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THERMODYNAMICS OF AMINE SOLUTIONS

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ABSTRACT

An association model is presented to reproduce the vapor-liquid equilibria of binary mixtures of simple aliphatic amines in saturated hydrocarbons over the whole mole fraction range with good accuracy in terms of linear association, with allowance for a non-polar interaction term. The model is able to explain the spectroscopic property of dilute solutions of aniline in cyclohexane and also to represent the vapor-liquid equilibrium and excess enthalpy data of binary amine-organic compound mixtures with an addition of solvation equilibrium between the terminal amino group of the amine chains and a solvating molecule. The predictive ability of the model is shown by good agreement between calculated and experimental vapor-liquid and liquid-liquid equilibrium results for ternary mixtures of aniline with hydrocarbons.

INTRODUCTION

The self-association of simple aliphatic amines in saturated hydrocarbons has been studied from the vapor pressure isotherms by means of the theory of ideal associated solution using a two-constant model [1,2]. The model contains the dimerization constant and the other for the formation of higher polymers. Wolff and Landeck [2] stated that the equations of the model permit at least a formal description of the considered solutions with only minor faults almost over the entire range of mole fractions. It is not possible to describe the thermodynamic properties of liquid mixtures of aniline with organic compounds by use of the ideal association theory, because the theory is unable to predict phase-separation observed in aniline-saturated hydrocarbon mixtures.

In this paper, we propose an association model with a non-polar interaction term for the accurate representation of the vapor pressure isotherms of binary mixtures of simple aliphatic amines with saturated hydrocarbons and tetrachloromethane as well as the phase equilibrium and excess enthalpy data of binary aniline-organic compound mixtures. Predicted ternary

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vapor–liquid and liquid–liquid equilibrium results obtained from the proposed model with only binary parameters are compared with experimental data for mixtures of aniline with hydrocarbons.

ASSOCIATION MODEL

Our proposed model assumes linear association for the amine in accordance with the previous approaches [1,2] and solvation between the terminal amino group of the amine chains and an active unassociated compound, with allowance for a non-polar interaction term given by the NRTL equation [3]. In ternary amine mixtures, A stands for the amine, B for the active unassociated compound, and C for the saturated hydrocarbon.

Three equilibrium constants for the formation of chemical complexes, A_2, A_{i+1}, and A_iB, are defined in terms of mole fractions, respectively.

$$A_1 + A_1 = A_2 \qquad K_2 = x_{A_2}/x_{A_1}^2 \tag{1}$$

$$A_i + A_1 = A_{i+1} \qquad K = x_{A_{i+1}}/x_{A_i}x_{A_1} \text{ for all } i > 1 \tag{2}$$

$$A_i + B = A_iB \qquad K_{AB} = x_{A_iB}/x_{A_i}x_{B_1} \tag{3}$$

The temperature dependence of K_2, K and K_{AB} is given by the van't Hoff relation

$$\partial \ln K_2/\partial(1/T) = -h_2/R \quad \partial \ln K/\partial(1/T) = -h/R$$
$$\partial \ln K_{AB}/\partial(1/T) = -h_{AB}/R \tag{4}$$

The activity coefficient of any component I in the ternary mixture is expressed by

$$\ln \gamma_I = \ln\left(\frac{x_{I_1}}{x_{I_1}^* x_I}\right) + \frac{\sum_J \tau_{JI} G_{JI} x_J}{\sum_K G_{KI} x_K} + \sum_J \frac{x_J G_{IJ}}{\sum_K G_{KJ} x_K}\left(\tau_{IJ} - \frac{\sum_R x_R \tau_{RJ} G_{RJ}}{\sum_K G_{KJ} x_K}\right) \tag{5}$$

where $x_{I_1}^* = 1$ for an unassociated component,

$$\tau_{JI} = a_{JI}/T \tag{6}$$

$$G_{JI} = \exp(-\alpha_{JI}\tau_{JI}) \tag{7}$$

and the nonrandomness parameter $\alpha_{JI}(=\alpha_{IJ})$ is set as 0.3 [3]. The binary parameters, a_{JI} and a_{IJ}, are obtained from experimental phase equilibrium data reduction.

The nominal mole fraction of each component is expressed in terms of the monomeric mole fractions of the components.

$$x_A = (1 + K_{AB}x_{B_1})\left[x_{A_1} + K_2 x_{A_1}^2(2-z)/(1-z)^2\right]/S \tag{8}$$

$$x_B = \left\{x_{B_1} + K_{AB}x_{B_1}\left[x_{A_1} + K_2 x_{A_1}^2/(1-z)\right]\right\}/S \tag{9}$$

$$x_C = x_{C_1}/S \tag{10}$$

where $z = Kx_{A_1}$ and the stoichiometric sum S is given by

$$S = \left(1 + K_{AB}x_{B_1}\right)\left[x_{A_1} + K_2 x_{A_1}^2 (2 - z)/(1 - z)^2\right] + K_{AB}x_{B_1}\left[x_{A_1} + K_2 x_{A_1}^2/(1 - z)\right] + x_{B_1} + x_{C_1} \tag{11}$$

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

$$\sum_{i=1}^{\infty} x_{A_i}(\text{linear}) + \sum_{i=1}^{\infty} x_{A_i B} + x_{B_1} + x_{C_1} = \left(1 + K_{AB}x_{B_1}\right)\left[x_{A_1} + K_2 x_{A_1}^2/(1 - z)\right] + x_{B_1} + x_{C_1} = 1 \tag{12}$$

Equations (8)–(12) are used to solve x_{A_1}, x_{B_1}, and x_{C_1}, if the equilibrium constants are known.

At pure amine state eqn. (12) reduces to

$$x_{A_1}^* + K_2 x_{A_1}^{*2}/(1 - z^*) = 1 \tag{13}$$

The excess enthalpy of the ternary mixture is expressed by the sum of chemical and physical contribution terms.

$$h^E = h^E_{\text{chem}} + h^E_{\text{phys}} \tag{14}$$

$$\begin{aligned} h^E_{\text{chem}} = {} & \Big\{\left(1 + K_{AB}x_{B_1}\right)\left[h_2 K_2 x_{A_1}^2/(1 - z) + hK_2 K x_{A_1}^3/(1 - z)^2\right] \\ & + h_{AB}K_{AB}x_{B_1}\left[x_{A_1} + K_2 x_{A_1}^2/(1 - z)\right]\Big\}/S \\ & - x_A\left[h_2 K_2 x_{A_1}^{*2}/(1 - z^*) + hK_2 K x_{A_1}^{*3}/(1 - z^*)^2\right]/S^* \end{aligned} \tag{15}$$

$$h^E_{\text{phys}} = R\sum_I x_I \left[\frac{\sum_J x_J \dfrac{\partial(\tau_{JI}G_{JI})}{\partial(1/T)}}{\sum_K G_{KI}x_K} - \frac{\sum_J \tau_{JI}G_{JI}x_J \sum_K x_K \dfrac{\partial G_{KI}}{\partial(1/T)}}{\left(\sum_K G_{KI}x_K\right)^2}\right] \tag{16}$$

In binary excess enthalpy fit, the energy parameters are assumed to be temperature-dependent linearly.

$$a_{JI} = C_I + D_I(T - 273.15) \tag{17}$$

The infrared spectroscopic data [4] provide a fraction of the number of the monomeric aniline in the stoichiometric number of aniline molecules, β.

$$\beta = \epsilon_a/\epsilon_M = \frac{x_{A_1}}{\sum_{i=1}^{\infty} i x_{A_i}} = \frac{1}{1 + K_2 x_{A_1}(2 - z)/(1 - z)^2} \tag{18}$$

where ϵ_a is the apparent molar absorptivity and ϵ_M is the extrapolated value of ϵ_a at infinite dilution of aniline, the molar absorptivity of monomer.

TABLE 1

Association parameters for pure amines

Substance	K_2	K	$-h_2$ (kJ mol^{-1})	$-h$ (kJ mol^{-1})	Temp. (°C)	Ref.
Methylamine	1.1	2.5	10.0	9.0	20	2
Ethylamine	1.0	2.3	10.0	9.0	20	2
Dimethylamine	0.9	1.5	9.0	9.0	20	1
n-Propylamine	1.0	1.9	7.0	8.0	20	2
n-Butylamine	0.6	1.2	9.0	9.0	60	This work
Diethylamine	0.3	0.4	9.0	9.0	60	This work
n-Hexylamine	0.8	0.9	9.0	9.0	60	This work
Dipropylamine	0.2	0.1			60	This work
Diisopropylamine	0.1	0.2			60	This work
Aniline	2.34	4.65	10.0	9.0	50	This work

CALCULATED RESULTS AND DISCUSSION

Reproduction of binary experimental data

The association constants and enthalpies of hydrogen bond of pure amines are listed in Table 1. These association parameters of some aliphatic amines were taken from Wolff and Landeck [2] and those of the other aliphatic amines were obtained in this work from the constants of the Wilson equation as described previously [1,2]. The infrared spectroscopic data of dilute solutions of aniline in cyclohexane at different temperatures [4] enabled us to obtain the set of association constants of aniline at each temperature as given in Table 2. This was done by minimizing the following objective function

$$F=\sum_{i=1}^{N}\left[\frac{(x_{A_i}-\hat{x}_{A_i})^2}{\sigma_x^2}+\frac{(\beta_i-\hat{\beta}_i)^2}{\sigma_\beta^2}\right] \tag{19}$$

TABLE 2

Results obtained in fitting the model to spectroscopic data of aniline–cyclohexane mixtures

Temp. (°C)	K_2	K	Root-mean-square deviation $\delta\beta$ ($\times 10^3$)
20	3.34 (0.14) [a]	7.39 (0.32) [a]	3.4
30	3.11 (0.12)	5.78 (0.30)	3.4
35	2.78 (0.10)	5.71 (0.25)	3.4
40	2.83 (0.09)	5.13 (0.24)	2.9
50	2.34 (0.08)	4.65 (0.27)	3.6
60	2.07 (0.08)	4.23 (0.27)	4.3
70	1.85 (0.10)	3.66 (0.36)	6.0

[a] Parentheses show estimated standard deviation.

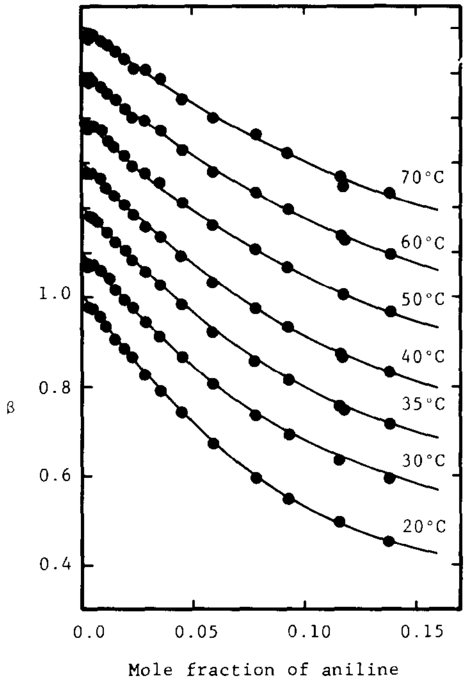

Fig. 1. Infrared spectroscopic data for fraction of monomer for aniline + cyclohexane. Calculated (———). Experimental (●) [4]. Note that the ordinates for 30, 35, 40, 50, 60 and 70°C curves are displaced upwards by 0.1, 0.2, 0.3, 0.4, 0.5 and 0.6, respectively, to avoid overlap.

where a circumflex designates the calculated true value corresponding to each experimental point and the estimated standard deviations in the measured values were taken as: $\sigma_x = 0.005$ and $\sigma_\beta = 0.02$. We used the β data in the region of aniline concentration less than 1.5 M [4]. K_2 and K at 50°C were selected for aniline. The enthalpies of hydrogen bonds were derived from the plot of ln K vs. $1/T$ as shown in Fig. 1. Figure 2 shows that the model reproduces the infrared spectroscopic data with satisfactory accuracy.

Vapor–liquid equilibrium data were reduced by use of eqn. (20).

$$\phi_I y_I P = x_I \gamma_I \phi_I^{\mathrm{s}} P_I^{\mathrm{s}} \exp\left[v_I^{\mathrm{L}} (P - P_I^{\mathrm{s}})/RT \right] \tag{20}$$

where y is the vapor-phase mole fraction, P is the total pressure, and P^{s} is the pure-component vapor pressure, which is calculated from the Antoine equation. Table 3 lists Antoine constants [5–7]. The pure-liquid molar volumes v^{L} are estimated from the modified Rackett equation [8]. The fugacity coefficients, ϕ at P and ϕ^{s} at P^{s}, are calculated by

$$\ln \phi_I = \left[2 \sum_I y_I B_{IJ} - \sum_I \sum_J y_I y_J B_{IJ} \right] \frac{P}{RT} \tag{21}$$

where the second virial coefficients B_{IJ} are estimated from the generalized method of Hayden and O'Connell [9].

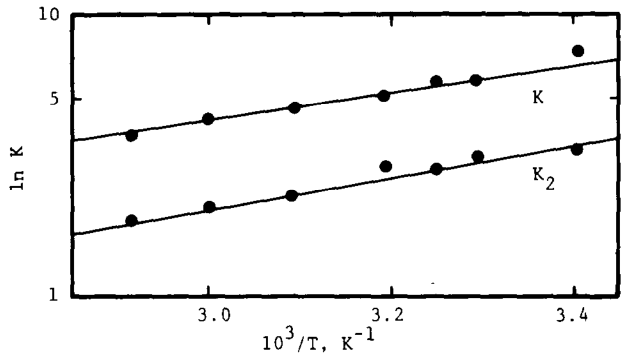

Fig. 2. Temperature dependence of K_2 and K obtained from infrared spectroscopic data for aniline. Lines correspond to values of K_2, K, h_2 and h given in Table 1.

Parameter estimation, based on the maximum likelihood principle [10], was performed by minimizing the objective function

$$F=\sum_{i=1}^{N}\left[\frac{(P_i-\hat{P}_i)^2}{\sigma_P^2}+\frac{(T_i-\hat{T}_i)^2}{\sigma_T^2}+\frac{(x_{A_i}-\hat{x}_{A_i})^2}{\sigma_x^2}+\frac{(y_{A_i}-\hat{y}_{A_i})^2}{\sigma_y^2}\right] \tag{22}$$

where $\sigma_P = 1.0$ Torr, $\sigma_T = 0.05°C$, $\sigma_x = 0.001$, and $\sigma_y = 0.003$.

TABLE 3

Antoine parameters for pure compounds

Substance	Antoine constants [a]			Ref.
	A	B	C	
Methylamine	7.33690	1011.532	233.286	5
Ethylamine	7.38605	1137.300	235.850	5
Dimethylamine	7.08212	960.242	221.667	5
n-Propylamine	6.92651	1044.051	210.836	5
n-Butylamine	7.21300	1308.400	224.190	5
Diethylamine	5.80159	583.279	144.145	5
n-Hexylamine	7.17000	1486.100	213.800	5
Dipropylamine	7.20663	1415.400	218.000	5
Diisopropylamine	7.80430	1758.500	273.150	5
Aniline	7.46441	1840.790	216.923	5
Tetrachloromethane	6.89406	1219.583	227.160	6
Acetone	7.23157	1277.030	237.230	6
n-Butane	6.82485	943.453	239.711	7
Benzene	6.90565	1211.033	220.790	6
Cyclohexane	6.84498	1203.526	222.863	6
n-Hexane	6.87776	1171.530	224.366	6
Toluene	6.95464	1344.800	219.482	6
Methylcyclohexane	6.82689	1272.864	221.630	6
n-Heptane	6.90240	1268.115	216.900	6
n-Nonane	6.93513	1428.811	201.619	6

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

TABLE 4

Solvation equilibrium constants and enthalpies of complex formation

Mixture (A–B)	K_{AB}	$-h_{AB}$ (kJ mol^{-1})	Temp. (°C)
Methylamine–tetrachloromethane	1.5	7	20
Dimethylamine–tetrachloromethane	1.5	7	20
Diethylamine–tetrachloromethane	1.2	7	20
Aniline–acetone	4.0	14	40
Aniline–benzene	1.5	7	25
Aniline–tetrachloromethane	0.2	5	25
Aniline–toluene	1.5	7	25

Binary solubility data provide a set of parameters by solving eqn. (23) for component I using the Newton–Raphson iterative method.

$$(\gamma_I x_I)^{\mathrm{I}} = (\gamma_I x_I)^{\mathrm{II}} \tag{23}$$

where the superscripts I and II denote two liquid phases in equilibrium.

Table 4 gives the solvation equilibrium constants and enthalpies of complex formation between unlike molecules. The values of K_{AB} were tentatively assumed in this work, because experimental values of K_{AB} were not available to us. h_{AB} for methylamine–tetrachloromethane and ethylamine–tetrachloromethane were taken from Wolff and Würtz [11] and the same value was assumed for dimethylamine–tetrachloromethane. h_{AB} for aniline–tetrachloromethane was assumed to be equal to that of benzene–

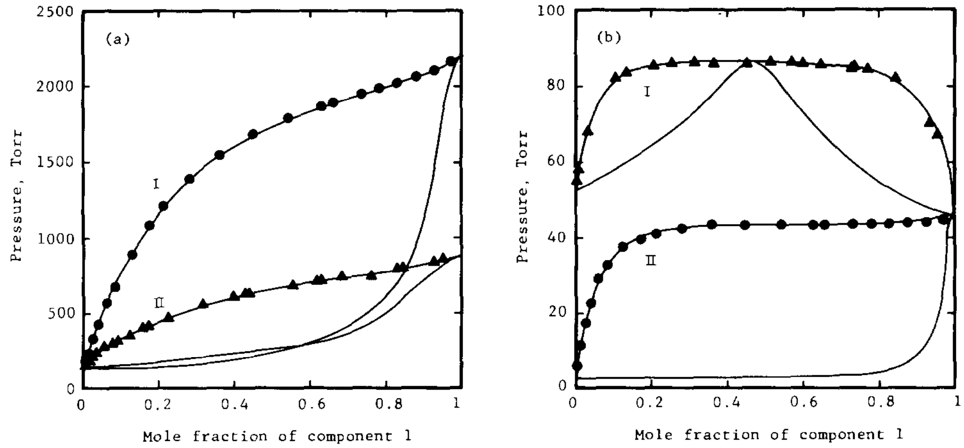

Fig. 3. Vapor–liquid equilibria for aliphatic amine + saturated hydrocarbon. Experimental: (a), I, methylamine + n-hexane at 20°C (●) [16], II, ethylamine + n-hexane at 20°C (▲) [15]; (b), I, methylamine + n-butane at −55°C (▲) [15], II, methylamine + n-hexane at −55° C (●) [16]. Calculated (———).

TABLE 5

Binary results obtained in fitting the model to vapor–liquid equilibria of aliphatic amine mixtures

Mixture (A–B)	Temp. (°C)	No. of data points	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	0.6	0.01	0.1		−111.95	256.30	15
	−20	21	0.6	0.04	0.4		−89.10	217.35	15
	15	21	0.6	0.08	0.7		−42.45	139.85	15
Methylamine–*n*-hexane	−55	21	0.5	0.00	0.1		36.13	92.24	16
	−20	21	1.1	0.02	0.3		225.86	−75.09	16
	20	21	0.4	0.06	0.8		284.39	−142.61	16
Methylamine–*n*-nonane	−40	20	0.9	0.01	0.2		368.19	−126.50	15
	−20	20	1.6	0.04	0.3		471.69	−189.39	15
	0	20	0.7	0.04	1.0		517.98	−231.45	15
	20	20	1.5	0.05	1.2		559.80	−275.41	15
Ethylamine–*n*-butane	−55	24	1.3	0.01	0.2		−305.02	539.13	15
	−20	24	2.6	0.08	1.7		−318.00	529.82	15
	20	24	0.9	0.13	2.4		−320.42	492.62	15
Ethylamine–*n*-hexane	−40	24	0.6	0.00	0.0		−273.86	432.22	15
	−20	24	1.1	0.02	0.2		−241.49	340.61	15
	0	24	1.6	0.03	0.3		−219.46	281.11	15
	20	24	1.8	0.08	0.8		−273.90	360.96	15

Dimethylamine–*n*-hexane	−50	10	0.4	0.00	0.0		−216.35	326.49	17
	−20	10	0.9	0.02	0.2		−189.89	259.27	17
	20	10	1.4	0.07	1.4		−261.33	348.17	17
n-Propylamine–*n*-hexane	−20	22	0.2	0.00	0.0		−280.06	453.36	15
	0	22	0.5	0.00	0.0		−286.19	431.18	15
	20	22	2.0	0.06	0.5		−425.76	674.07	15
n-Butylamine–*n*-hexane	60	7	1.4	0.05	0.1	11.1	−266.79	415.65	18
n-Butylamine–*n*-heptane	55	17	1.3	0.03	0.1	9.8	341.38	−249.59	19
	75	18	1.6	0.09	0.5	8.4	−150.94	191.26	19
Diethylamine–*n*-hexane	60	7	0.4	0.03	0.1	3.9	381.11	−280.67	18
Diethylamine–*n*-heptane	35	24	1.1	0.02	0.3	6.1	527.93	−337.64	19
	55	21	1.0	0.03	0.3	5.4	458.43	−318.80	19
n-Hexylamine–*n*-hexane	25	7	0.7	0.01	0.1	3.9	−293.03	423.03	20
	50	15	0.7	0.01	0.2	7.5	−225.55	303.27	20
	60	7	1.1	0.03	0.7	13.3	−283.47	383.69	18
Dipropylamine–*n*-hexane	60	7	3.0	0.01	0.1	14.4	114.65	−85.58	18
Diisopropylamine–*n*-hexane	60	7	2.0	0.03	0.3	13.9	483.59	−306.67	18
Methylamine–tetrachloromethane	−20	20	1.9	0.06	0.7		−326.28	598.83	11
	20	20	4.0	0.07	2.6		−306.20	627.45	11
Dimethylamine–tetrachloromethane	−20	22	1.2	0.03	0.3		−381.80	694.78	21
	20	22	4.9	0.17	2.4		−352.15	597.51	21
Diethylamine–tetrachloromethane	20	11	3.3	0.05	0.2	8.3	539.51	−262.45	22
	40	11	0.7	0.05	0.3	2.2	12.11	64.29	22

TABLE 6

Binary results obtained in fitting the model to phase equilibria of aniline mixtures

Mixture (A–B)	Temp. (°C)	No. of data points	Root-mean-square deviations				Parameters (K)		Ref.
			δP (Torr)	δT (°C)	δx ($\times 10^3$)	δy ($\times 10^3$)	a_{AB}	a_{BA}	
Aniline–acetone	40	12	1.4	0.02	0.6		−601.37	976.04	23
	113.52	13	0.6	0.04	1.1		−608.58	991.57	23
Aniline–benzene	25	27	0.8	0.01	0.1		−483.42	698.92	24
	70	11	2.0	0.04	0.9	1.5	−466.37	760.09	24
Aniline–cyclohexane	70	12	2.0	0.04	0.9	2.3	−160.31	465.28	5
Aniline–methylcyclohexane	80	14	1.0	0.02	0.8	1.8	−24.15	279.19	25
	90	16	0.8	0.02	0.9	1.3	−6.70	253.14	25
	100.02	13	0.9	0.02	1.2	1.1	−21.44	262.37	25
Aniline–tetrachloromethane	25	13	1.1	0.00	0.2	0.3	−334.77	563.84	26
	50	17	2.9	0.00	1.4	0.8	−374.31	646.20	26
Aniline–toluene	40	11	0.9	0.00	0.0		−386.76	744.26	24
	80	10	1.4	0.02	0.5	2.8	−422.87	682.39	24
	90	16	1.6	0.02	0.7	2.9	−434.89	708.61	24
	100.02	12	2.1	0.04	1.1	3.6	−454.15	742.59	24
Benzene–cyclohexane	25	11	0.2	0.00	0.0	0.9	137.89	10.89	5
	69.98	7	0.1	0.00	0.0	2.5	140.87	−7.87	5
Benzene–*n*-heptane	24.98	10	0.4	0.00	0.0		235.55	−7.64	25
Benzene–*n*-hexane	25	10	0.1	0.00	0.0	0.5	306.28	−71.96	5
Cyclohexane–*n*-heptane	25	11	0.4	0.00	0.0	1.8	6.48	27.12	27
Toluene–cyclohexane	25	11	0.2	0.00	0.0		46.87	102.64	5
Toluene–methylcyclohexane	80	12	0.1	0.01	0.0	1.0	136.89	−31.01	25
	90	14	1.5	0.06	0.5	2.5	74.70	19.13	25
	100.02	15	0.3	0.01	0.0	1.0	122.66	−25.68	25
Toluene–*n*-heptane	40	10	0.3	0.00	0.0		157.56	−20.96	25
Aniline–cyclohexane	20	MS[a]					−70.32	378.36	28
	25	MS					−85.12	388.92	29
Aniline–*n*-heptane	25	MS					169.26	236.54	29
	40	MS					206.33	172.37	30
Aniline–*n*-hexane	20	MS					127.67	249.34	31

[a] MS = mutual solubilities.

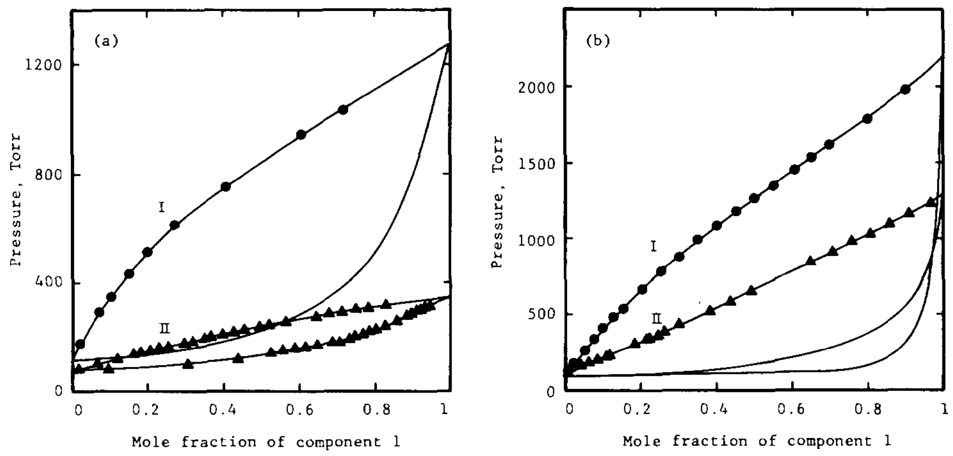

Fig. 4. Vapor–liquid equilibria for (a) aliphatic amine + saturated hydrocarbon and (b) aliphatic amine + tetrachloromethane. Experimental: (a), I, dimethylamine + *n*-hexane at 20°C (●) [17], II, diethylamine + *n*-heptane at 35°C (▲) [19]; (b) I, methylamine + tetrachloromethane at 20°C (●) [11], II, dimethylamine + tetrachloromethane at 20°C (▲) [21]. Calculated (———).

tetrachloromethane [12]. h_{AB} for aniline–benzene was taken from Whetsel and Lady [13]. h_{AB} for aniline–acetone was approximately obtained by taking the difference between h of the aniline chains and the extrapolated value of experimental h^E/x_1x_2 at infinite dilution of aniline using a correlating equation given by Christensen et al. [14].

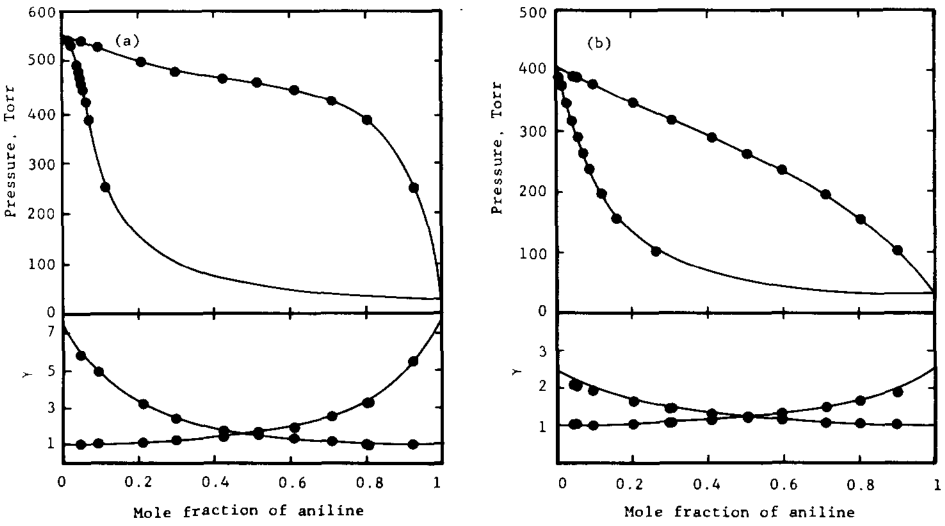

Fig. 5. Vapor–liquid equilibria for (a) aniline + methylcyclohexane at 90°C and (b) aniline + toluene at 90°C. Experimental (●): (a) [25], (b) [24]. Calculated (———).

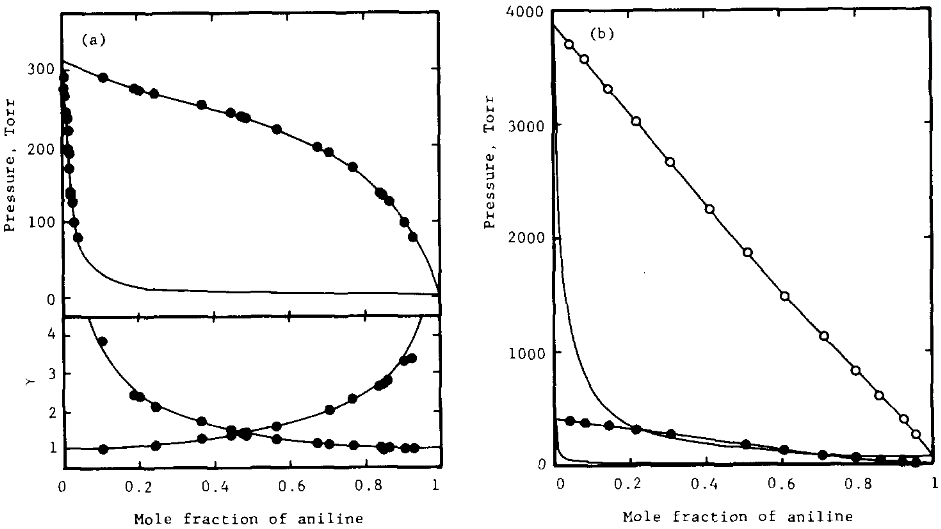

Fig. 6. Vapor–liquid equilibria for (a) aniline + tetrachloromethane at 50°C and (b) aniline + acetone at 40 and 113.52°C. Experimental: (a) (●) [26], (b) 40°C (●), 113.52°C (○) [23]. Calculated (———).

Binary calculated results of phase equilibrium data are summarized in Table 5 for aliphatic amine mixtures and in Table 6 for aniline mixtures. Figures 3–6 show the calculated and experimental vapor–liquid equilibrium results for representative binary mixtures.

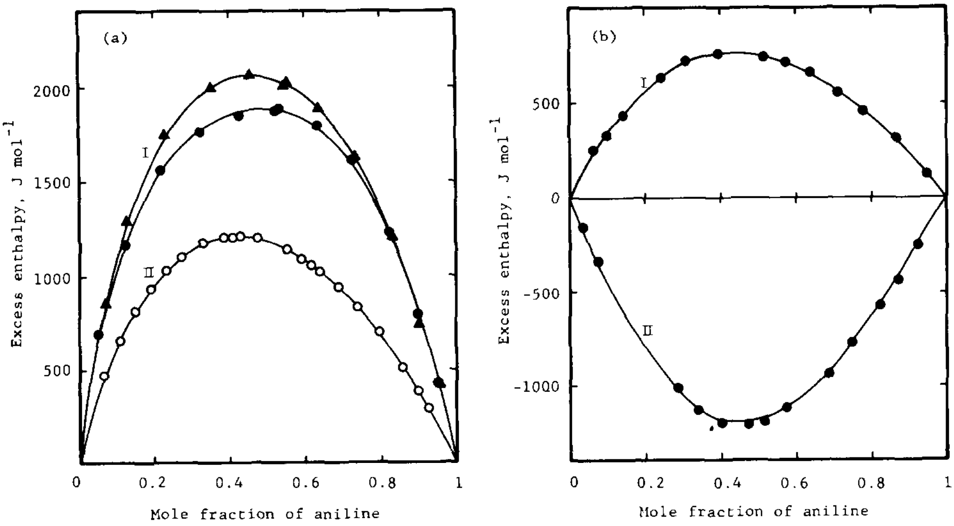

Fig. 7. Molar excess enthalpies for aniline mixtures. Experimental: (a) I, aniline + cyclohexane at 35°C (●) and 50°C (▲) [33], II, aniline + tetrachloromethane at 25°C (○) [14]; (b) I, aniline + benzene at 30°C (●) [32], II, aniline + acetone at 25°C (●) [14]. Calculated (———).

TABLE 7

Binary results obtained in fitting the model to molar excess enthalpies of aniline mixtures

Mixture (A–B)	Temp. (°C)	No. of data points	Root-mean-square deviations			Parameters				Ref.
			δh^E (J mol^{-1})	δT (°C)	δx ($\times 10^3$)	C_A (K)	C_B (K)	D_A	D_B	
Aniline–acetone	25	13	12.5	0.16	4.4	2394.07	1833.74	6.9388	5.2191	14
Aniline–benzene	30	14	4.9	0.05	1.6	1128.91	878.40	4.2536	3.9931	32
Aniline–cyclohexane	35	12	7.6	0.04	2.7	1452.80	288.79	2.4431	−0.9642	33
	50	12	4.9	0.02	2.3	1432.71	92.70	3.0862	−1.3353	33
Aniline–tetrachloromethane	25	24	3.6	0.04	1.4	293.00	1037.02	0.6980	4.8447	14

TABLE 8

Predicted results of ternary vapor–liquid equilibria for mixtures of aniline with hydrocarbons

Mixture	Temp. (°C)	No. of data points	Abs. arith. mean deviations		Ref.
			Vapor mole fraction ($\times 10^3$)	Pressure (Torr)	
Aniline–			1.2		
benzene–	70	10	8.4	6.16	5
cyclohexane			9.0		
Aniline–			1.0		
toluene–	80	7	4.4	2.10	25
methylcyclohexane			4.1		
Aniline–			1.5		
toluene–	90	9	4.6	4.09	25
methylcyclohexane			4.5		
Aniline–			1.2		
toluene–	100.02	9	4.0	4.48	25
methylcyclohexane			4.1		

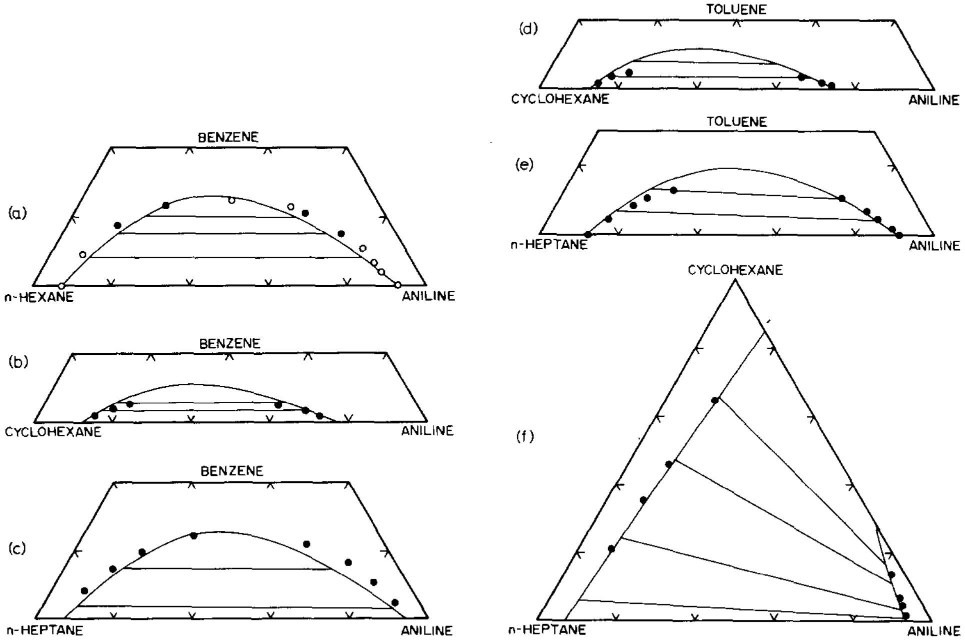

Fig. 8. Liquid–liquid equilibria for ternary aniline + hydrocarbon mixtures. Experimental: (●) tie-line, (○) solubility; (a) *n*-hexane + benzene + aniline at 20°C [31]; (b) cyclohexane + benzene + aniline at 20°C [30]; (c) *n*-heptane + benzene + aniline at 25°C [30]; (d) cyclohexane + toluene + aniline at 20°C [30]; (e) *n*-heptane + toluene + aniline at 40°C [30]; (f) *n*-heptane + cyclohexane + aniline at 25°C [30]. Calculated (———).

TABLE 9

Comparison of calculated and experimental vapor–liquid equilibrium data for ternary mixtures

Experimental					Deviations [a]			
x_A	x_B	y_A	y_B	P (Torr)	δy_A	δy_B	δy_C	δP (Torr)
					$(\times 10^3)$			
Aniline(A)–benzene(B)–cyclohexane(C) at 70°C								
0.1602	0.6209	0.0070	0.6686	523.24	-0.3	2.0	-1.7	2.78
0.1673	0.4188	0.0086	0.4435	531.25	-0.3	6.3	-6.0	2.69
0.1660	0.1965	0.0110	0.2255	521.65	-0.7	-4.8	5.4	2.12
0.3651	0.4756	0.0131	0.6220	453.20	-0.8	11.0	-10.2	6.24
0.3737	0.3133	0.0139	0.3983	475.35	-1.0	-12.3	13.3	5.62
0.3721	0.1564	0.0154	0.1917	482.23	-1.2	-7.3	8.4	3.30
0.5248	0.3553	0.0176	0.5839	400.96	-2.2	9.6	-7.4	15.43
0.5300	0.2268	0.0173	0.3394	437.69	-2.1	-9.6	11.7	12.86
0.5170	0.1153	0.0173	0.1648	455.42	-2.1	-13.4	15.5	4.56
0.8332	0.0810	0.0352	0.2599	265.48	-2.1	-7.9	10.0	-6.07
Root-mean-square deviation					1.5	9.0	9.8	7.50
Aniline(A)–toluene(B)–methylcyclohexane(C) at 80°C								
0.1001	0.8059	0.0140	0.8080	289.87	0.2	4.2	-4.4	-1.61
0.0976	0.6774	0.0141	0.6249	316.64	0.5	3.7	-4.1	-0.87
0.1035	0.4515	0.0166	0.3924	345.98	0.5	-3.0	2.5	-1.62
0.1016	0.2224	0.0200	0.1920	368.29	0.4	-5.3	4.9	-0.95
0.1014	0.0866	0.0225	0.0775	376.21	-0.5	-4.0	4.5	-1.67
0.3020	0.3530	0.0329	0.3371	316.52	-1.0	-2.7	3.7	1.46
0.5250	0.3580	0.0490	0.5090	246.51	-3.8	8.0	-4.2	6.54
Root-mean-square deviation					1.5	4.7	4.1	2.79
Aniline(A)–toluene(B)–methylcyclohexane(C) at 90°C								
0.0995	0.8065	0.0156	0.8154	402.87	-0.2	-4.9	5.1	0.56
0.0977	0.6773	0.0159	0.6321	437.54	-0.7	-5.9	6.6	-1.34
0.1020	0.4554	0.0185	0.3995	476.13	-1.1	2.2	-1.1	-0.44
0.1013	0.2217	0.0220	0.1950	505.05	-0.7	7.7	-7.0	-0.10
0.1012	0.0868	0.0246	0.0804	515.51	0.4	6.4	-6.9	0.89
0.3030	0.3550	0.0385	0.3425	430.93	0.7	-0.6	0.0	-4.67
0.5230	0.3600	0.0580	0.5160	336.22	3.8	-13.0	9.1	-11.75
0.5020	0.2540	0.0511	0.2949	395.16	3.7	-0.6	-3.1	-10.94
0.5050	0.1320	0.0509	0.1311	432.32	2.3	-0.5	-1.8	-6.07
Root-mean-square deviation					2.0	6.1	5.4	5.96

TABLE 9 (continued)

Experimental					Deviations [a]			
x_A	x_B	y_A	y_B	P (Torr)	δy_A $(\times 10^3)$	δy_B	δy_C	δP (Torr)
Aniline(A)–toluene(B)–methylcyclohexane(C) at 100.02°C								
0.0986	0.8074	0.0174	0.8146	549.93	0.6	7.7	−8.3	−1.05
0.0972	0.6768	0.0176	0.6374	593.06	0.9	4.9	−5.7	0.13
0.1014	0.4566	0.0204	0.4056	641.94	1.2	−0.4	−0.8	−0.04
0.1006	0.2244	0.0235	0.2005	679.28	0.2	−6.5	6.3	0.78
0.1004	0.0886	0.0269	0.0791	691.05	−0.2	−2.3	2.5	−1.93
0.3020	0.3580	0.0444	0.3516	577.40	0.4	0.1	−0.5	4.31
0.5210	0.3620	0.0671	0.5209	450.74	−3.1	12.6	−9.5	13.60
0.4980	0.2580	0.0600	0.3030	525.24	−2.5	1.4	1.1	12.06
0.5060	0.1310	0.0596	0.1344	571.74	−1.9	0.0	1.9	6.48
Root-man-square deviation					1.6	5.7	5.2	6.64

[a] Deviation = experimental value − calculated one.

In the correlation of binary excess enthalpy data, the coefficients of eqn. (17) were obtained by minimizing the following objective function.

$$F=\sum_{i=1}^{N}\left[\frac{(x_{A_i}-\hat{x}_{A_i})^2}{\sigma_x^2}+\frac{(T_i-\hat{T}_i)^2}{\sigma_T^2}+\frac{(h_i^E-\hat{h}_i^E)^2}{\sigma_h^2}\right] \tag{24}$$

where $\sigma_x = 0.0005$, $\sigma_T = 0.05$°C, and $\sigma_h = 0.01\ h^E$ J mol^{-1}.

Calculated results for excess enthalpies are given in Table 7. The calculated results are compared with the experimental data of four aniline mixtures in Fig. 7.

Prediction of ternary vapor–liquid and liquid–liquid equilibria

Table 8 contains a summary for the absolute arithmetic mean deviations between the calculated and experimental values in vapor-phase mole fractions and total pressure for the four ternary mixtures investigated in this work. Table 9 gives a detailed comparison of the experimental and calculated vapor–liquid equilibrium data of the ternary mixtures. Figure 8 shows the agreement between the calculated and experimental solubility envelopes of the five ternary mixtures of aniline with hydrocarbons.

In conclusion, the proposed model is successful in the quantitative reproduction of the thermodynamic and spectroscopic properties of binary amine mixtures. The model permits good predictions of both vapor–liquid and liquid–liquid equilibria for ternary aniline mixtures using binary phase equilibrium data for the constituent binary pairs.

LIST OF SYMBOLS

A, B, C	amine, nonassociating component and saturated hydrocarbon
a_{IJ}	NRTL constant
C_I, D_I	constants of eqn. (17)
F	objective function
G_{IJ}	coefficient as defined by $\exp(-\alpha_{IJ}\tau_{IJ})$
h_2	enthalpy of formation of dimer
h	enthalpy of hydrogen bond formation in i-mer
h_{AB}	enthalpy of formation of chemical complex $\mathrm{A}_i\mathrm{B}$
h^{E}	molar excess enthalpy
K_2	association constant of dimer formation
K	association constant of chain i-mer formation, $i > 1$
K_{AB}	solvation constant of formation of chemical complex $\mathrm{A}_i\mathrm{B}$
P	total pressure
P_I^{s}	saturation pressure of pure component I
R	gas constant
S	stoichiometric sum
T	absolute temperature
v_I^{L}	liquid molar volume of pure component I
x_I	liquid-phase mole fraction of component I
y_I	vapor-phase mole fraction of component I
z	coefficient as defined by Kx_{A_1}

Greek letters

α_{IJ}	nonrandomness parameter of NRTL equation
β	coefficient as defined by eqn. (18)
γ_I	activity coefficient of component I
ϵ_{a}, ϵ_{M}	apparent molar absorptivity and molar absorptivity of monomer
σ_x, σ_β, σ_P, σ_T, σ_y, σ_h	standard deviations in liquid-phase mole fraction, β, pressure, temperature, vapor-phase mole fraction, and excess enthalpy
τ_{JI}	coefficient as defined by a_{JI}/T
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 pressure P_I^{s}

Subscripts

A, B, C	amine, unassociating component, and saturated hydrocarbon
A_1, A_i	amine monomer and i-mer
$\mathrm{A}_i\mathrm{B}$	complex formation between amine i-mer and component B
chem	chemical
I, J, K	components
phys	physical

Superscripts

E	excess
L	liquid
s	saturation
*	pure amine
^	calculated

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