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Liquid–liquid equilibria for aniline + benzene + *n*-heptane and methanol + aniline + *n*-heptane + benzene at 25°C

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Abstract

Experimental tie-line data have been measured for aniline + benzene + *n*-heptane and methanol + aniline + *n*-heptane + benzene at 25°C. The experimental results have been satisfactorily correlated with the modified Wilson equation including binary, ternary and quaternary parameters obtained in fitting the equation to published and present experimental data.

LIST OF SYMBOLS

a_{ij}	binary energy parameter for i–j pair
F	objective function as defined by eqn. (5)
R	universal gas constant
T	absolute temperature
V_i	liquid molar volume of pure component i
x_i	liquid mole fraction of component i

Greek letters

α_{ij}	binary parameter in modified Wilson model for i–j pair
γ_i	activity coefficient of component i
δ	deviations of experimental values from calculated results
Λ_{ij}	Wilson-like parameter for i–j pair
Λ_{jki}, Λ_{jkli}	modified Wilson ternary and quaternary parameters

Subscripts

calc	calculated
exptl	experimental
i, j, k, l	components

INTRODUCTION

As part of continuing studies on the measurements of liquid–liquid equilibria (LLE) of ternary and quaternary systems, this paper reports tie-lines for aniline + benzene + *n*-heptane and methanol + aniline + *n*-heptane + benzene at 25°C. The experimental results have been well correlated with those calculated from the modified Wilson models having binary, ternary, and quaternary parameters [1, 2]. Binary energy parameters are available for the following systems: methanol + aniline at 20°C [3]; methanol + benzene at 35°C [4]; aniline + benzene at 25°C [5]; *n*-heptane + benzene at 45°C [6]; methanol + *n*-heptane at 25°C [1]. Ternary tie-lines at 25°C have been reported for the methanol + aniline + *n*-heptane [7] and methanol + benzene + *n*-heptane systems [8].

EXPERIMENTAL

Aniline (Kanto Chemical Co. Inc., special grade) and *n*-heptane (Kanto Chemical Co. Inc., spectro-analysis grade) were used without further purification. Methanol (Wako Pure Chemical Industries Ltd., first grade) was subjected to fractional distillation after shaking with calcium oxide. Benzene (Kanto Chemical Co. Inc., first grade) was purified by repeated fractional recrystallization. The densities of these chemicals, measured with an Anton Paar densimeter (DMA40) at 25°C, were in excellent agreement with published values [9] as shown in Table 1.

Tie-line measurements were carried out as described previously [10]. The compositions of two liquids in equilibrium were determined by combining use of a Shimadzu gas chromatograph (GC-8C) and a Shimadzu Chromatopac (C-R3A). The experimental error of measured mole fractions was at most 0.002.

Tables 2 and 3 give the experimental tie-line values of the ternary aniline + benzene + *n*-heptane and quaternary methanol + aniline + *n*-heptane + benzene systems at 25°C.

TABLE 1

Densities of pure components at 25°C

Component	Density/g mol^{-1}	
	Obs.	Lit. [9]
Aniline	1.01746	1.01750
Methanol	0.78668	0.78637
Benzene	0.87371	0.87360
n-Heptane	0.67953	0.67946

TABLE 2

Experimental tie-line values for aniline(1) + benzene(2) + n-heptane(3) at 25°C

Phase I			Phase II		
x_1	x_2	x_3	x_1	x_2	x_3
0.1116	0.0628	0.8256	0.8820	0.0493	0.0687
0.1473	0.1154	0.7373	0.8110	0.1066	0.0824
0.1812	0.1750	0.6438	0.7387	0.1484	0.1129
0.2172	0.2014	0.5814	0.6878	0.1769	0.1353
0.3161	0.2451	0.4388	0.5648	0.2265	0.2087

TABLE 3

Experimental tie-line values for methanol(1) + aniline(2) + n-heptane(3) + benzene(4) obtained by mixing pure n-heptane and benzene with $\{x'_1\text{methanol} + (1 - x'_1)\text{aniline}\}$ at 25°C

Phase I				Phase II			
x_1	x_2	x_3	x_4	x_1	x_2	x_3	x_4
$x'_1 = 0.75$							
0.1114	0.0568	0.7807	0.0511	0.6678	0.2095	0.0975	0.0252
0.1513	0.0685	0.6876	0.0926	0.6260	0.2062	0.1173	0.0505
0.1900	0.0780	0.6134	0.1186	0.6033	0.1873	0.1393	0.0698
0.2221	0.0935	0.5520	0.1324	0.5671	0.1869	0.1606	0.0854
0.2492	0.0957	0.5153	0.1398	0.5540	0.1745	0.1762	0.0953
$x'_1 = 0.50$							
0.0602	0.0834	0.8017	0.0547	0.4405	0.4567	0.0727	0.0301
0.0838	0.1150	0.6483	0.1229	0.4029	0.4154	0.1016	0.0801
0.0997	0.1383	0.6081	0.1539	0.3755	0.3918	0.1283	0.1044
0.1293	0.1645	0.5342	0.1720	0.3535	0.3670	0.1526	0.1267
0.1495	0.1750	0.4953	0.1802	0.3319	0.3439	0.1842	0.1400
$x'_1 = 0.25$							
0.0155	0.0839	0.8497	0.0507	0.2074	0.6970	0.0627	0.0329
0.0262	0.1224	0.7265	0.1249	0.1929	0.6338	0.0853	0.0880
0.0407	0.1720	0.6129	0.1744	0.1776	0.5788	0.1114	0.1322
0.0516	0.2213	0.5279	0.1992	0.1670	0.5389	0.1328	0.1613
0.0654	0.2457	0.4730	0.2159	0.1388	0.4786	0.1960	0.1866

ANALYSIS OF EXPERIMENTAL RESULTS

The experimental tie-line results have been correlated using the modified Wilson equation having binary, ternary and quaternary parameters [2]. The modified Wilson equation gives the activity coefficient of component 1 in a quaternary mixture

$$\begin{aligned}
\ln \gamma_1 = &- \ln\left[\left(\sum_j^4 \alpha_{1j}\Lambda_{1j}x_j + \Lambda_{231}x_2x_3 + \Lambda_{241}x_2x_4 + \Lambda_{341}x_3x_4 + \Lambda_{2341}x_2x_3x_4\right)\Big/ \sum_j^4 \alpha_{1j}x_j\right] \\
&- x_1\left(\frac{1 - \Lambda_{231}x_2x_3 - \Lambda_{241}x_2x_4 - \Lambda_{341}x_3x_4 - 2\Lambda_{2341}x_2x_3x_4}{\sum_j^4 \alpha_{1,j}\Lambda_{1j}x_j + \Lambda_{231}x_2x_3 + \Lambda_{241}x_2x_4 + \Lambda_{341}x_3x_4 + \Lambda_{2341}x_2x_3x_4} - \frac{\alpha_{11}}{\sum_j^4 \alpha_{1,j}x_j}\right) \\
&- x_2\left[\frac{\alpha_{21}\Lambda_{21} + \Lambda_{132}x_3(1-x_1) + \Lambda_{142}x_4(1-x_1) - \Lambda_{342}x_3x_4 + \Lambda_{1342}x_3x_4(1-2x_1)}{\sum_j^4 \alpha_{2j}\Lambda_{2j}x_j + \Lambda_{132}x_1x_3 + \Lambda_{142}x_1x_4 + \Lambda_{342}x_3x_4 + \Lambda_{1342}x_1x_3x_4} - \frac{\alpha_{21}}{\sum_j^4 \alpha_{2j}x_j}\right] \\
&- x_3\left[\frac{\alpha_{31}\Lambda_{31} + \Lambda_{123}x_2(1-x_1) + \Lambda_{143}x_4(1-x_1) - \Lambda_{243}x_2x_4 + \Lambda_{1243}x_2x_4(1-2x_1)}{\sum_j^4 \alpha_{3j}\Lambda_{3j}x_j + \Lambda_{123}x_1x_2 + \Lambda_{143}x_1x_4 + \Lambda_{243}x_2x_4 + \Lambda_{1243}x_1x_2x_4} - \frac{\alpha_{31}}{\sum_j^4 \alpha_{3j}x_j}\right] \\
&- x_4\left[\frac{\alpha_{41}\Lambda_{41} + \Lambda_{124}x_2(1-x_1) + \Lambda_{134}x_3(1-x_1) - \Lambda_{234}x_2x_3 + \Lambda_{1234}x_2x_3(1-2x_1)}{\sum_j^4 \alpha_{4j}\Lambda_{4j}x_j + \Lambda_{124}x_1x_2 + \Lambda_{134}x_1x_3 + \Lambda_{234}x_2x_3 + \Lambda_{1234}x_1x_2x_3} - \frac{\alpha_{41}}{\sum_j^4 \alpha_{4j}x_j}\right]
\end{aligned} \tag{1}$$

where α_{ij} and Λ_{ij} are the binary parameters. The values of α_{ij} are unity for completely miscible mixtures and are empirically assigned values, which are slightly larger than unity, for partially miscible mixtures. Λ_{ij} is defined by

$$\Lambda_{ij} = (V_j/V_i)\exp(-a_{ij}/T) \tag{2}$$

$\Lambda_{jki(i \neq j \neq k)}$ and $\Lambda_{jkli(i \neq j \neq k \neq l)}$ are also the ternary and quaternary parameters to be determined from the experimental tie-line results.

The expressions of $\ln \gamma_2$, $\ln \gamma_3$ and $\ln \gamma_4$ are obtained successively by cyclic advancement of the subscripts in eqn. (1) by changing 1 to 2, 2 to 3, 3 to 4, and 4 to 1.

Table 4 shows the binary Wilson-like parameters. The values of the energy parmeters a_{ij} for partially miscible mixtures were obtained by solving

TABLE 4

Binary Wilson-like parameters

System (1 + 2)	Temp./°C	Parameters			
		a_{12}/K	a_{21}/K	α_{12}	α_{21}
Aniline + benzene	25	269.28	9.08	1.0	1.0
Aniline + *n*-heptane	25	979.99	797.62	1.1	1.1
n-Heptane- + benzene	45	216.55	55.20	1.0	1.0
Methanol + aniline	20	338.35	− 52.29	1.0	1.0
Methanol + benzene	35	889.85	92.17	1.0	1.0
Methanol + *n*-heptane	25	1158.4	552.61	1.0	1.1

the thermodynamic equation (eqn. (3)) for each component at two equilibrated liquid phases I and II and satisfying simultaneously eqn. (4).

$$(x_i\gamma_i)^{\mathrm{I}} = (x_i\gamma_i)^{\mathrm{II}} \tag{3}$$

$$\sum_i x_i^{\mathrm{I}} = 1 \quad \text{and} \quad \sum_i x_i^{\mathrm{II}} = 1 \tag{4}$$

The ternary parameters of the modified Wilson equation were obtained by minimizing the following objective function with a simplex method [11].

$$F = \left[\sum_i \sum_j \sum_k (x_{ijk,\,\mathrm{calc}} - x_{ijk,\,\mathrm{exptl}})^2/6M\right]^{0.5} \tag{5}$$

where $i = 1, 2, 3$ (components), $j = 1, 2$ (phases) and $k = 1, 2, \ldots M$ (tie-lines). Table 5 gives the ternary calculated results. Figure 1 shows the experimental tie-lines and the calculated results for the three ternary systems. Table 6 gives also the quaternary calculated results and Table 7 shows

TABLE 5

The results of fitting the modified Wilson equation to ternary tie-lines at 25°C

System (1 + 2 + 3)	Type	Number of data points	Ternary parameters		F/mol%
Aniline + benzene + *n*-heptane	I	5	Λ_{231}	0.0653	0.36
			Λ_{132}	−0.0237	
			Λ_{123}	−0.1809	
Methanol + aniline + *n*-heptane	II	9	Λ_{231}	0.0728	0.59
			Λ_{132}	−0.3346	
			Λ_{123}	0.0658	
Methanol + benzene + *n*-heptane	I	8	Λ_{231}	0.1746	0.44
			Λ_{132}	0.1967	
			Λ_{123}	0.0823	

TABLE 6

The results of fitting the modified Wilson equation to the quaternary tie-line results at 25°C

System (1 + 2 + 3 + 4)	No. of data points	Quaternary parameters		Deviations/mol%	
				AAM [a]	RMS [b]
Methanol + aniline + *n*-heptane + benzene	15	Λ_{2341}	−0.0430	0.87	0.98
		Λ_{1342}	0.0923	1.86 [c]	2.27 [c]
		Λ_{1234}	−1.5948		
		Λ_{1234}	3.6738		

[a] AAM, absolute arithmetic mean deviation. [b] RMS, root-mean-squared deviation. [c] Predicted value based on the binary and ternary parameters.

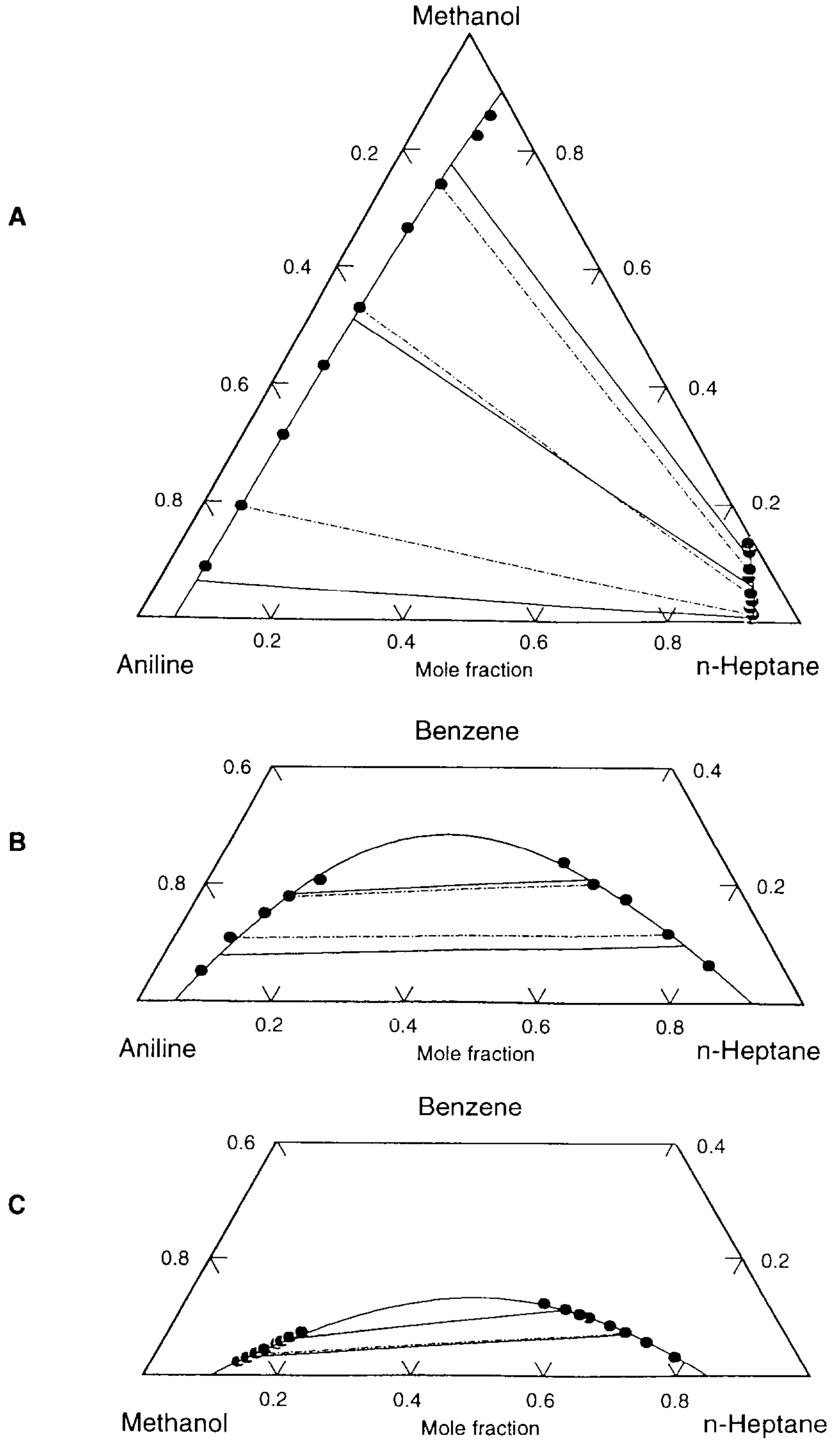

Fig. 1. Calculated liquid–liquid equilibria for three ternary systems at 25°C: ●– · – · –●, experimental tie line; ——, calculated from the modified Wilson equation with binary and ternary parameters. A, Aniline + methanol + *n*-heptane [7]; B, aniline + benzene + *n*-heptane, this work; C, methanol + benzene + *n*-heptane [8].

TABLE 7

Detailed calculated results for methanol(1) + aniline(2) + *n*-heptane(3) + benzene(4) at 25°C

	Phase I		Phase II	
	AAM [a]	RMS [b]	AAM	RMS
δx_1	0.0117	0.0131	0.0122	0.0127
δx_2	0.0114	0.0129	0.0125	0.0137
δx_3	0.0115	0.0127	0.0056	0.0077
δx_4	0.0026	0.0030	0.0024	0.0027

[a] AAM, absolute arithmetic mean deviation between the experimental and calculated liquid mole fractions. [b] RMS, root-mean-squared deviation between the experimental and calculated liquid mole fractions.

the detailed deviations between the experimental and calculated liquid mole fractions.

We may conclude that the experimental tie-line results for the ternary and quaternary systems studied here have been well correlated with the modified Wilson equation having binary, ternary and quaternary parameters.

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