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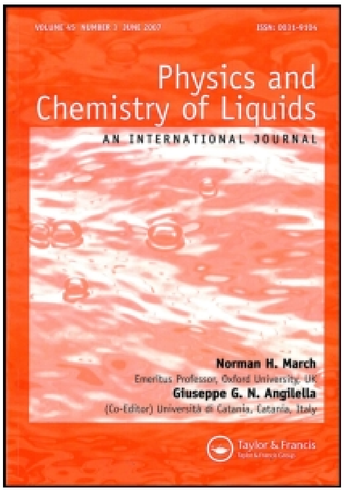

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Isobaric Vapour-Liquid Equilibria in the Binary Systems Formed by Anisole with Benzonitrile and Nitrobenzene

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ISOBARIC VAPOUR–LIQUID EQUILIBRIA IN THE BINARY SYSTEMS FORMED BY ANISOLE WITH BENZONITRILE AND NITROBENZENE

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Isobaric VLE data were measured for the binary systems of anisole with benzonitrile and nitrobenzene over the entire composition range by an indirect method using a Swietoslawski-type ebulliometer at three pressures. The experimental *t–x* data were found to be well represented by Wilson and NRTL models.

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

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INTRODUCTION

The present investigation is in continuation of our study on isobaric vapour-liquid equilibria of binary liquid mixtures containing anisole as the common component. The experimental data for the binary systems anisole-benzene and anisole-chlorobenzene are already reported[1]. This paper presents measurements on the temperature (*t*)–composition (*x*) relationships for the binary systems anisole-benzonitrile and anisole-nitrobenzene, on which no published information is available.

EXPERIMENTAL SECTION

The VLE measurements were carried out in a Swietoslawski-type ebulliometer[2]. The ebulliometer was connected to a vacuum system and the pressures were measured

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by a mercury manometer with an accuracy of ± 1 mm Hg. The temperatures were measured with a carefully calibrated mercury-in-glass thermometer, to an accuracy of ± 0.1 C. The measurements were carried out at the sub-atmospheric pressures of 200, 500 and 709/712 mm Hg.

The boiling-points of the systems anisole-benzonitrile and anisole-nitrobenzene were determined over the entire composition range at the three 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.*,[2]. The temperature was measured at equilibrium, as indicated by the steady drop-rate and constancy in the temperature at each pressure.

PURITY OF THE MATERIALS

All the chemicals used in this study were obtained from Fluka with a guaranteed purity of $>99\%$ GC. They were used as received, without further treatment. The purity of the samples was, however, ascertained by measuring some of the physical properties. A comparison with the literature values is given in Table 1.

RESULTS AND DISCUSSION

The experimental t–x data were correlated with Wilson[3] and NRTL[4] equations. The details of these models can be obtained from the above references or from our earlier work[1].

In the above two cases, the gas phase is assumed to be ideal and hence the fugacity coefficient is taken to be unity. The total pressure in each case is calculated

Table 1 Physical properties of pure components.

Component	*Temperature (K)*	*Density(g ml^{-1})*	*Refractive Index*	*Reference*
Anisole	293.15	0.9940	1.5175	this work
			1.5179	6
		0.99402		8
Benzonitrile	293.15		1.5290	this work
			1.5289	7
	303.15	0.9965		this work
		0.99628		8
Nitrobenzene	293.15		1.5530	this work
			1.55296	7
	303.15	1.1937		this work
		1.19341		8
		1.1936		9

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Table 2 Antoine constants[5] of the pure liquids.

Component	*A*	*B*	*C*
Anisole	7.05269	1489.99	203.57
Benzonitrile	6.74631	1436.72	181.00
Nitrobenzene	7.11560	1746.60	201.80

Table 3 VLE data for the system anisole(1) + benzonitrile(2) at 200 mm Hg $N = 15$, $\bar{e}$(Wilson) = 1.1, $\bar{e}$(NRTL) = 1.0.

		Wilson equation			*NRTL equation*		
x_1	t_{expt} °C	t_{cal} °C	$y_{1,cal}$	e	t_{cal} °C	$y_{1,cal}$	e
0.0741	139.0	138.4	0.1788	−1.8	138.4	0.1791	−1.8
0.1424	136.0	135.4	0.3122	−2.1	135.3	0.3129	−2.2
0.2007	133.4	132.9	0.4088	−1.6	132.9	0.4094	−1.7
0.2832	129.9	129.7	0.5247	−0.6	129.7	0.5247	−0.6
0.4120	125.3	125.2	0.6681	−0.3	125.3	0.6674	−0.1
0.4858	122.9	122.9	0.7342	−0.1	122.9	0.7334	0.1
0.4960	123.1	122.6	0.7426	−1.8	122.6	0.7417	−1.6
0.5954	120.0	119.7	0.8155	−1.2	119.7	0.8150	−0.9
0.6702	117.9	117.6	0.8615	−1.0	117.7	0.8613	−0.8
0.7368	115.9	115.9	0.8971	0.0	116.0	0.8971	0.2
0.8076	114.5	114.2	0.9301	−1.1	114.2	0.9304	−0.9
0.8783	112.8	112.6	0.9588	−0.8	112.6	0.9592	−0.7
0.9345	111.8	111.4	0.9790	−1.6	111.4	0.9793	−1.5

from

$$P_{t,\mathrm{cal}} = \gamma_1 P_1 x_1 + \gamma_2 P_2 x_2$$

where x_i, P_i, and γ_i represent the mole fraction, vapour pressure and activity coefficients, respectively. The P_is were calculated using the Antoine constants given in Dean[5]. The percent deviation in the total pressure, defined as

$$e = 100(P_{t,\mathrm{exp}} - P_{t,\mathrm{cal}})/P_{t,\mathrm{exp}}$$

is given along with the t–x data in Tables 3–8. The percent average absolute deviation, $\bar{e}$, defined as

$$\bar{e} = \frac{\sum |e|}{N}$$

where N is the number of data points, is also given in Tables 3–8. The optimum model parameters in each case, obtained by minimizing sum of the squares of the deviation in the total pressure using Nedler–Mead optimization technique, are presented along with root mean square error in temperature in Tables 9–10.

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Table 4 VLE data for the system anisole(1) + benzonitrile(2) at 500 mm Hg. $N = 15$, $\bar{e}$ (Wilson) = 1.0, $\bar{e}$ (NRTL) = 0.9.

		Wilson equation			*NRTL equation*		
x_1	t_{expt} °C	t_{cal} °C	$y_{1,cal}$	e	t_{cal} °C	$y_{1,cal}$	e
0.0741	169.9	169.9	0.1681	0.0	169.9	0.1694	−0.1
0.1424	166.4	166.6	0.2958	0.4	166.5	0.2978	0.1
0.2007	163.6	163.9	0.3895	0.8	163.8	0.3915	0.5
0.2832	159.8	160.5	0.5035	1.7	160.4	0.5048	1.4
0.4120	154.7	155.6	0.6473	2.3	155.5	0.6473	2.1
0.4858	152.2	153.0	0.7150	2.1	152.9	0.7145	2.0
0.4960	152.3	152.6	0.7236	0.9	152.6	0.7231	0.8
0.5954	149.3	149.4	0.7997	0.3	149.4	0.7990	0.3
0.6702	146.8	147.2	0.8484	1.0	147.2	0.8478	1.0
0.7368	144.7	145.3	0.8866	1.6	145.3	0.8862	1.6
0.8076	143.0	143.4	0.9224	1.0	143.4	0.9223	1.1
0.8783	141.3	141.6	0.9540	0.7	141.6	0.9541	0.7
0.9345	140.4	140.2	0.9765	−0.6	140.2	0.9766	−0.6

Table 5 VLE data for the system anisole(1) + benzonitrile(2) at 709 mm Hg. $N = 15$, $\bar{e}$ (Wilson) = 0.6, $\bar{e}$ (NRTL) = 0.5.

		Wilson equation			*NRTL equation*		
x_1	t_{expt} °C	t_{cal} °C	$y_{1,cal}$	e	t_{cal} °C	$y_{1,cal}$	e
0.0741	184.0	183.8	0.1642	−0.6	183.7	0.1660	−0.8
0.1424	180.2	180.3	0.2899	0.2	180.2	0.2925	−0.2
0.2007	177.4	177.6	0.3826	0.3	177.4	0.3851	−0.1
0.2832	173.6	174.0	0.4958	0.8	173.8	0.4976	0.3
0.4120	168.4	168.8	0.6398	1.0	168.7	0.6400	0.7
0.4858	165.7	166.2	0.7080	1.1	166.1	0.7076	0.9
0.4960	166.1	165.8	0.7167	−0.9	165.7	0.7162	−1.1
0.5954	162.6	162.4	0.7939	−0.5	162.4	0.7931	−0.6
0.6702	160.2	160.1	0.8436	−0.4	160.1	0.8428	−0.4
0.7368	157.9	158.1	0.8827	0.5	158.1	0.8821	0.5
0.8076	156.1	156.1	0.9196	0.0	156.1	0.9192	0.0
0.8783	154.4	154.2	0.9522	−0.6	154.2	0.9521	−0.5
0.9345	153.1	152.8	0.9755	−0.9	152.8	0.9755	−0.9

Table 6 VLE data for the system anisole(1) + nitrobenzene(2) at 200 mm Hg. $N = 17$, $\bar{e}$ (Wilson) = 1.4, $\bar{e}$ (NRTL) = 1.3.

		Wilson equation			*NRTL equation*		
x_1	t_{expt} °C	t_{cal} °C	$y_{1,cal}$	e	t_{cal} °C	$y_{1,cal}$	e
0.0766	153.6	152.7	0.2867	−2.9	152.7	0.2868	−2.9
0.1379	147.7	147.2	0.4429	−1.7	147.2	0.4426	−1.6
0.2054	142.4	142.0	0.5683	−1.4	142.0	0.5677	−1.3
0.2811	137.2	137.0	0.6711	−0.8	137.1	0.6704	−0.6
0.3598	132.7	132.5	0.7499	−0.7	132.6	0.7494	−0.5
0.4453	128.6	128.3	0.8141	−1.1	128.4	0.8138	−0.9
0.5026	126.2	125.8	0.8482	−1.6	125.8	0.8480	−1.3
0.5070	125.7	125.6	0.8506	−0.5	125.6	0.8504	−0.3
0.5680	123.4	123.1	0.8806	−1.1	123.2	0.8806	−0.8
0.6346	120.8	120.6	0.9081	−0.6	120.7	0.9082	−0.4
0.6952	118.7	118.6	0.9293	−0.5	118.6	0.9295	−0.4
0.7826	116.4	115.8	0.9547	−2.0	115.9	0.9550	−1.9
0.8312	115.1	114.4	0.9668	−2.4	114.4	0.9670	−2.4
0.8801	113.8	113.1	0.9777	−2.6	113.1	0.9779	−2.6
0.9344	112.1	111.6	0.9885	−1.7	111.6	0.9886	−1.6

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Table 7 VLE data for the system anisole(1) + nitrobenzene(2) at 500 mm Hg. $N = 17$, $\bar{e}$ (Wilson) = 1.1, $\bar{e}$ (NRTL) = 1.1.

		Wilson equation			*NRTL equation*		
x_1	t_{expt} °C	t_{cal} °C	$y_{1,cal}$	e	t_{cal} °C	$y_{1,cal}$	e
0.0766	185.5	185.4	0.2562	−0.5	185.3	0.2575	−0.6
0.1379	179.3	179.7	0.4045	0.9	179.6	0.4056	0.7
0.2054	173.7	174.3	0.5287	1.2	174.2	0.5294	1.0
0.2811	168.3	168.9	0.6343	1.3	168.9	0.6346	1.2
0.3598	163.3	164.0	0.7179	1.7	164.0	0.7179	1.6
0.4453	158.7	159.3	0.7877	1.6	159.3	0.7876	1.6
0.5026	155.8	156.5	0.8255	1.8	156.5	0.8253	1.8
0.5070	155.7	156.3	0.8281	1.5	156.3	0.8280	1.5
0.5680	152.8	153.6	0.8619	1.9	153.6	0.8617	2.0
0.6346	150.1	150.8	0.8931	1.8	150.8	0.8930	1.8
0.6952	148.1	148.4	0.9173	0.8	148.5	0.9173	0.9
0.7826	145.2	145.3	0.9468	0.3	145.3	0.9468	0.3
0.8312	144.0	143.7	0.9608	−0.9	143.7	0.9609	−0.9
0.8801	142.2	142.2	0.9736	−0.2	142.2	0.9737	−0.1
0.9344	140.6	140.5	0.9863	−0.2	140.5	0.9864	−0.2

Table 8 VLE data for the system anisole(1) + nitrobenzene(2) at 712 mm Hg. $N = 17$, $\bar{e}$ (Wilson) = 0.5, $\bar{e}$ (NRTL) = 0.6.

		Wilson equation			*NRTL equation*		
x_1	t_{expt} °C	t_{cal} °C	$y_{1,cal}$	e	$t_{1,cal}$ °C	$y_{1,cal}$	e
0.0766	200.0	199.5	0.2450	−1.5	199.4	0.2467	−1.8
0.1379	193.8	193.7	0.3899	−0.5	193.6	0.3916	−0.8
0.2054	188.2	188.1	0.5133	−0.4	188.0	0.5145	−0.7
0.2811	182.5	182.6	0.6197	0.0	182.5	0.6204	−0.2
0.3598	177.5	177.6	0.7050	−0.1	177.5	0.7052	−0.2
0.4453	172.6	172.7	0.7769	0.1	172.7	0.7768	0.0
0.5026	169.7	169.8	0.8161	0.0	169.8	0.8160	0.0
0.5070	169.5	169.6	0.8189	0.0	169.6	0.8187	0.0
0.5680	166.6	166.7	0.8541	0.1	166.7	0.8539	0.1
0.6346	163.8	163.8	0.8868	−0.2	163.8	0.8866	−0.2
0.6952	161.4	161.3	0.9123	−0.3	161.3	0.9122	−0.3
0.7826	158.3	158.0	0.9434	−0.8	158.0	0.9434	−0.8
0.8312	156.8	156.3	0.9583	−1.3	156.5	0.9583	−1.3
0.8801	155.0	154.7	0.9719	−0.8	154.7	0.9719	−0.8
0.9344	153.4	153.0	0.9854	−1.2	153.0	0.9855	−1.1

Table 9 Model parameters for Wilson and NRTL equations and the root mean square error in temperature for anisole + benzonitrile system.

Model	*Parameters*	*RMS error in temperature*
Wilson	$\lambda_{12} - \lambda_{11} = 26327.7$ K $\lambda_{21} - \lambda_{22} = -18399.4$ K	0.4 K
NRTL ($\alpha_{12}=0.12$)	$g_{12} - g_{22} = -49467.0$ K $g_{21} - g_{11} = 58275.7$ K	0.4 K

Table 10 Model parameters for Wilson and NRTL equations and the root mean square error in temperature for anisole + nitrobenzene system.

Model	*Parameters*	*RMS error in temperature*
Wilson	$\lambda_{12}-\lambda_{11}=$ 11750.2 K $\lambda_{21}-\lambda_{22}=-9301.1$ K	0.4 K
NRTL ($\alpha_{12}=0.12$)	$g_{12}-g_{22}=-31159.1$ K $g_{21}-g_{11}=$ 35313.7 K	0.4 K

CONCLUSIONS

None of the systems studied are far from ideal. Both the systems are well correlated by the two models. Because the pressures employed are sub-atmospheric, the assumption that the vapour phase is ideal is justified.

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