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THERMODYNAMICS OF ASSOCIATED SOLUTIONS. EXCESS THERMODYNAMIC PROPERTIES OF MIXTURES OF ANILINE WITH HYDROCARBONS

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ABSTRACT

The binary vapor–liquid and liquid–liquid equilibria and molar excess enthalpies of mixtures containing aniline and a hydrocarbon are correlated with the UNIQUAC associated solution model. Ternary predictions of vapor–liquid and liquid–liquid equilibria for aniline mixtures are good with this model using only binary parameters.

INTRODUCTION

The UNIQUAC associated solution model has been used to represent the excess thermodynamic properties of various kinds of liquid mixtures: phase equilibria and excess enthalpies of binary and ternary alcohol solutions [1–6]; vapor–liquid equilibria of binary aliphatic amine-saturated hydrocarbon mixtures [6]; phase equilibria of aqueous solutions [7]. In this paper we show that the UNIQUAC associated solution model can be applied to the accurate description of phase equilibrium and excess molar enthalpy data for solutions of aniline with hydrocarbons.

ASSOCIATION MODEL

We will briefly summarize the UNIQUAC associated solution model for a ternary mixture containing aniline and hydrocarbons. A stands for aniline, B for the aromatic hydrocarbon, and C for the saturated hydrocarbon. Aniline self-associates in the mixture in the form of open chains formed by successive reactions

$$A_1 + A_i = A_{i+1} \text{ for all } i \geqslant 1 \tag{1}$$

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Aniline and the aromatic hydrocarbon form chemical species A_iB according to the solvation reaction

$$A_i + B = A_iB \tag{2}$$

The equilibrium constants for the above reactions, respectively, are defined as

$$K_A = \left(\Phi_{A_{i+1}}/\Phi_{A_i}\Phi_{A_1}\right)i/(i+1) \tag{3}$$

$$K_{AB} = \left(\Phi_{A_iB}/\Phi_{A_i}\Phi_{B_1}\right)i/(ir_A + r_B) \tag{4}$$

The activity coefficients of aniline and the aromatic hydrocarbon are given as follows

$$\begin{aligned} \ln \gamma_A = {} & \ln\left(\Phi_{A_1}/\Phi_{A_1}^0 x_A\right) + r_A\left(1/V^0 - 1/V\right) \\ & -\left(\frac{Z}{2}\right)q_A\left[\ln(\Phi_A/\theta_A) + 1 - \Phi_A/\theta_A\right] \\ & + q_A\left[1 - \ln\left(\sum_J \theta_J\tau_{JA}\right) - \sum_J\left(\theta_J\tau_{AJ}/\sum_K \theta_K\tau_{KJ}\right)\right] \end{aligned} \tag{5}$$

$$\begin{aligned} \ln \gamma_B = {} & \ln\left(\Phi_{B_1}/x_B\right) + 1 - \gamma_B/V - \left(\frac{Z}{2}\right)q_B\left[\ln(\Phi_B/\theta_B) + 1 - \Phi_B/\theta_B\right] \\ & + q_B\left[1 - \ln\left(\sum_J \theta_J\tau_{JB}\right) - \sum_J\left(\theta_J\tau_{BJ}/\sum_K \theta_K\tau_{KJ}\right)\right] \end{aligned} \tag{6}$$

$\ln \gamma_C$ is expressed by changing the subscript B in eqn. (6) to C and Z is the coordination number taken as 10. Φ_I, the segment fraction, θ_I, the area fraction, and τ_{IJ}, the binary adjustable parameter, respectively, are given by

$$\Phi_I = r_I x_I/\sum_J r_J x_J \tag{7}$$

$$\theta_I = q_I x_I/\sum_J q_J x_J \tag{8}$$

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

The stoichiometric segment fractions Φ_A and Φ_B are related to the monomeric segment fractions Φ_{A_1} and Φ_{B_1}.

$$\Phi_A = \left[\Phi_{A_1}/(1 - K_A\Phi_{A_1})^2\right]\left[1 + r_A K_{AB}\Phi_{B_1}\right] \tag{10}$$

$$\Phi_B = \Phi_{B_1}\left[1 + r_B K_{AB}\Phi_{A_1}/(1 - K_A\Phi_{A_1})\right] \tag{11}$$

Φ_C is equal to Φ_{C_1}. The aniline monomer segment fraction, $\Phi_{A_1}^0$, in pure aniline is expressed by

$$\Phi_{A_1}^0 = \left[(2K_A + 1) - (1 + 4K_A)^{1/2}\right]/2K_A^2 \tag{12}$$

The true molar volume, V, in the mixture and that in pure aniline liquid, V^0, are given as

$$1/V = \Phi_{A_1}/\left[r_A\left(1 - K_A\Phi_{A_1}\right)\right] + \left(\Phi_{B_1}/r_B\right)\left[1 + K_{AB}r_B\Phi_{A_1}/\left(1 - K_A\Phi_{A_1}\right)\right] + \Phi_C/r_C \tag{13}$$

$$1/V^0 = \left(1 - K_A\Phi^0_{A_1}\right)/r_A \tag{14}$$

Excess molar enthalpy for the ternary mixture is

$$h^E = K_A h_A x_A\left(\Phi_{A_1} - \Phi^0_{A_1}\right) + K_{AB}h_{AB}\Phi_{B_1}r_A x_A\left(1 - K_A\Phi_{A_1}\right)/\left(1 + r_A K_{AB}\Phi_{B_1}\right) - R\sum_I q_I x_I \frac{\sum_J \theta_J \frac{\partial \tau_{JI}}{\partial(1/T)}}{\sum_J \theta_J \tau_{JI}} \tag{15}$$

The energy parameters are assumed to have a linear function of temperature.

$$a_{JI} = \mathrm{C}_I + \mathrm{D}_I(T - 273.15) \tag{16}$$

DATA REDUCTION

Binary vapor–liquid equilibrium data were reduced using the equation

$$\phi_I y_I P = \gamma_I x_I P_I^s \phi_I^s \exp\left[v_I^L\left(P - P_I^s\right)/RT\right] \tag{17}$$

where y_I, P, and P_I^s are the vapor-phase mole fraction, the total pressure, and the pure-component vapor pressure, respectively. The fugacity coefficients, ϕ_I at P and ϕ_I^s at P_I^s, were calculated by the volume-explicit virial equation of state, truncated after the second term. Second virial coefficients were calculated using the method of Hayden and O'Connell [8]. The pure-liquid molar volumes, v^L, were estimated from the modified Rackett equation [9]. The vapor pressures of pure components were calculated using the Antoine equation whose constants were taken from the literature [10,11].

The computer program used was similar to that developed by Prausnitz et al. [12], based on the maximum-likelihood principle. The adjustable parameters were obtained by minimizing the following objective function

$$S = \sum_{i=1}^{N}\left[\frac{\left(P_i - \hat{P}_i\right)^2}{\sigma_P^2} + \frac{\left(T_i - \hat{T}_i\right)^2}{\sigma_T^2} + \frac{\left(x_{Ai} - \hat{x}_{Ai}\right)^2}{\sigma_x^2} + \frac{\left(y_{Ai} - \hat{y}_{Ai}\right)^2}{\sigma_y^2}\right] \tag{18}$$

where a circumflex denotes the calculated variable. The estimated standard deviations for the measured variables were taken as $\sigma_P = 1.0$ Torr for pressure, $\sigma_T = 0.05$ K for temperature, $\sigma_x = 0.001$ for liquid-phase mole fraction, and $\sigma_y = 0.003$ for vapor-phase mole fraction.

The binary parameters for a partially miscible mixture were obtained by

TABLE 1

Values of the molecular structural constants and the Antoine constants for pure compounds

Substance	Structural constants		Antoine constants [a]			Ref.
	r	q	A	B	C	
Aniline	2.98	2.38	7.46441	1840.790	216.923	10
Cyclohexane	3.18	2.55	6.84498	1203.526	222.863	11
n-Hexane	3.61	3.09	6.87776	1171.530	224.366	11
Methylcyclohexane	3.72	2.98	6.82689	1272.864	221.630	11
n-Heptane	4.15	3.52	6.90240	1268.115	216.900	11
Benzene	2.56	2.05	6.90565	1211.033	220.790	11
Toluene	3.10	2.48	6.95464	1344.800	219.482	11

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

solving eqn. (19) for component I with a Newton–Raphson iterative method.

$$(\gamma_I x_I)^{\mathrm{I}} = (\gamma_I x_I)^{\mathrm{II}} \tag{19}$$

where the superscripts I and II represent two equilibrium liquid phases.

Table 1 shows the pure-component molecular structural parameters, estimated by the method of Vera et al. [13], and the Antoine parameters.

RESULTS AND DISCUSSION

In phase equilibrium data reduction we studied the capability of the UNIQUAC associated solution model using two different values for the association constant of aniline: (I) $K_{\mathrm{A}} = 50.2$ at 50°C, given by Brandani who presented a method for estimating the associated constant for pure self-associating liquid compounds [14]; (II) $K_{\mathrm{A}} = 15$ at 50°C, tentatively assumed in this work. The molar enthalpy of hydrogen bond formation in pure aniline was taken as $h_{\mathrm{A}} = -15.4$ kJ mol^{-1}, which is equal to the enthalpy of dilution of aniline in cyclohexane at 35°C [15]. The molar enthalpy of complex formation between aniline and an aromatic hydrocarbon, $h_{\mathrm{AB}} = -10.8$ kJ mol^{-1}, was estimated by taking the difference between the enthalpy of dilution of aniline in cyclohexane and that of aniline in benzene [16]. h_{A} and h_{AB} were assumed to be independent of temperature. The value of the solvation constant was assumed as 1 at 50°C for aniline–aromatic hydrocarbon mixtures. The temperature dependence of the equilibrium constants is given by the van't Hoff relation.

Binary calculated results are listed in Table 2 and the binary parameters presented there are used to calculate ternary liquid–liquid equilibria without introducing any additional ternary parameters. The UNIQUAC associated solution model reduces to the original UNIQUAC model when we do not

TABLE 2

Root-mean-square deviations obtained in binary phase equilibrium data reduction and binary parameters used for predicting ternary liquid–liquid equilibria

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–benzene	25	27	I [a]	0.99	0.00	0.1		295.82	−152.03	17
			II [b]	2.29	0.00	0.2		1195.61	−282.66	
			III [c]	0.60	0.00	0.0		−27.86	148.00	
Aniline–toluene	40	11	I	0.94	0.00	0.0		101.92	−6.91	17
			II	1.03	0.00	0.0		347.27	−188.73	
			III	1.06	0.00	0.0		−34.75	212.61	
Benzene–cyclohexane	25	11		0.23	0.00	0.1	0.9	10.21	56.92	18
Benzene–*n*-hexane	25	10		0.10	0.00	0.1	0.4	32.15	49.41	18
Benzene–*n*-heptane	24.98	10		0.48	0.00	0.0		−10.91	111.54	19
Cyclohexane–*n*-heptane	25	11		0.46	0.00	0.1	1.2	−30.05	45.62	20
Cyclohexane–toluene	25	10		0.13	0.00	0.0		45.50	12.55	18
Toluene–*n*-heptane	40	10		0.30	0.00	0.0		−53.49	109.77	19
Aniline–cyclohexane	20	MS [d]	I					164.63	14.59	21
			II					221.68	−33.00	
			III					77.54	270.39	
	25	MS	I					145.16	23.33	22
			II					203.95	−26.66	
			III					63.87	273.70	
Aniline–*n*-heptane	25	MS	I					156.14	31.72	22
			II					226.64	−37.49	
			III					76.20	317.82	
	40	MS	I					159.98	18.32	23
			II					226.58	−44.85	
			III					75.19	282.88	
Aniline–*n*-hexane	20	MS	I					209.59	0.50	24
			II					269.68	−52.44	
			III					109.88	277.56	

[a] I, $K_A = 15$ at 50°C and $h_A = -15.4$ kJ mol^{-1}.

[b] II, $K_A = 50.2$ at 50°C and $h_A = -15.4$ kJ mol^{-1}.

[c] III, $K_A = 0$ and $K_{AB} = 0$ (original UNIQUAC model).

[d] MS = mutual solubilities.

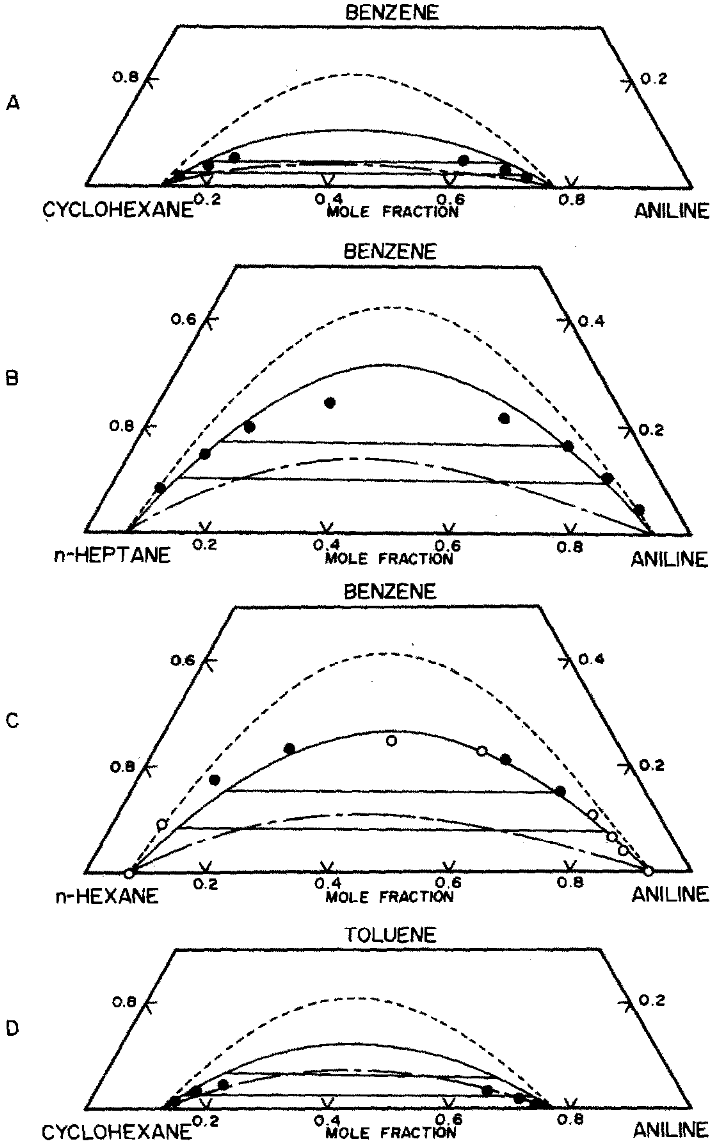

Fig. 1. Ternary liquid–liquid equilibria for mixtures of aniline with hydrocarbons. Experimental (●) tie-line, (○) solubility. (A) Cyclohexane–benzene–aniline at 20°C [23]; (B) *n*-heptane–benzene–aniline at 25°C [23]; (C) *n*-hexane–benzene–aniline at 20°C [24]; (D) cyclohexane–toluene–aniline at 20°C [23]; (E) *n*-heptane–toluene–aniline at 40°C [23]; (F) *n*-heptane–cyclohexane–aniline at 25°C [23]. Calculated: (- - - - - -) UNIQUAC model; (———) $K_A = 15$ at 50°C and $h_A = -15.4$ kJ mol^{-1} were used; (- — -) $K_A = 50.2$ at 50°C and $h_A = -15.4$ kJ mol^{-1} were used.

assume the association of aniline molecules ($K_A = 0$) and the solvation constant between aniline and the aromatic hydrocarbon ($K_{AB} = 0$). Figure 1 compares calculated and experimental liquid–liquid equilibria for five ternary

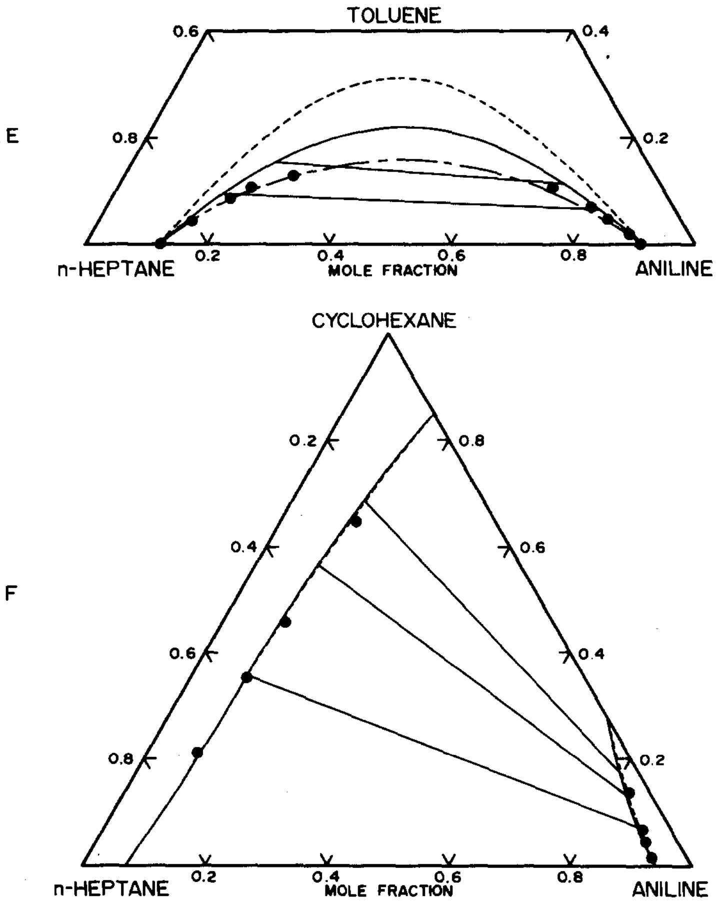

Fig. 1 (continued).

mixtures of type I, where only one binary is partially miscible, and for one ternary mixture of type II, where two binaries are partially miscible and the third binary is completely miscible. For a type II mixture, good agreement is obtained by the three approaches. For type I mixtures predictions using the original UNIQUAC model are grossly in error and the UNIQUAC associated solution model with $K_A = 50.2$ at 50°C gives the smallest two-phase region. Table 3 lists results of vapor–liquid equilibrium data for binaries constituting ternary mixtures obtained from the UNIQUAC associated solution model and some results are shown in Figs. 2 and 3. Table 4 summarizes vapor–liquid equilibrium predictions for ternary mixtures. Better agreement is obtained between calculated and experimental pressures and vapor-phase mole fractions using $K_A = 15$ at 50°C and detailed results are given in Table 5. The calculated results of phase equilibria suggest that the association constant of aniline should be considerably less than that estimated by Brandani's method [14]. Binary calculated excess enthalpy results are given in Table 6 and are shown in Fig. 4.

TABLE 3

Root-mean-square deviations obtained in binary vapor–liquid equilibrium data reduction and binary parameters used for predicting ternary vapor–liquid equilibria

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–benzene	70	11	I [a]	1.99	0.07	0.9	1.2	286.09	−150.29	17
			II [b]	7.35	0.26	3.1	2.8	703.77	−307.85	
Aniline–	70	12	I	2.69	0.11	0.8	1.8	229.71	−57.19	18
cyclohexane			II	6.90	0.27	1.8	2.1	347.25	−139.11	
Aniline–methyl-	80	14	I	2.91	0.09	0.6	1.6	239.28	−73.17	19
cyclohexane			II	8.51	0.25	1.9	2.6	372.65	−163.85	
	90	16	I	3.13	0.12	0.8	1.4	252.93	−84.49	19
			II	9.33	0.35	2.9	3.1	403.72	−180.61	
	100.02	13	I	3.24	0.15	1.3	1.4	256.16	−90.75	19
			II	10.09	0.48	3.7	3.2	412.14	−191.75	
Aniline–toluene	80	10	I	1.26	0.02	0.3	1.6	244.99	−128.79	17
			II	5.98	0.12	1.5	5.0	562.68	−292.52	
	90	16	I	1.08	0.03	0.5	1.1	233.15	−123.81	17
			II	6.01	0.15	2.0	4.3	549.87	−294.91	
	100.02	12	I	1.34	0.04	0.7	1.9	223.65	−122.16	17
			II	7.25	0.24	3.2	3.8	583.93	−313.84	
Benzene–										
cyclohexane	69.98	7		0.15	0.01	0.2	2.1	−10.23	71.71	18
Methylcyclo-	80	12		0.15	0.00	0.1	0.8	37.50	1.44	19
hexane–	90	14		1.60	0.06	0.3	1.8	71.24	−31.33	19
toluene	100.02	15		0.25	0.01	0.1	0.9	38.76	−2.20	19

[a] I, $K_A = 15$ at 50°C and $h_A = -15.4$ kJ mol^{-1}.

[b] II, $K_A = 50.2$ at 50°C and $h_A = -15.4$ kJ mol^{-1}.

TABLE 4

Predicted results of ternary vapor–liquid equilibria

Mixture	Temp. (°C)	No. of data points	Abs. arith. mean deviations						Ref.
			Vapor mole fraction ($\times 10^3$)		Pressure				
					(Torr)		(%)		
			I [a]	II [b]	I	II	I	II	
Aniline–			0.7	0.9					
benzene–	70	10	6.1	6.6	4.83	12.30	1.19	2.55	18
cyclohexane			5.6	6.7					
Aniline–			0.5	1.1					
toluene–	80	7	3.4	3.1	4.55	11.57	1.37	3.51	19
methylcyclohexane			2.9	2.6					
Aniline–			0.7	1.4					
toluene–	90	9	3.2	4.2	4.00	14.29	0.87	3.24	19
methylcyclohexane			2.7	3.3					
Aniline–			0.5	1.9					
toluene–	100.2	9	2.0	2.6	5.77	18.67	0.96	3.14	19
methylcyclohexane			1.7	2.5					

[a] I, $K_A = 15$ at 50°C and $h_A = -15.4$ kJ mol^{-1}.

[b] II, $K_A = 50.2$ at 50°C and $h_A = -15.4$ kJ mol^{-1}.

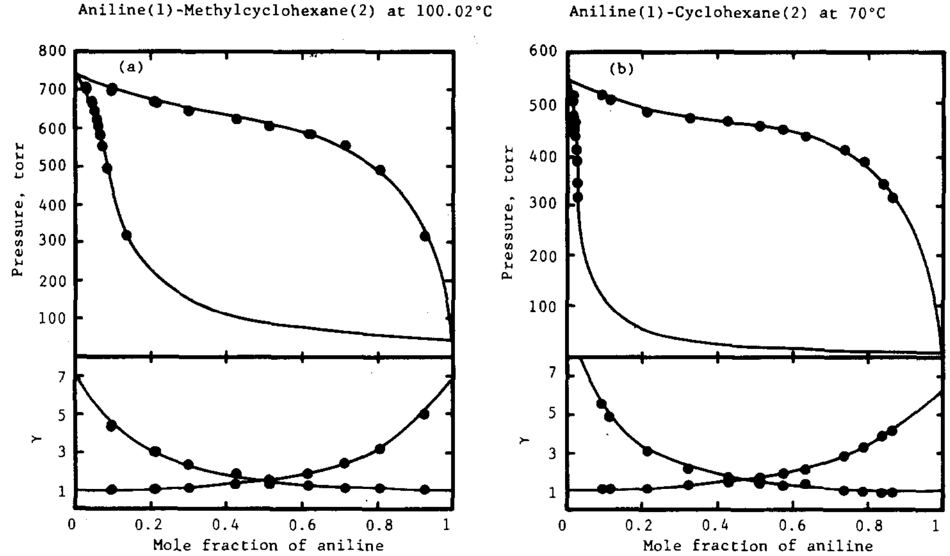

Fig. 2. Vapor–liquid equilibria for (a) aniline–methylcyclohexane at 100.02°C and (b) aniline–cyclohexane at 70°C. Experimental (●): (a) aniline–methylcyclohexane [19]; (b) aniline–cyclohexane [18]. Calculated (———), $K_A = 15$ at 50°C and $h_A = -15.4$ kJ mol^{-1} were used.

In conclusion, the UNIQUAC associated solution model is able to correlate binary phase equilibrium and excess enthalpy data well for aniline–hydrocarbon mixtures and to predict ternary vapor–liquid and liquid–liquid

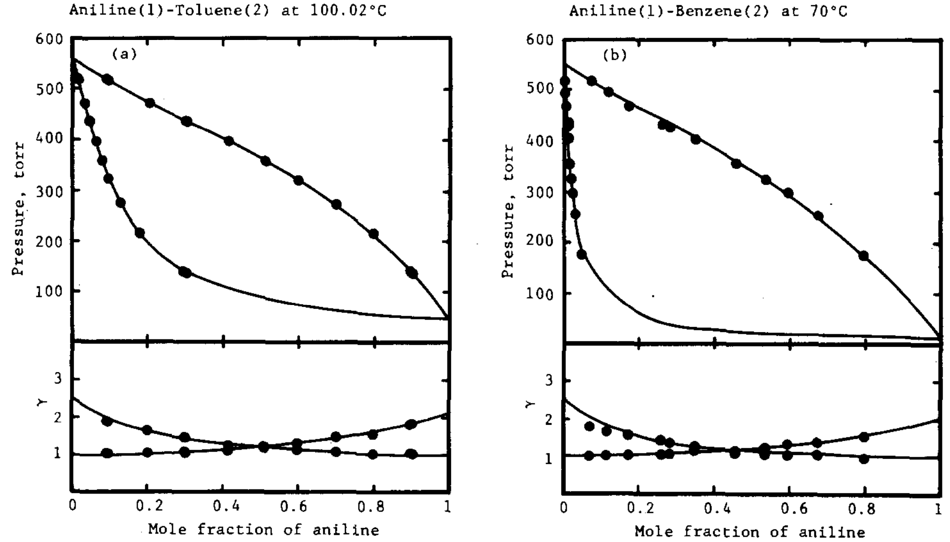

Fig. 3. Vapor–liquid equilibria for (a) aniline–toluene at 100.02°C and (b) aniline–benzene at 70°C. Experimental (●) [17]. Calculated (———), $K_A = 15$ at 50°C and $h_A = -15.4$ kJ mol^{-1} were used.

TABLE 5

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

Experimental					Deviations [a]			
x_1	x_2	y_1	y_2	P (Torr)	$10^3\ \delta y_1$	$10^3\ \delta y_2$	$10^3\ \delta y_3$	δP (Torr)
Aniline (1)–benzene (2)–cyclohexane (3) at 70°C								
0.1602	0.6209	0.0070	0.6686	523.24	−0.3	6.2	−5.9	−5.03
0.1673	0.4188	0.0086	0.4435	531.25	−0.3	−5.2	5.5	−6.44
0.1660	0.1965	0.0110	0.2255	521.65	−0.3	0.1	0.2	−7.23
0.3651	0.4756	0.0131	0.6220	453.20	−0.3	1.5	−1.2	−5.05
0.3737	0.3133	0.0139	0.3983	475.35	−0.5	11.9	−11.4	−5.51
0.3721	0.1564	0.0154	0.1917	482.23	−0.7	−0.4	1.1	−3.69
0.5248	0.3553	0.0176	0.5839	400.96	−1.2	6.5	−5.3	1.99
0.5300	0.2268	0.0173	0.3394	437.69	−1.2	10.3	−9.1	0.78
0.5170	0.1153	0.0173	0.1648	455.42	−1.6	7.4	−5.8	−1.09
0.8332	0.0810	0.0352	0.2599	265.48	−0.7	11.0	−10.3	−11.52
Root-mean-square deviation					0.8	7.3	6.7	5.72
Aniline (1)–toluene (2)–methylcyclohexane (3) at 80°C								
0.1001	0.8059	0.0140	0.8080	289.87	−0.1	1.9	−1.8	−4.03
0.0976	0.6774	0.0141	0.6249	316.64	−0.2	2.3	−2.1	−4.25
0.1035	0.4515	0.0166	0.3924	345.98	−0.3	4.1	−3.7	−5.69
0.1016	0.2224	0.0200	0.1920	368.29	−0.2	3.4	−3.2	−5.32
0.1014	0.0866	0.0225	0.0775	376.21	−0.6	3.4	−2.8	−6.38
0.3020	0.3530	0.0329	0.3371	316.52	−0.1	2.3	−2.2	−5.24
0.5250	0.3580	0.0490	0.5090	246.51	−1.7	6.4	−4.8	−0.96
Root-mean-square deviation					0.7	3.7	3.1	4.84
Aniline (1)–toluene (2)–methylcyclohexane (3) at 90°C								
0.0995	0.8065	0.0156	0.8154	402.87	−0.2	2.8	−2.6	−4.07
0.0977	0.6773	0.0159	0.6321	437.54	−0.3	1.8	−1.5	−3.85
0.1020	0.4550	0.0185	0.3995	476.13	−0.3	3.3	−3.0	−5.72
0.1013	0.2217	0.0220	0.1950	505.05	−0.4	4.6	−4.2	−6.19
0.1012	0.0868	0.0246	0.0804	515.51	−0.8	4.9	−4.1	−7.30
0.3030	0.3550	0.0385	0.3425	430.93	0.4	−0.8	0.3	−6.90
0.5230	0.3600	0.0580	0.5160	336.22	−0.9	3.2	−2.3	−0.85
0.5020	0.2540	0.0511	0.2949	395.16	−1.6	1.6	0.0	−0.96
0.5050	0.1320	0.0509	0.1311	432.32	−1.2	−5.4	6.6	−0.14
Root-mean-square deviation					0.8	3.5	3.4	4.77
Aniline (1)–toluene (2)–methylcyclohexane (3) at 100.02°C								
0.0986	0.8074	0.0174	0.8146	549.93	0.1	−0.9	0.8	−5.27
0.0972	0.6768	0.0176	0.6374	593.06	−0.2	1.9	−1.8	−6.21
0.1014	0.4566	0.0204	0.4056	641.94	−0.3	1.1	−0.9	−7.45
0.1006	0.2244	0.0235	0.2005	679.28	−1.0	4.3	−3.3	−6.82
0.1004	0.0886	0.0269	0.0791	691.05	−0.8	0.9	−0.2	−9.85
0.3020	0.3580	0.0444	0.3516	577.40	1.4	−1.3	−0.1	−9.60
0.5210	0.3620	0.0671	0.5209	450.74	0.0	1.8	−1.9	−2.45
0.4980	0.2580	0.0600	0.3030	525.24	−0.3	−0.3	0.6	−2.89
0.5060	0.1310	0.0596	0.1344	571.74	−0.7	−4.9	5.6	−1.41
Root-mean-square deviation					0.7	2.5	2.4	6.45

[a] Deviation = experimental value − calculated one, and $K_A = 15$ at 50°C and $h_A = -15.4$ kJ mol^{-1} were used.

TABLE 6

Results of excess enthalpy data reduction for binary aniline–hydrocarbon mixtures [a]

Mixture (A–B)	Temp. (°C)	No. of data points	Abs. arith. mean dev. ($J\ mol^{-1}$)	Parameters				Ref.
				C_A (K)	C_B (K)	D_A	D_B	
Aniline–cyclohexane	35	12	17.7	534.39	364.55	0.9539	−0.0919	15
	50	12	8.8	437.89	306.44	0.7078	−0.1039	15
Aniline–benzene	30	9	11.8	28.67	28.18	1.4850	−1.4850	25
	30	14	7.2	−14.72	−79.14	8.8128	−4.6030	26
Aniline–toluene	30	9	15.7	19.49	225.51	−0.1581	0.3955	25
	50	9	13.1	−152.59	6716.1	−0.8914	−77.735	25

[a] $K_A = 15$ at 50°C and $h_A = 15.4$ kJ mol^{-1}.

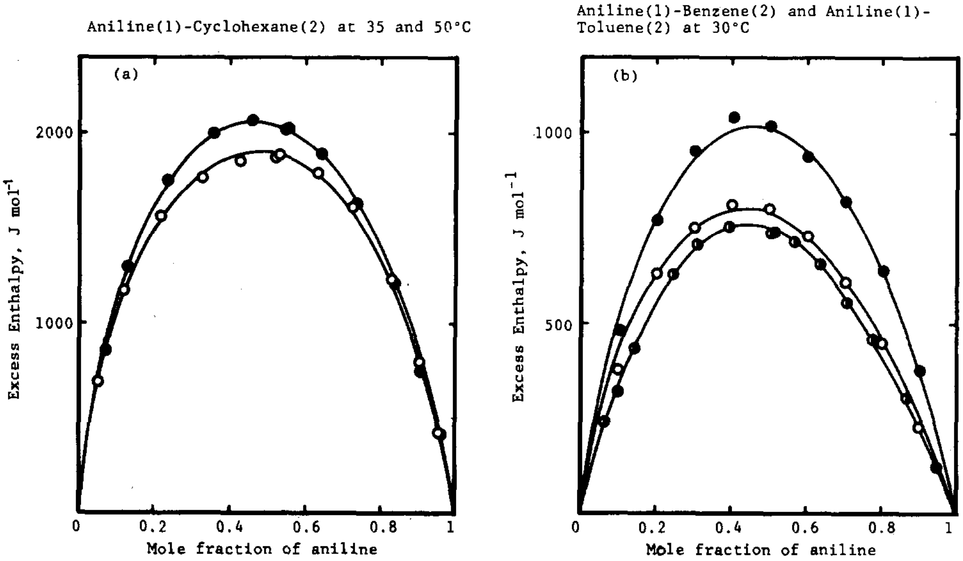

Fig. 4. Excess molar enthalpies for (a) aniline–cyclohexane at 35 and 50°C and (b) aniline–benzene and aniline–toluene at 30°C. Experimental: (a) aniline–cyclohexane at 35 (○) and 50°C (●) [15]; (b) aniline–benzene (○) [25], (◑) [26] and aniline–toluene (●) [25]. Calculated (———), $K_A = 15$ at 50°C and $h_A = -15.4$ kJ mol^{-1} were used.

equilibria for mixtures containing aniline and hydrocarbons with good accuracy.

LIST OF SYMBOLS

A, B, C,	aniline, aromatic hydrocarbon, and saturated hydrocarbon
a_{IJ}	binary interaction parameter

h_{A}	molar enthalpy of hydrogen bond formation
h_{AB}	molar enthalpy of formation of chemical species $\mathrm{A}_i\mathrm{B}$
h^{E}	excess molar enthalpy
K_{A}	association equilibrium constant
K_{AB}	solvation equilibrium constant of chemical species $\mathrm{A}_i\mathrm{B}$
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
S	objective function defined by eqn. (18)
T	absolute temperature
V	true molar volume of mixture given by eqn. (13)
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	lattice coordination number (equal to 10)

Greek letters

γ_I	activity coefficient of component I
θ_I	area 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
τ_{JI}	$\exp(-a_{JI}/T)$
Φ_I	segment fraction of component I
Φ_{A_1}	segment fraction of aniline monomer
Φ_{B_1}	segment fraction of monomeric aromatic hydrocarbon
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	aniline, aromatic hydrocarbon, and saturated hydrocarbon
A_1, A_i, B_1	aniline monomer and i-mer, and monomeric aromatic hydrocarbon
$\mathrm{A}_i\mathrm{B}$	complex containing i molecules of aniline and one molecule of aromatic hydrocarbon
AB	binary complex containing aniline and aromatic hydrocarbon
i	i-mer or number of data points
I, J, K	components I, J, and K

Superscripts

s	saturated
0	pure aniline
L	liquid

REFERENCES

1 I. Nagata and Y. Kawamura, Z. Phys. Chem., Neue Folge, 107 (1977) 141.
2 I. Nagata and Y. Kawamura, Chem. Eng. Sci., 34 (1979) 601.
3 I. Nagata and Y. Kawamura, Thermochim. Acta, 34 (1979) 43.
4 I. Nagata and Y. Ogasawara, Thermochim. Acta, 52 (1982) 155.
5 I. Nagata, Fluid Phase Equilibria, 19 (1985) 153.
6 V. Brandani and F. Evangelista, Fluid Phase Equilibria, 17 (1984) 281.
7 I. Nagata, Thermochim. Acta, 89 (1985) 39.
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. Gmehling and U. Onken, Vapor-Liquid Equilibrium Data Collection, Vol. I, Part 1, DECHEMA, Frankfurt am Main, 1977, p. 497.
11 J.A. Riddick and W.B. Bunger, Organic Solvents, 3rd edn., Wiley-Interscience, New York, 1970, pp. 77, 78, 85, 86, 107, 109.
12 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.
13 J.H. Vera, S.G. Sayegh and G.A. Ratcliff, Fluid Phase Equilibria, 1 (1977) 113.
14 V. Brandani, Fluid Phase Equilibria, 12 (1983) 87.
15 G.L. Nicolaides and C.A. Eckert, J. Chem. Eng. Data, 23 (1978) 152.
16 I. Velasco, S. Otín and C. Gutiérrez-Losa, J. Chim. Phys., 76 (1979) 381.
17 J. Gmehling, U. Onken and W. Arlt, Vapor-Liquid Equilibrium Data Collection, Vol. I, Part 7, DECHEMA, Frankfurt am Main, 1980, pp. 255, 259, 427-430.
18 J. Gmehling, U. Onken and W. Arlt, Vapor-Liquid Equilibrium Data Collection, Vol. I, Part 6a, DECHEMA, Frankfurt am Main, 1980, pp. 232, 237, 251, 279, 542, 639.
19 J. Gmehling, U. Onken and W. Arlt, Vapor-Liquid Equilibrium Data Collection, Vol. I, Part 6b, DECHEMA, Frankfurt am Main, 1980, pp. 15-17, 39-41, 136, 170, 464-466.
20 J. Gmehling, U. Onken and B. Kolbe, Vapor-Liquid Equilibrium Data Collection, Vol. I, Part 6c, DECHEMA, Frankfurt am Main, 1983, p. 269.
21 E. Angelescu and R. Giusca, Z. Phys. Chem., Abt. A, 191 (1942) 145.
22 T.G. Hunter and T. Brown, Ind. Eng. Chem., 39 (1947) 1343.
23 J.M. Sørensen and W. Arlt, Liquid-Liquid Equilibrium Data Collection, Vol. V, Part 3, DECHEMA, Frankfurt am Main, 1980, pp. 264, 265, 303, 304, 317.
24 G. Maffiolo and J. Vidal, Bull. Soc. Chim. Fr., (1971) 2810.
25 J.J. Christensen, R.W. Hanks and R.M. Izatt, Handbook of Heats of Mixing, Wiley-Interscience, New York, 1982, pp. 99, 1349.
26 I. Velasco, S. Otín and C. Gutiérrez-Losa, Int. Data Ser., Ser. A, (1979) 8.