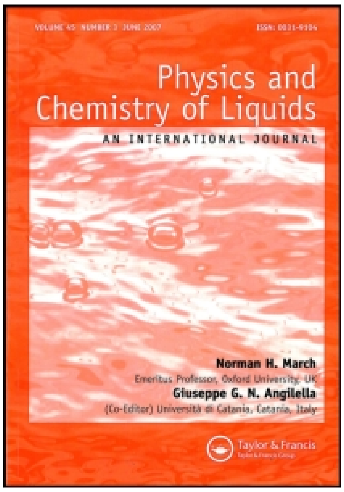

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Isobaric Vapour-Liquid Equilibrium Data for the Binary Systems of Anisole with Benzene and Chlorobenzene

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ISOBARIC VAPOUR-LIQUID EQUILIBRIUM DATA FOR THE BINARY SYSTEMS OF ANISOLE WITH BENZENE AND CHLOROBENZENE

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Isobaric VLE data were obtained for the binary systems of anisole with benzene and chlorobenzene over the entire composition range by an indirect method using a standard Swietoslawski-type ebulliometer at 3 different pressures. The experimental *t-x* data were correlated with Wilson & NRTL methods. Both these methods represent the data adequately.

KEY WORDS: Vapour-liquid equilibrium, *t-x* relationship, boiling point.

INTRODUCTION

The present investigation forms a part of the study on the vapour-liquid equilibrium properties of binary liquid mixtures containing anisole as the common component. Although the VLE data for the anisole-benzene system have already been reported in the literature, the work has either been reported in a not-easily-available journal[1] or has been carried out[2,3] under conditions different from the one presently being reported. Similarly, the anisole-chlorobenzene system has been studied at a different pressure and the information[4] is difficult to obtain.

Our studies on these systems have been carried out at three different pressures–200,500, and 710/713 mm Hg. This paper presents measurements on the temperature (t)–liquid composition(x) relationships.

EXPERIMENTAL SECTION

The VLE measurements were conducted in a Swietoslawski ebulliometer[5]. The ebulliometer was connected to a vacuum system and the pressures were measured by a mercury manometer with an accuracy of ± 1 mm Hg. The temperature was measured with a carefully calibrated mercury-in-glass thermometer, with an accuracy of 0.1°C.

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The boiling points of the systems anisole–benzene and anisole–chlorobenzene were determined over the entire composition range at three different pressures. Mixtures of different compositions were prepared gravimetrically and placed in the ebulliometer. The heating rate was adjusted to yield the desired condensate drop-rate of around 30 per minute, keeping in view the suggestion of Hala *et al*[5]. The boiling point was first determined at 200 mm Hg. The temperature was recorded after observing its constancy for about half an hour. Then the pressure was raised to 500 mm Hg and a higher pressure and the procedure repeated.

PURITY OF THE MATERIALS

Both anisole and chlorobenzene were obtained from Fluka and were of high purity (>99%, GC). Benzene (spectroscopic grade) was obtained from SD fine chemicals (India). No further purification of the chemicals was attempted. The purity of the chemicals was, however, checked by measuring the physical properties of these compounds. The comparison of measured physical properties with literature is shown in Table 1.

RESULTS AND DISCUSSION

The experimental *t-x* measurements at the three different pressures are presented in Tables 2–7. The experimental data are correlated with Wilson and NRTL equations.

Table 1 Comparison of physical properties of pure components with literature values.

Component	*Boiling point (500 mm)*	*Refractive Index (20 °C)*	*Reference*
Anisole	138.4	1.5175	this work
	138.7[a]	1.51791	6
		1.5170	7
		1.51700	8
		1.5179	9
Benzene	67.0	1.5010	this work
	67.1[a]	1.50108	6
		1.5011	7
		1.50112	8
		1.5011	9
Chlorobenzene	116.9	1.5250	this work
	116.9[a]	1.5248	6
		1.5248	7
		1.52481	8
		1.525	9

[a] Calculated using Antoine constants from *Lange's Handbook of Chemistry*, Dean, J. A. Ed., McGraw-Hill Book Co., New York, 1979.

Table 2 VLE data for anisole-benzene system at 200 mm Hg.

x_1, *mol. fr.*	t_{exp} °C	*Wilson eqn.*		*NRTLeqn.*	
		t_{cal} °C	$y_{1,cal}$	t_{cal} °C	$y_{1,cal}$
0.0859	44.1	44.3	0.0047	44.3	0.0048
0.1689	46.5	46.6	0.0106	46.6	0.0106
0.2193	48.3	48.1	0.0149	48.1	0.0149
0.2926	50.4	50.5	0.0226	50.5	0.0226
0.4117	55.6	55.0	0.0402	54.9	0.0401
0.4970	59.3	58.8	0.0588	58.7	0.0586
0.5615	62.6	62.1	0.0781	62.0	0.0779
0.6253	66.3	65.8	0.1042	65.7	0.1038
0.6874	70.1	70.1	0.1395	70.0	0.1388
0.7567	75.2	75.7	0.1976	75.6	0.1966
0.8157	80.5	81.5	0.2733	81.3	0.2717
0.8677	87.8	87.6	0.3744	87.5	0.3723
0.9348	97.2	97.5	0.5931	97.4	0.5907

Table 3 VLE data for anisole-benzene system at 500 mm Hg.

x_1, *mol. fr.*	t_{exp} °C	*Wilson eqn.*		*NRTLeqn.*	
		t_{cal} °C	$y_{1,cal}$	t_{cal} °C	$y_{1,cal}$
0.0859	69.6	69.6	0.0068	69.6	0.0069
0.1689	72.6	72.2	0.0152	72.2	0.0153
0.2193	74.7	74.0	0.0213	74.0	0.0214
0.2926	77.0	76.8	0.0321	76.7	0.0322
0.4117	81.8	81.9	0.0564	81.9	0.0563
0.4970	86.7	86.3	0.0815	86.2	0.0813
0.5615	90.1	90.0	0.1071	89.9	0.1067
0.6253	94.6	94.3	0.1407	94.1	0.1401
0.6874	98.5	99.0	0.1849	98.8	0.1839
0.7567	103.9	105.1	0.2546	104.9	0.2530
0.8157	109.3	111.2	0.3405	111.0	0.3383
0.8677	116.9	117.4	0.4481	117.3	0.4454
0.9348	126.3	127.1	0.6594	127.0	0.6567

i) Wilson equation[10]:

$$\ln \gamma_1 = -\ln(x_1 + \Lambda_{12} x_2) + x_2 \left[\frac{\Lambda_{12}}{x_1 + \Lambda_{12} x_2} - \frac{\Lambda_{21}}{x_2 + \Lambda_{21} x_1} \right]$$

$$\ln \gamma_2 = -\ln(x_2 + \Lambda_{21} x_1) + x_1 \left[\frac{\Lambda_{21}}{x_2 + \Lambda_{21} x_1} - \frac{\Lambda_{12}}{x_1 + \Lambda_{12} x_2} \right]$$

Table 4 VLE data for anisole-benzene system at 713 mm Hg.

x_1, *mol.fr.*	t_{exp} °*C*	*Wilson eqn.*		*NRTL eqn.*	
		t_{cal} °*C*	$y_{1,cal}$	t_{cal} °*C*	$y_{1,cal}$
0.0859	81.2	80.7	0.0078	80.7	0.0079
0.1689	84.3	83.5	0.0174	83.5	0.0175
0.2193	85.6	85.4	0.0243	85.4	0.0245
0.2926	88.1	88.3	0.0366	88.3	0.0367
0.4117	93.9	93.8	0.0639	93.7	0.0639
0.4970	99.2	98.4	0.0920	98.3	0.0918
0.5615	102.7	102.4	0.1203	102.2	0.1199
0.6253	107.2	106.8	0.1571	106.6	0.1563
0.6874	111.5	111.6	0.2048	111.4	0.2036
0.7567	117.3	117.9	0.2788	117.7	0.2769
0.8157	123.0	124.1	0.3679	123.9	0.3654
0.8677	130.8	130.5	0.4768	130.3	0.4739
0.9348	140.0	140.0	0.6833	139.9	0.6806

Table 5 VLE data for anisole-chlorobenzene system at 200 mm Hg.

x_1, *mol.fr.*	t_{exp} °*C*	*Wilson eqn.*		*NRTL eqn.*	
		t_{cal} °*C*	$y_{1,cal}$	t_{cal} °*C*	$y_{1,cal}$
0.0728	90.2	89.7	0.0322	89.7	0.0312
0.1338	91.1	90.7	0.0623	90.8	0.0610
0.1970	92.5	91.9	0.0967	92.0	0.0956
0.2797	94.1	93.5	0.1473	93.6	0.1470
0.3622	95.2	95.1	0.2047	95.3	0.2057
0.4454	97.1	96.8	0.2706	97.0	0.2731
0.5035	98.4	98.1	0.3219	98.2	0.3252
0.4982	97.8	97.9	0.3170	98.1	0.3203
0.5681	99.7	99.5	0.3845	99.6	0.3884
0.6413	101.1	101.1	0.4632	101.2	0.4671
0.7274	104.5	103.1	0.5674	103.2	0.5702
0.7890	104.7	104.6	0.6506	104.6	0.6518
0.8669	106.6	106.6	0.7672	106.5	0.7662
0.9237	108.2	108.0	0.8610	107.9	0.8591

where,

$$\Lambda_{12} = \frac{V_2}{V_1}\exp\left[-\frac{(\lambda_{12}-\lambda_{11})}{RT}\right]$$

and,

$$\Lambda_{21} = \frac{V_1}{V_2}\exp\left[-\frac{(\lambda_{21}-\lambda_{22})}{RT}\right]$$

Table 6 VLE data for anisole-chlorobenzene system at 500 mm Hg.

x_1, *mol.fr.*	t_{exp} °C	*Wilson eqn.*		*NRTLeqn.*	
		t_{cal} °C	$y_{1,cal}$	t_{cal} °C	$y_{1,cal}$
0.0728	117.8	118.2	0.0368	118.2	0.0364
0.1338	119.0	119.3	0.0707	119.4	0.0704
0.1970	120.5	120.5	0.1089	120.6	0.1090
0.2797	121.9	122.2	0.1642	122.2	0.1653
0.3622	123.5	123.9	0.2258	123.9	0.2280
0.4454	125.2	125.6	0.2952	125.6	0.2982
0.5035	126.5	126.9	0.3483	126.9	0.3516
0.4982	126.2	126.8	0.3433	126.8	0.3466
0.5681	127.7	128.3	0.4123	128.3	0.4154
0.6413	129.3	130.0	0.4913	129.9	0.4935
0.7274	131.6	132.0	0.5940	131.8	0.5942
0.7890	133.1	133.4	0.6744	133.2	0.6729
0.8669	134.9	135.3	0.7852	135.1	0.7818
0.9237	136.2	136.7	0.8727	136.6	0.8691

Table 7 VLE data for anisole-chlorobenzene system at 710 mm Hg.

x_1, *mol.fr.*	t_{exp} °C	*Wilson eqn.*		*NRTL eqn.*	
		t_{cal} °C	$y_{1,cal}$	t_{cal} °C	$y_{1,cal}$
0.0728	130.8	130.6	0.0387	130.6	0.0385
0.1338	132.1	131.7	0.0741	131.7	0.0741
0.1970	133.2	132.9	0.1138	133.0	0.1144
0.2797	135.2	134.6	0.1708	134.6	0.1724
0.3622	136.6	136.3	0.2340	136.3	0.2366
0.4454	138.2	138.1	0.3046	138.0	0.3078
0.5035	139.6	139.3	0.3583	139.3	0.3616
0.4982	139.2	139.2	0.3533	139.1	0.3565
0.5681	140.9	140.8	0.4226	140.6	0.4254
0.6413	142.5	142.4	0.5017	142.2	0.5033
0.7274	144.7	144.4	0.6037	144.2	0.6031
0.7890	145.8	145.9	0.6830	145.6	0.6806
0.8669	147.7	147.8	0.7916	147.5	0.7874
0.9237	149.2	149.2	0.8768	149.0	0.8727

Here V_1 and V_2 are the liquid molar volumes which are calculated through Rackett[11] equation. λ's, the energies of interaction between the molecules designated in the subscripts.

ii) NRTL equation[12]:

$$\ln \gamma_1 = x_2^2\left[\tau_{21}\left[\frac{G_{21}}{x_1 + x_2 G_{21}}\right]^2 + \frac{\tau_{12} G_{12}}{(x_2 + x_1 G_{12})^2}\right]$$

$$\ln \gamma_2 = x_1^2\left[\tau_{12}\left[\frac{G_{12}}{x_2 + x_1 G_{12}}\right]^2 + \frac{\tau_{21} G_{21}}{(x_1 + x_2 G_{21})^2}\right]$$

Table 8 Model parameters for Wilson and NRTL equations along with root mean square error in temperature. (Anisole-benzene system)

Model	*Parameters*	*RMS error in temperature*
Wilson	$\Delta\lambda_{12} = -1456.4°K$	0.6°K
	$\Delta\lambda_{21} = 1708.3°K$	
NRTL	$\Delta g_{12} = -18289.7°K$	0.6°K
$(\alpha = 0.12)$	$\Delta g_{21} = 20095.8°K$	

Table 9 Model parameters for Wilson and NRTL equations along with root mean square error in temperature. (Anisole-chlorobenzene system)

Model	*Parameters*	*RMS error in temperature*
Wilson	$\Delta\lambda_{12} = 16418.9°K$	0.4°K
	$\Delta\lambda_{21} = -13362.0°K$	
NRTL	$\Delta g_{12} = 63181.0°K$	0.4°K
$(\alpha = 0.12)$	$\Delta g_{21} = -52245.3°K$	

where,

$$\ln G_{12} = -\alpha_{12}\tau_{12},$$
$$\ln G_{21} = -\alpha_{12}\tau_{21},$$
$$\tau_{12} = \Delta g_{12}/RT,$$
$$\tau_{21} = \Delta g_{21}/RT,$$
$$\Delta g_{12} = g_{12} - g_{22},$$
$$\Delta g_{21} = g_{21} - g_{11},$$
$$\alpha_{12} = 0.12.$$

Here g's are the energies of interaction between different molecular species designated by the subscripts.

In the above two cases, the gas phase is assumed to be ideal and hence the fugacity coefficient is taken to be unity. The optimum model parameters (Tables 8, 9) in each case were obtained by minimizing sum of the squares of the deviation in total pressure, using Nedler-Mead optimization technique.

CONCLUSION

Both the systems are well correlated by the two models. Because the pressures employed are low, the assumption that the vapour phase is ideal is justified.

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