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Ternary liquid–liquid equilibria for [(aniline + saturated hydrocarbon) + methanol or ethanol]

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Abstract

Tie-line data have been measured for the ternary systems [(aniline + methanol) + cyclohexane or *n*-hexane or *n*-heptane] and [(aniline + ethanol) + cyclohexane or *n*-hexane or *n*-heptane] at 25 °C. All the tie-line data were well correlated with the extended UNIQUAC model having binary and ternary parameters.

INTRODUCTION

Ternary liquid–liquid equilibrium data have not been reported for mixtures containing aniline, an aliphatic alcohol, and one saturated hydrocarbon [1,2]. This paper presents experimental tie-line data at 25 °C for six ternary systems: aniline + methanol + cyclohexane, aniline + methanol + *n*-hexane, aniline + methanol + *n*-heptane, aniline + ethanol + cyclohexane, aniline + ethanol + *n*-hexane, and aniline + ethanol + *n*-heptane. The experimental results are correlated using the extended UNIQUAC model with binary and ternary parameters [3]. Vapour–liquid equilibrium data for five binary systems constituting the ternary systems studied here were available from the literature. Those for aniline + methanol at 20 °C [4]; for aniline + ethanol at 40 °C [5]; for ethanol + cyclohexane at 20 °C [6]; for ethanol + *n*-hexane at 25 °C [7]; for ethanol + *n*-heptane at 30 °C [8] Mutual solubility data for methanol + saturated hydrocarbon at 25 °C were taken from previous papers. Those for methanol + cyclohexane [9]; for methanol + *n*-hexane or *n*-heptane [10]. Mutual solubilities for aniline + cyclohexane or *n*-hexane or *n*-heptane have been measured in this work. All these phase equilibrium data are used to obtain the binary parameters of the extended UNIQUAC model [11].

EXPERIMENTAL

Chemicals

Aniline and cyclohexane (Wako Pure Chemical Industries Ltd., guaranteed reagent grade), *n*-hexane (Wako Pure Chemical Industries Ltd., spec-

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tro-grade), and *n*-heptane (Kanto Chemical Co. Inc., spectro-grade) were used directly as received. C.P. methanol and ethanol were fractionally distilled in glass columns packed with McMahon packing after drying over calcium oxide. Densities of the chemicals used, measured with an Anton Paar densimeter (DMA40) at 25 ° C, agreed well with literature values [12].

Tie-line measurements

Each ternary biphasic mixture in a glass equilibrium cell was vigorously agitated with a magnetic stirrer in a thermostated water bath for 2 h at 25 ° C and left to settle at equilibrium for 2 h. Samples of each of the two equilibrated liquid phases were withdrawn by a Hamilton syringe and analyzed using a Shimadzu gas chromatograph (GC-8A) connected with a Shimadzu Chromatopac (C-R3A). The error of measured mole fractions was at most 0.002.

RESULTS AND DATA ANALYSIS

Tables 1 and 2 give the experimental tie-line results for the six systems. The extended UNIQUAC approach [3] is used to correlate ternary liquid–liquid equilibria using binary plus additional ternary parameters, and provides the excess Gibbs free energy for a ternary mixture by

$$\frac{g^{E}}{RT}=\sum_{i}^{3}x_i\ln\frac{\Phi_i}{x_i}-\frac{Z}{2}\sum_{i}^{3}q_ix_i\ln\frac{\Phi_i}{\theta_i}-q_1'x_1\ln(\theta_1\tau_{11}+\theta_2\tau_{21}+\theta_3\tau_{31}+\theta_2\theta_3\tau_{231})$$
$$-q_2'x_2\ln(\theta_1\tau_{12}+\theta_2\tau_{22}+\theta_3\tau_{32}+\theta_1\theta_3\tau_{132})$$
$$-q_3'x_3\ln(\theta_1\tau_{13}+\theta_2\tau_{23}+\theta_3\tau_{33}+\theta_1\theta_2\tau_{123})\qquad(1)$$

where Z is the coordination number set as 10, Φ is the segment fraction, θ is the surface fraction, τ_{ij} are binary parameters, and τ_{ijk} are ternary parameters.

$$\Phi_i=x_ir_i/\sum_j x_jr_j\qquad(2)$$

$$\theta_i=x_iq_i/\sum_j x_jq_j\qquad(3)$$

$$\tau_{ij}=\exp(-a_{ij}/T)\qquad(4)$$

Here, r, q and q' are pure-component structural parameters. The ternary terms vanish whenever the ternary mixture degenerates to a binary one.

TABLE 1

Tie-line data for aniline + methanol + saturated hydrocarbon at 25 ° C

Phase I			Phase II		
x_1	x_2	x_3	x_1	x_2	x_3
Aniline(1) + methanol(2) + cyclohexane(3)					
0.7147	0	0.2853	0.1905	0	0.8095
0.6310	0.0777	0.2913	0.1793	0.0192	0.8015
0.5261	0.1772	0.2967	0.1687	0.0497	0.7816
0.4861	0.2133	0.3006	0.1664	0.0641	0.7695
0.4024	0.2854	0.3122	0.1546	0.0966	0.7488
0.3296	0.3468	0.3236	0.1443	0.1336	0.7221
0.3061	0.3703	0.3236	0.1363	0.1436	0.7201
0.2651	0.4197	0.3152	0.1160	0.1602	0.7238
0.2087	0.5035	0.2878	0.0815	0.1604	0.7581
0.1419	0.6095	0.2486	0.0470	0.1601	0.7929
0.0622	0.7352	0.2026	0.0187	0.1444	0.8369
Aniline(1) + methanol(2) + *n*-hexane(3)					
0.9250	0	0.0750	0.0731	0	0.9269
0.8465	0.0814	0.0721	0.0688	0.0048	0.9264
0.7157	0.2087	0.0756	0.0640	0.0117	0.9243
0.6198	0.3010	0.0792	0.0589	0.0204	0.9207
0.5433	0.3737	0.0830	0.0550	0.0286	0.9164
0.4863	0.4279	0.0858	0.0538	0.0378	0.9084
0.3650	0.5379	0.0971	0.0490	0.0578	0.8932
0.3363	0.5634	0.1003	0.0469	0.0610	0.8921
0.2546	0.6324	0.1130	0.0400	0.0833	0.8767
0.1558	0.7098	0.1344	0.0298	0.1266	0.8436
0.0785	0.7603	0.1612	0.0218	0.1795	0.7987
Aniline(1) + methanol(2) + *n*-heptane(3)					
0.9445	0	0.0555	0.0756	0	0.9244
0.8568	0.0879	0.0553	0.0712	0.0056	0.9232
0.7502	0.1927	0.0571	0.0663	0.0120	0.9217
0.6277	0.3124	0.0599	0.0645	0.0231	0.9124
0.5064	0.4306	0.0630	0.0559	0.0349	0.9092
0.4020	0.5301	0.0679	0.0511	0.0488	0.9001
0.2617	0.6653	0.0730	0.0395	0.0763	0.8842
0.1742	0.7397	0.0861	0.0315	0.0899	0.8786
0.0773	0.8238	0.0989	0.0170	0.1194	0.8636
0.0397	0.8585	0.1018	0.0108	0.1350	0.8542

The activity coefficient of component 1 is expressed by

$$\ln \gamma_1 = \ln\frac{\Phi_1}{x_1} + 1 - \frac{\Phi_1}{x_1} - \frac{Z}{2} q_1 \left(\ln\frac{\Phi_1}{\theta_1} + 1 - \frac{\Phi_1}{\theta_1} \right) - q_1' \ln\left(\sum_j^3 \theta_j \tau_{j1} + \theta_2 \theta_3 \tau_{231} \right)$$
$$+ q_1 \sum_j^3 (q_j'/q_j)\theta_j - \frac{q_1' \theta_1 (\tau_{11} - \theta_2 \theta_3 \tau_{231})}{\sum_j^3 \theta_j \tau_{j1} + \theta_2 \theta_3 \tau_{231}}$$

TABLE 2

Tie-line data for aniline + ethanol + saturated hydrocarbon at 25 °C

Phase I			Phase II		
x_1	x_2	x_3	x_1	x_2	x_3
Aniline(1) + ethanol(2) + cyclohexane(3)					
0.7147	0	0.2853	0.1905	0	0.8095
0.6696	0.0172	0.3132	0.2197	0.0060	0.7743
0.6318	0.0271	0.3411	0.2304	0.0110	0.7586
0.6037	0.0329	0.3634	0.2506	0.0147	0.7347
0.5878	0.0369	0.3753	0.2662	0.0178	0.7160
0.5657	0.0384	0.3959	0.2783	0.0198	0.7019
0.5409	0.0400	0.4191	0.2903	0.0229	0.6868
0.5207	0.0401	0.4392	0.3058	0.0263	0.6679
Aniline(1) + ethanol(2) + *n*-hexane(3)					
0.9250	0	0.0750	0.0731	0	0.9269
0.8218	0.0846	0.0936	0.0694	0.0101	0.9205
0.7464	0.1483	0.1053	0.0817	0.0221	0.8962
0.6181	0.2420	0.1399	0.0970	0.0574	0.8456
0.5653	0.2734	0.1613	0.1110	0.0800	0.8090
0.5143	0.2971	0.1886	0.1268	0.1046	0.7686
0.4718	0.3131	0.2151	0.1494	0.1350	0.7156
0.4103	0.3181	0.2716	0.1878	0.1805	0.6317
0.3746	0.3095	0.3159	0.2093	0.2047	0.5860
Aniline(1) + ethanol(2) + *n*-heptane(3)					
0.9445	0	0.0555	0.0756	0	0.9244
0.8575	0.0794	0.0631	0.0833	0.0093	0.9074
0.7771	0.1472	0.0757	0.0833	0.0214	0.8953
0.7131	0.1992	0.0877	0.0916	0.0364	0.8720
0.6517	0.2462	0.1021	0.1021	0.0553	0.8426
0.6025	0.2804	0.1171	0.1186	0.0762	0.8052
0.5497	0.3137	0.1370	0.1264	0.1012	0.7724
0.5063	0.3362	0.1575	0.1397	0.1243	0.7360
0.4657	0.3518	0.1825	0.1563	0.1545	0.6892
0.4193	0.3610	0.2197	0.1816	0.1928	0.6256
0.3484	0.3437	0.3079	0.2362	0.2583	0.5055

$$-\frac{q_1(q_2'/q_2)\theta_2\left[\tau_{12}+(1-\theta_1)\theta_3\tau_{132}\right]}{\sum_j^3\theta_j\tau_{j2}+\theta_1\theta_3\tau_{132}}-\frac{q_1(q_3'/q_3)\theta_3\left[\tau_{13}+(1-\theta_1)\theta_2\tau_{123}\right]}{\sum_j^3\theta_j\tau_{j3}+\theta_1\theta_2\tau_{123}} \qquad (5)$$

where $\ln\gamma_2$ is obtained by the cyclic advancement of the subscripts $1\to 2$, $2\to 3$ and $3\to 1$ and by setting $\tau_{312}=\tau_{132}$ and $\tau_{213}=\tau_{123}$; $\ln\gamma_3$ is analogously derived by putting $\tau_{321}=\tau_{231}$.

Vapour–liquid equilibrium data for binary mixtures constituting the ternary mixtures studied were correlated with the extended UNIQUAC model using a computer program as described by Prausnitz et al. [13] and eqns. (6) and (7)

$$P\phi_i y_i = \gamma_i x_i P_i^s \phi_i^s \exp\left[v_i^L (P - P_i^s)/RT\right] \tag{6}$$

$$\ln \phi_i = \left(2\sum_j y_i B_{ij} - \sum_{ij}\sum y_i y_j B_{ij}\right)\frac{P}{RT} \tag{7}$$

where P is the total pressure, ϕ the fugacity coefficient, y the vapor mole fraction, P^s the pure-component vapour pressure, ϕ^s the pure-component fugacity coefficient, v^L the molar pure-liquid volume estimated from a modified Rackett equation [14], R the gas constant, and B the pure and cross second virial coefficients calculated from the Hayden–O'Connell method [15].

Mutual solubility data were used to obtain binary parameters, which satisfy eqn. (8) for any component i

$$(x_i\gamma_i)^\alpha = (x_i\gamma_i)^\beta \tag{8}$$

where the superscripts α and β indicate conjugated liquid phases.

Table 3 shows the values of pure component structural parameters. Binary parameters and the root-mean-square deviations between experimental and the most probable calculated results are given in Table 4.

A set of ternary parameters for each system was sought using a program which minimizes the objective function given by

$$F = 100\left[\sum_k \min \sum_{ij}\sum \left(x_{ijk} - \hat{x}_{ijk}\right)^2/6M\right]^{0.5}$$

$$i = 1, 2, 3;\ j = \alpha, \beta;\ k = 1, \ldots M. \tag{9}$$

where min indicates minimum values, M the number of experimental points, and $\hat{x}$ the calculated mole fraction. Figure 1 shows the experimental and calculated results for the six systems. The predictions based on only

TABLE 3

Pure component structural parameters

Component	r	q	q'
Aniline	3.72	2.82	$q^{0.2}$
Methanol	1.43	1.43	1.00
Ethanol	2.11	1.97	0.92
Cyclohexane	3.97	3.01	$q^{0.2}$
n-Hexane	4.50	3.86	$q^{0.2}$
n-Heptane	5.17	4.40	$q^{0.2}$

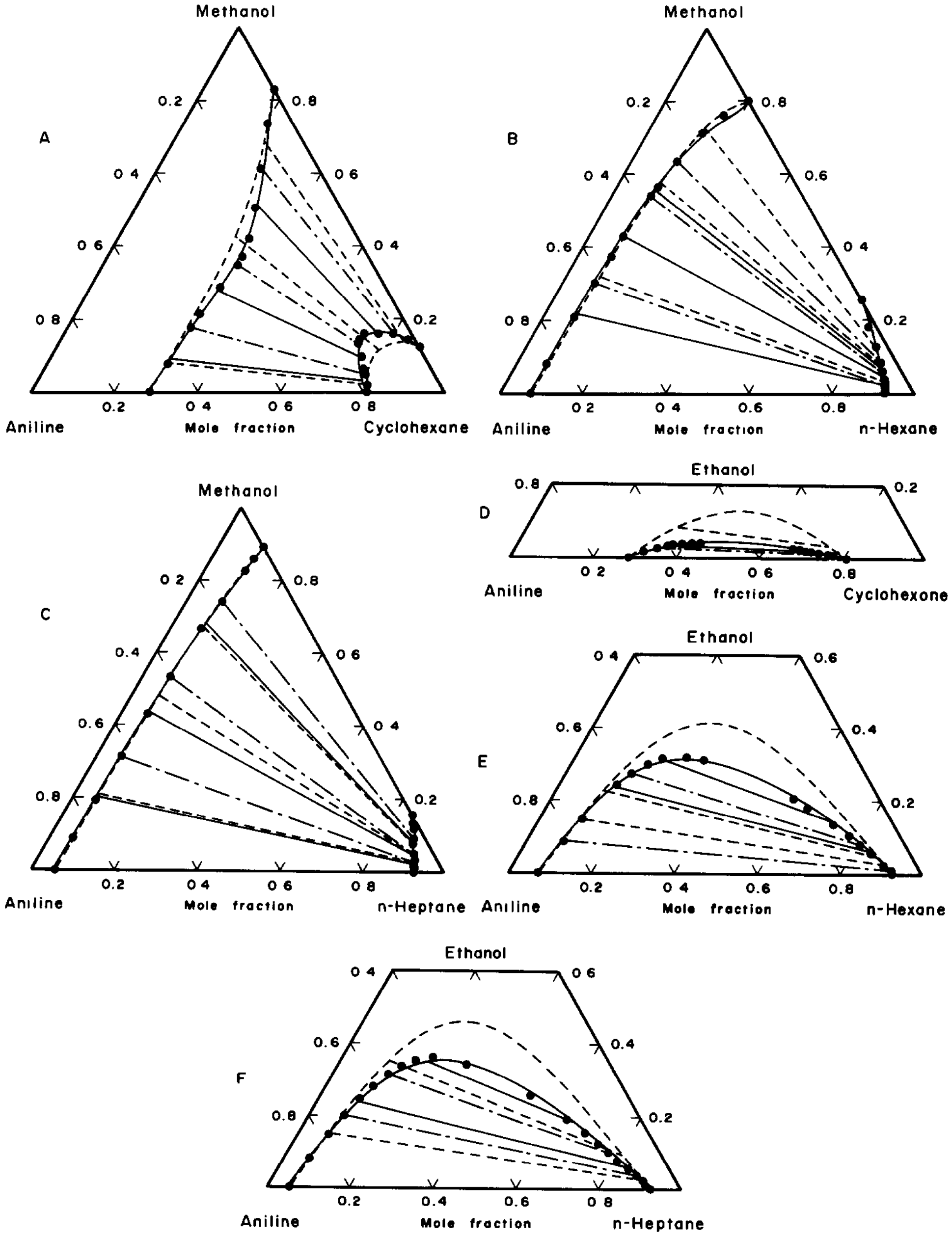

Fig. 1. Experimental tie-lines and calculated binodal curves at 25 ° C: A, aniline + methanol + cyclohexane; B, aniline + methanol + *n*-hexane; C, aniline + methanol + *n*-heptane; D, aniline + ethanol + cyclohexane; E, aniline + ethanol + *n*-hexane; F, aniline + ethanol + *n*-heptane. (●- - - - -●) Experimental tie-line. Calculated: (- - - - - -) with binary parameters alone; (———) binary and ternary parameters.

TABLE 4

Binary parameters and root-mean-square deviations

System	Temp. (°C)	No. of data points	Root-mean-square deviations				Parameters (K)	
			δP (Torr)	δT (K)	δx ($\times 10^3$)	δy ($\times 10^3$)	a_{12}	a_{21}
Aniline(1) + methanol(2)	20	13	0.15	0.00	0.0		307.93	−65.67
Aniline(1) + ethanol(2)	40	13	0.11	0.00	0.0		229.39	76.21
Ethanol(1) + cyclohexane(2)	20	7	0.29	0.00	0.0		182.81	1334.28
Ethanol(1) + *n*-hexane(2)	25	25	0.75	0.02	0.2		242.40	1261.74
Ethanol(1) + *n*-heptane(2)	30	31	0.53	0.00	0.2		250.19	1334.94
Aniline(1) + cyclohexane(2)	25	MS [a]					343.26	509.46
Aniline(1) + *n*-hexane(2)	25	MS					382.79	618.20
Aniline(1) + *n*-heptane(2)	25	MS					383.90	632.44
Methanol(1) + cyclohexane(2)	25	MS					280.74	1122.7
Methanol(1) + *n*-hexane(2)	25	MS					376.05	1230.9
Methanol(1) + *n*-heptane(2)	25	MS					409.70	1357.8

[a] MS = mutual solubilities.

TABLE 5

Ternary parameters of the extended UNIQUAC model and root-mean-square deviation at 25 °C

System	τ_{231}	τ_{132}	τ_{123}	F (mol%)
Aniline(1) + methanol(2) + cyclohexane(3)	0.0989	−0.0017	−0.1492	0.560
Aniline(1) + methanol(2) + *n*-hexane(3)	0.4083	−0.1271	−0.0080	0.535
Aniline(1) + methanol(2) + *n*-heptane(3)	0.1233	−0.0344	−0.0192	0.254
Aniline(1) + ethanol(2) + cyclohexane(3)	0.2001	0.4652	−0.2092	0.279
Aniline(1) + ethanol(2) + *n*-hexane(3)	0.6865	−0.1965	−0.2050	0.379
Aniline(1) + ethanol(2) + *n*-heptane(3)	0.4035	−0.0667	−0.1149	0.382

binary parameters agree well with the experimental values for the (aniline + methanol) + *n*-hexane or *n*-heptane systems. Table 5 gives the results of fitting the model to the ternary tie-line data.

LIST OF SYMBOLS

a_{ij}	binary interaction parameter related to τ_{ij}
B_{ij}	second virial coefficient for i–j pair
F	objective function as defined by eqn. (9)
g^E	excess molar Gibbs energy
P	total pressure
P_i^s	vapor pressure of pure component i
q_i	molecular area parameter of pure component i

q_i'	molecular interaction area parameter of pure component i
R	universal gas constant
r_i	molecular volume parameter of pure component i
T	absolute temperature
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, here set as 10

Greek letters

α, β	conjugated liquid phases
γ_i	activity coefficient of component i
θ_i	surface fraction of component i
τ_{ij}	binary parameter as defined by $\exp(-a_{ij}/T)$
τ_{ijk}	ternary parameter
Φ_i	segment fraction of component i
ϕ_i	vapor-phase fugacity coefficient of component i at T and P
ϕ_i^s	vapor-phase fugacity coefficient of pure component i at T and P_i^s

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