]; (b) n-butylamine (1)–n-heptane (2) at 75°C [22]. Calculated (———).

TABLE 5

Calculated results obtained in vapor–liquid equilibrium data reduction for mixtures containing one amine and one active nonassociating component or one alcohol

Mixture (A–B)	Temp. (°C)	No. of data points	Type of model	Root-mean-square deviations				Parameters (K)		Ref.
				δP (Torr)	δT (°C)	δx ($\times 10^3$)	δy ($\times 10^3$)	a_{AB}	a_{BA}	
Methylamine–tetrachloromethane	−20	20		1.05	0.02	0.6		−114.31	233.40	24
	20	20		0.54	0.05	1.3		−134.62	239.95	24
Dimethylamine–tetrachloromethane	−20	22		1.00	0.01	0.2		−127.50	269.77	25
	20	22		2.41	0.12	2.8		−137.17	282.55	25
Diethylamine–tetrachloromethane	20	11		3.36	0.07	0.9	7.1	207.52	−109.20	26
	40	11		0.91	0.04	0.3	2.0	−38.11	102.12	26
n-Butylamine–ethanol	40	10	I [a]	0.85	0.01	0.3	3.8	−41.41	−261.95	27
			II [b]	4.99	0.02	0.6	7.0	−271.10	270.18	
n-Butylamine–1-propanol	40	12	I	0.79	0.01	0.4	2.6	−69.74	−222.41	27
			II	3.71	0.00	0.1	9.6	−215.43	215.10	
n-Butylamine–1-butanol	40	8	I	1.72	0.02	0.6	5.4	−18.55	−162.77	28
			II	1.71	0.01	0.9	3.2	481.86	−238.28	
Aniline–methanol	20	13	I	1.22	0.01	0.1		321.88	−323.10	27
			II	0.80	0.01	0.1		292.32	−58.76	
	65	13	I	4.99	0.14	2.8		351.09	−350.59	27
			II	0.77	0.05	0.5		33.00	21.99	
Aniline–ethanol	40	13	I	2.26	0.02	0.3		303.21	−301.85	27
			II	0.23	0.00	0.0		241.45	4.41	
	77.66	13	I	4.37	0.17	3.2		335.43	−336.51	27
			II	0.25	0.01	0.2		88.89	26.34	

[a] Single solvation model. [b] Multisolvation model.

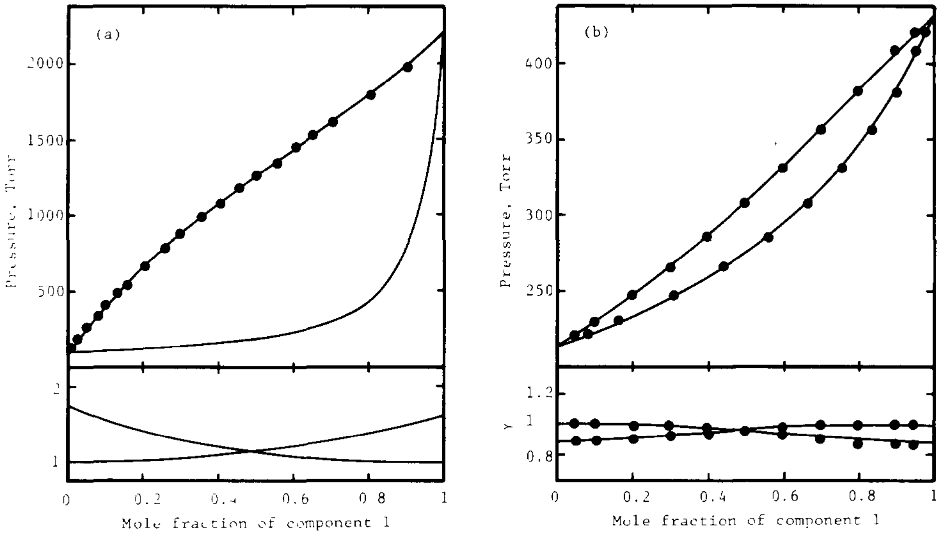

Fig. 3. Vapor–liquid equilibria for aliphatic amine–tetrachloromethane mixtures. Experimental (●): (a) methylamine (1)–tetrachloromethane (2) at 20°C [24]; (b) diethylamine (1)–tetrachloromethane (2) at 40°C [26]. Calculated (———).

presents the values of the solvation constant and enthalpy of complex formation. Table 4 indicates that the results for binary mixtures containing one aliphatic amine and one saturated hydrocarbon obtained from the UNIQUAC associated-solution model are comparable to those obtained from the original UNIQUAC model in terms of root-mean-square deviations for pressure, for temperature, for liquid-phase mole fraction and for vapor-phase mole fraction. Figures 1 and 2 compare calculated values with experimental results for some representative mixtures. Brandani and Evangelista [2] stated that, for the amine systems containing one inert component, to obtain a good fit it is necessary to consider a solvent effect. However, the present results show clearly that for these systems the UNIQUAC associated-solution model with the small values of the association constant for aliphatic amines works well without introducing K_{AB}. Table 5 presents the results for binary mixtures containing one amine and tetrachloromethane or one alcohol and calculated and experimental results are shown for four mixtures in Figs. 3 and 4. For n-butylamine–ethanol and n-butylamine–1-propanol the single solvation model works better than the multisolvation model does and for n-butylamine–1-butanol the two models give similar results. On the other hand, for aniline–methanol and aniline–ethanol the multisolvation model provides much better results than the single solvation model does. Table 6 gives the results of excess enthalpy for three binary mixtures containing one amine and one alcohol and calculated and experimental values are illustrated in Fig. 5. These results

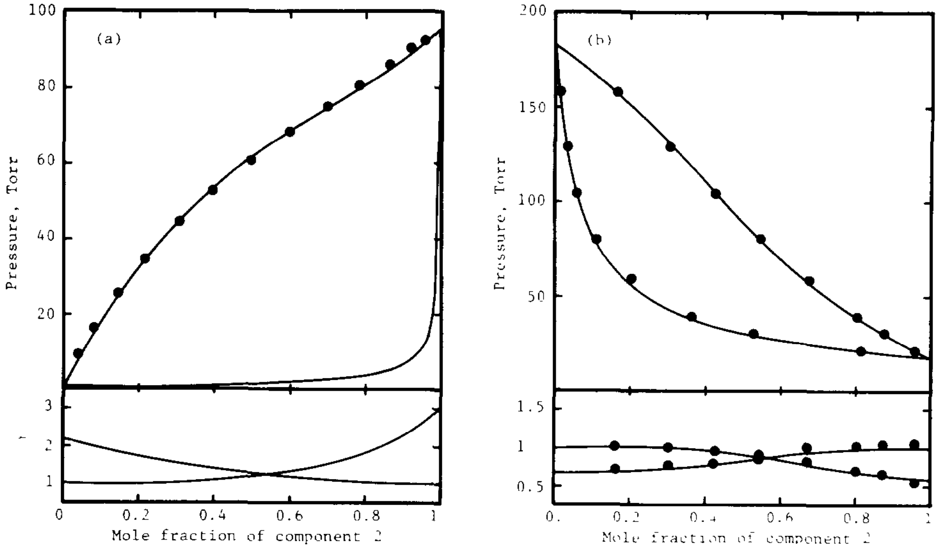

Fig. 4. Vapor-liquid equilibria for amine-alcohol mixtures. Experimental (●): (a) aniline (1)-methanol (2) at 20°C [27]; (b) n-butylamine (1)-1-butanol (2) at 40°C [28]. Calculated (———).

imply that the two solvation models can accurately reproduce experimental excess enthalpy data for amine-alcohol mixtures. Since any reliable ternary phase equilibrium and excess molar enthalpy data for mixtures containing

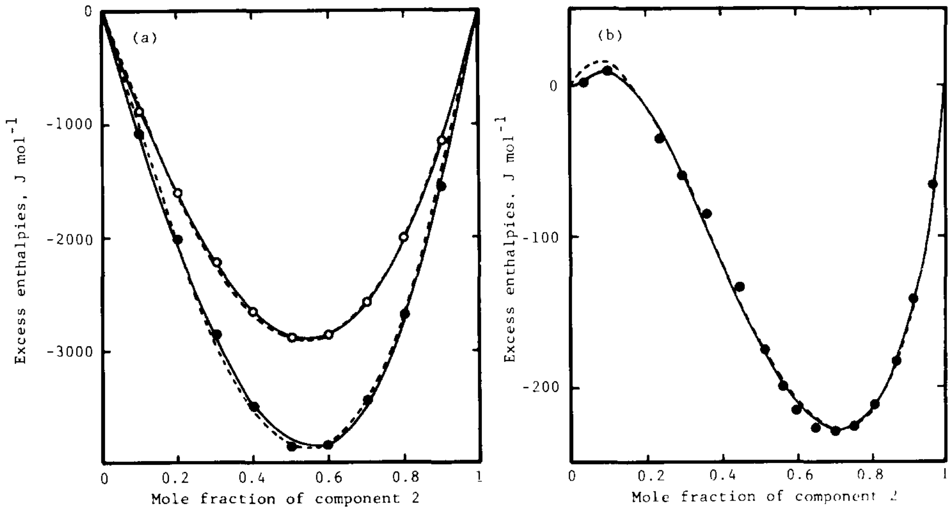

Fig. 5. Excess molar enthalpies for amine-alcohol mixtures. Experimental: (a) n-butylamine (1)-methanol (2) at 25°C (●) [30], n-butylamine (1)-ethanol (2) at 40°C (○) [31]; (b) aniline (1)-methanol (2) at 25°C (●) [32]. Calculated (———, single solvation model), (- - - - -, multisolvation model).

TABLE 6

Calculated results obtained in excess enthalpy data reduction for amine–alcohol mixtures

Mixture (A–B)	Temp. (°C)	No. of data points	Type of model	Abs. arith. mean dev. (J mol^{-1})	Parameters				Ref.
					C_A (K)	C_B (K)	D_A	D_B	
n-Butylamine–methanol	25	9 [a]	I [b]	31.7	−198.43	−86.229	9.1184	−4.4956	30
			II [c]	28.4	−225.23	506.60	4.6066	−10.542	
n-Butylamine–ethanol	40	9 [a]	I	5.0	−143.41	−161.17	5.1332	−2.2962	31
			II	18.6	135.08	−218.43	−6.4097	5.7088	
Aniline–methanol	25	16	I	4.0	105.90	−30.79	5.1344	0.5841	32
			II	4.7	364.61	304.47	−4.3816	1.5411	

[a] Experimental values were obtained at equally spaced interval 0.1 mole fraction from smoothing polynomials given by Christensen et al. [29].

[b] Single solvation model.

[c] Multisolvation model.

one amine, one alcohol and one nonassociating component do not seem to exist in the literature, further computation of the ternary excess properties for these mixtures was not carried out.

In conclusion, the UNIQUAC associated-solution model describes well vapor–liquid equilibrium and excess molar enthalpy data for binary mixtures containing one amine and one nonassociating component or one alcohol.

ACKNOWLEDGEMENT

Mr. K. Ohtsubo is acknowledged for his computational work.

LIST OF SYMBOLS

A, B	self-associating component and nonassociating or self-associating component
a_{IJ}	binary interaction parameter
C_I, D_I	coefficients of eqn. (26)
F	objective function as defined by eqn. (42)
H^E	excess molar enthalpy
h_A, h_B	enthalpies of hydrogen-bond formation of self-associating components
h_{AB}	enthalpy of complex formation between unlike molecules
K_A, K_B	association constants for self-associating components
K_{AB}	solvation constant between unlike molecules
P	total pressure
P_I^s	saturated vapor 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
$\bar{S}_A$, $\bar{S}_B$	sums as defined by eqns. (30) and (31)
S_A, S_B	sums as defined by eqns. (32) and (33)
T	absolute temperature
$\bar{U}_A$, $\bar{U}_B$	quantities as defined by eqns. (36) and (37)
U_A, U_B	quantities as defined by eqns. (38) and (39)
V	true molar volume of the mixture
V_I^0	true molar volume of pure self-associating component I
v_I^L	molar liquid volume of pure component I
x_I	liquid-phase mole fraction of component I
y_I	vapor-phase mole fraction of component I
Z	lattice coordination number taken 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-phase mole fraction and vapor-phase mole fraction, respectively
τ_{IJ}	coefficient as defined by $\exp(-a_{IJ}/T)$
Φ_I	segment fraction of component I
Φ_{A_1}, Φ_{B_1}	monomer segment fractions of components A and B
ϕ_I	vapor-phase fugacity coefficient of component I
ϕ_I^s	vapor-phase fugacity coefficient of pure component I at system temperature T and vapor pressure P_I^s

Subscripts

A, B	self-associating component and nonassociating or self-associating component
A_1, B_1	monomers of components A and B
A_i, B_i	i-mers of self-associating components A and B
AB	binary complex
A_iB	complex containing i molecules of self-associating component A and one molecule of component B
A_iB_j	complex containing i molecules of self-associating component A and j molecules of self-associating component B
I, J	components
i, j, k, l, m	degree of association

Superscripts

^{0}	pure-liquid reference state
$\hat{}$	calculated property

REFERENCES

1 V. Brandani, Fluid Phase Equilibria, 12 (1983) 87.
2 V. Brandani and F. Evangelista, Fluid Phase Equilibria, 17 (1984) 281.
3 I. Nagata and K. Ohtsubo, Thermochim. Acta, 97 (1986) 37.
4 I. Nagata, Fluid Phase Equilibria, 19 (1985) 153.
5 I. Nagata and K. Gotoh, Thermochim. Acta, 99 (1986) 145.
6 I. Nagata and K. Ohtsubo, Thermochim. Acta, 102 (1986) 185.
7 I. Nagata and K. Gotoh, Thermochim. Acta, 102 (1986) 207.
8 J.G. Hayden and J.P. O'Connell, Ind. Eng. Chem., Process Des. Dev., 14 (1975) 209.
9 C.F. Spencer and R.P. Danner, J. Chem. Eng. Data, 17 (1972) 236.
10 J.M. Prausnitz, T.F. Anderson, E.A. Grens, C.A. Eckert, R. Hsieh and J.P. O'Connell,

Computer Calculations for Multicomponent Vapor–Liquid and Liquid–Liquid Equilibria, Prentice-Hall, Englewood Cliffs, NJ, 1980, Chaps. 3, 4, 6 and Appendices C, D.
11 J. Gmehling, U. Onken and W. Arlt, Vapor–Liquid Equilibrium Data Collection, Vol. I, Part 6a, DECHEMA, Frankfurt am Main, 1980, pp. 19, 28, 251, 491, 512, 518, 519, 584–586.
12 J.A. Riddick and W.B. Bunger, Organic Solvents, 3rd edn., Wiley-Interscience, New York, pp. 78, 86, 97, 145, 146, 148, 151.
13 T. Boublik, V. Fried and E. Hála, The Vapour Pressures of Pure Substances, Elsevier, Amsterdam, 1973, p. 174.
14 J.H. Vera, S.G. Sayegh and G.A. Ratcliff, Fluid Phase Equilibria, 1 (1977) 113.
15 J.A. Nelder and R. Mead, Comput. J., 7 (1965) 308.
16 I. Nagata, Thermochim. Acta, 107 (1986) 199.
17 I. Nagata and K. Tamura, Thermochim. Acta, 101 (1986) 305.
18 H. Wolff, A. Höpfner and H.M. Höpfner, Ber. Bunsenges. Phys. Chem., 68 (1964) 410.
19 H. Wolff and A. Höpfner, Ber. Bunsenges. Phys. Chem., 66 (1962) 149.
20 H. Wolff and R. Würtz, J. Phys. Chem., 74 (1970) 1600.
21 R.L. Humphrey and M. Van Winkle, J. Chem. Eng. Data, 12 (1967) 526.
22 T.M. Letcher and J.W. Bayles, J. Chem. Eng. Data, 16 (1971) 266.
23 M. Kern, L. Abello, D. Caceres and G. Pannetier, Bull. Soc. Chim. Fr., (1970) 3849.
24 H. Wolff and R. Würtz, Ber. Bunsenges. Phys. Chem., 72 (1968) 101.
25 H. Wolff and H.-E. Höppel, Ber. Bunsenges. Phys. Chem., 70 (1966) 874.
26 H. Kilian and H.-J. Bittrich, Z. Phys. Chem. (Leipzig), 230 (1965) 383.
27 J. Gmehling, U. Onken and W. Arlt, Vapor–Liquid Equilibrium Data Collection, Vol. I, Part 2c, DECHEMA, Frankfurt am Main, 1982, pp. 192, 193, 351, 407, 408, 506.
28 J. Gmehling, U. Onken and W. Arlt, Vapor–Liquid Equilibrium Data Collection, Vol. I, Part 2b, DECHEMA, Frankfurt am Main, 1978, p. 163.
29 C. Christensen, J. Gmehling, P. Rasmussen and U. Weidlich, Heats of Mixing Data Collection, Vol. III, Part 1, DECHEMA, Frankfurt am Main, 1984, pp. 270, 410.
30 M.K. DuttaChoudhury and H.B. Mathur, Indian J. Chem., A14 (1976) 735.
31 M.K. DuttaChoudhury and H.B. Mathur, J. Chem. Eng. Data, 19 (1974) 145.
32 K. Nakanishi and H. Touhara, J. Chem. Thermodyn., 18 (1986) 657.