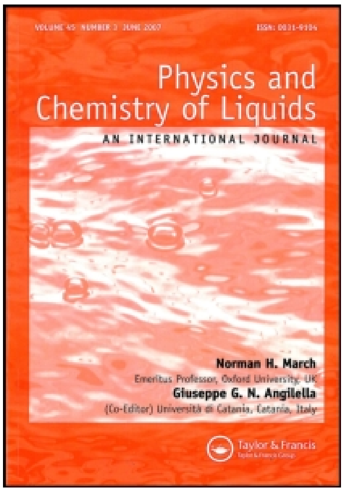

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Activity Coefficients and Excess Gibbs Free Energies for the Systems Chlorobenzene(1)–Nitrobenzene(2) and 1,2-Dichlorobenzene(1)–Nitrobenzene(2)

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Vapour–liquid equilibrium data for the systems chlorobenzene(1)–nitrobenzene(2) and 1,2-dichlorobenzene(1)–nitrobenzene(2) were obtained by the indirect method from the composition *vs* boiling point ($x - t$) measurements made in the Swiestoslawski type ebulliometer. The measurements were made at 200 mm Hg and 700 mm Hg. The experimental $t - x$ data were used to estimate Wilson parameters and then used to calculate activity coefficients, vapour compositions and theoretical boiling points for the binary mixtures. The activity coefficients determined were used to obtain excess Gibbs free energies G^E. The observed and calculated values are interpreted in terms of specific interaction.

1 INTRODUCTION

Distillation is one of the most expensive separation processes. In the present energy saving world, cost of the distillation process must always be calculated, even if only to justify on economic grounds in comparison with the other separation processes. For this vapour–liquid equilibrium (VLE) data are necessary. The design and operation of stage-wise or differential containing equipment require reliable VLE. As a part of continuing equilibrium study of halogen substituted aromatic hydrocarbons with nitrosubstituted aromatic hydrocarbons, VLE on chlorobenzen(1)–nitrobenzene(2) and 1,2-dichlorobenzene(1)–nitrobenzene(2) were obtained at 200 mm Hg. and 700 mm Hg., because data on the systems have not been reported in literature.

2 EXPERIMENTAL

Chlorobenzene (E. Merck, India) was dried with calcium chloride and distilled in a 1-metre fractionating column and the middle fraction was collected. 1,2-dichlorobenzene (Sarabhai Chemicals, Baroda) was further purified in a fractionating column under the reduced pressure and the middle fraction was collected.

Nitrobenzene (BDH) was dried over anhydrous calcium chloride for two days and the dried sample was distilled using one meter fractionating column under the reduced pressure.

The purity of the samples was checked by densities, refractive indices and boiling points. The densities were measured using a bicapillary pycnometer with an accuracy of 5 parts in 10^5. The refractive indices were determined using an Abbe's refractometer which gave an accuracy of ± 0.0002. The boiling points were obtained using Swietoslawski type ebulliometer with an accuracy of ± 0.2°C. The values are presented in Table I along with the literature values.[1,2]

TABLE I

Densities, refractive indices and boiling points of the pure compounds

	Density, ρg cm^3 at 303.15 K		Refractive indices at 293.15 K		Boiling point	
Compound	Exptl.	Lit. (1)	Exptl.	Lit. (2)	Exptl.	Lit. (1)
Chlorobenzene	1.09555	1.09550	1.5250	1.5251	404.9	404.85
1,2-dichlorobenzene	1.29449	1.29457	1.5525	1.5524	453.3	253.61
Nitrobenzene	1.19336	1.19341	1.5525	1.5524*	483.6	482.95

* 17°C.

The vapour–liquid equilibrium measurements were studied in a Swietoslawski type ebulliometer.[3] The ebulliometer was connected to a vacuum system. The pressure was measured using mercury manometer with an accuracy of ± 1 mm Hg. The temperature was measured using a PT100 thermometer which gave an accuracy of ± 0.1°C. The detailed procedure was described previously.[3]

Isobaric binary systems The isobaric boiling points of the system: Chlorobenzene(1)–nitrobenzene(2) and 1,2-dichlorobenzene(1)–nitrobenzene(2) were determined over the entire range of composition. Mixtures of different compositions were prepared by taking quantitities (by weight) of the pure materials. The boiling points for the known binary compositions were measured at 200 mm Hg and 700 mm Hg. The boiling point of a specified composition was first measured at 200 mm Hg. Then the pressure was raised to 700 mm Hg and the boiling point was determined. The system was brought back to 200 mm Hg. where the boiling point was determined and finally the measurement was repeated at 700 mm Hg, thereby obtaining duplicate sets of both the pressures of interest. The procedure also helps us to detect any possible dissociation, and loss of materials in the mixture under study.

3 RESULTS

Isobaric $t - x$ data are used for the data reduction. The model for expressing the composition and temperature dependence is chosen to be Wilson equation.[4]

$$\ln \delta_1 = -\ln[x_1 + \Lambda_{12}x_2] + x_2\left[\frac{\Lambda_{12}}{x_1 + \Lambda_{12}x_2} - \frac{\Lambda_{21}}{x_2 + \Lambda_{21}x_1}\right] \quad (1)$$

$$\ln \delta_2 = -\ln[x_2 + \Lambda_{21}x_1] + x_1\left[\frac{\Lambda_{21}}{x + \Lambda_{21}x_1} - \frac{\Lambda_{12}}{x_1 + \Lambda_{12}x_2}\right] \quad (2)$$

The Wilson parameters Λ_{12} and Λ_{21} are given by

$$\Lambda_{12} = \frac{V_2^L}{V_1^L}\exp - \frac{\lambda_{12} - \lambda_{11}}{RT} \quad (3)$$

$$\Lambda_{21} = \frac{V_1^L}{V_2^L}\exp - \frac{\lambda_{12} - \lambda_{22}}{RT} \quad (4)$$

where V_1^L and V_2^L are liquid molal volumes $(\lambda_{12} - \lambda_{11})$ and $(\lambda_{12} - \lambda_{22})$ are temperature independent (to some extent) Wilson parameters. λ's are the energies of interaction between the molecules designated in the subscripts. The optimum Wilson parameters Λ_{12} and Λ_{21} are obtained by minimizing the objective function ϕ, using Nelder–Mead optimization technique, are presented in Table II along with the standard deviation of the fit.

$$\phi = \Sigma\left(\frac{P_{\text{cal}}}{P_{\text{exp}}} - 1.0\right)^2 \quad (5)$$

TABLE II

Wilson parameters with standard deviation

System	Λ_{12}	Λ_{21}	$\sigma_{t°C}$
Chlorobenzene(1)-nitrobenzene(2) at 200 mm Hg.	377.266	−224.369	0.19
Chlorobenzene(1)-nitrobenzene(2) at 700 mm Hg.	203.149	73.440	0.39
1,2-dichlorobenzene(1)-nitrobenzene(2) at 200 mm Hg.	443.234	1539.330	0.15
1,2-dichlorobenzene(1)-nitrobenzene(2) at 700 mm Hg.	−444.934	996.877	0.14

4 DISCUSSION

Since the prediction of vapour liquid equilibrium data involves the vapour pressure data of pure compounds the same has been determined for chlorobenzene, 1,2-dichlorobenzene and nitrobenzene. The Antoine constants for the pure compounds were obtained by non-linear regression analysis of the experimental data. The obtained Antoine constants are presented in Table III. The measured boiling points, calculated boiling points using Wilson equation and the ideal boiling points are presented in Table IV to VI. The vapour compositions were calculated using the equation

$$y_1 = \frac{x_1 P_1 \delta_1}{P_{\text{cal}}} \tag{6}$$

The excess Gibbs free energies were calculated using activity coefficients

$$\frac{G^E}{RT} = x_1 \ln \delta_1 + x_2 \ln \delta_2 \tag{7}$$

The vapour compositions, activity coefficients and excess Gibbs free energies are presented in Table VIII to XI. The G^E, values are positive over the entire range of composition. It is observed, G^E values are increasing from chlorobenzene(1)-nitrobenzene(2) to 1,2-dichlorobenzene(2). From the figures we can conclude that the systems are slightly non-deal.

TABLE III

Antoine constants for the pure compounds with standard deviation

Compound	A	B	C	σp%
Chlorobenzene	15.4830	2941.06	200.49	0.3
1,2-dichlorobenzene	16.3376	3822.76	213.87	0.3
Nitrobenzene	16.3562	3992.91	200.27	0.4

TABLE IV

Chlorobenzene(1)–nitrobenzene(2) $t - x$ data at 200 mm Hg

x	t_{expt} °C	t_{cal} using Wilson equation °C	t_{ideal} °C	$t_{\mathrm{expt}} - t_{\mathrm{cal}}$ °C
0.1219	137.5	137.5	139.4	0.0
0.1219	137.5	137.5	139.4	0.0
0.2348*	125.0	124.9	126.1	1.1
0.2348*	125.9	124.9	126.1	1.0
0.3614	115.0	114.9	115.5	0.1
0.3614	115.0	114.9	115.5	0.1
0.4420	110.0	109.9	110.2	0.1
0.4420	110.1	109.9	110.2	0.2
0.5047	106.5	106.5	106.7	0.0
0.5047	106.5	106.5	106.7	0.0
0.6373	100.0	100.4	100.4	−0.4
0.6373	100.1	100.4	100.4	−0.3
0.7098	97.5	97.5	97.5	0.0
0.7098	97.6	97.5	97.5	0.1
0.8526	92.8	92.6	92.5	0.2
0.8526	92.7	92.6	92.5	0.2
0.9248	90.0	90.4	90.4	−0.4
0.9248	90.2	90.4	90.4	−0.2

* Points rejected from analysis.

TABLE V

Chlorobenzene(1)–nitrobenzene(2) $t - x$ data at 700 mm Hg

x_1	t_{expt} °C	t_{cal} using Wilson equation °C	t_{ideal} °C	$t_{\mathrm{expt}} - t_{\mathrm{cal}}$ °C
0.1219	183.0	183.1	187.2	−0.1
0.1219	183.1	183.1	187.2	−0.0
0.2348*	173.0	169.3	173.4	3.7
0.2348*	173.1	169.3	173.4	3.8
0.3614	158.5	158.4	161.7	0.1
0.3614	158.6	158.4	161.7	0.2
0.4420	153.5	153.0	155.5	0.5
0.4420	153.4	153.0	155.5	0.4
0.5047	148.8	149.3	151.3	−0.5
0.5047	148.9	149.3	151.3	−0.4
0.6373	142.6	142.6	143.8	0.0
0.6373	142.8	142.6	143.8	0.2
0.7098	139.0	139.5	140.2	−0.5
0.7098	138.9	139.5	140.2	−0.6
0.8526	134.4	133.9	134.1	0.5
0.8526	134.3	133.9	134.1	0.4
0.9248	131.7	131.3	131.4	0.4
0.9248	131.5	131.3	131.4	0.2

* Points rejected from analysis.

TABLE VI

1,2-dichlorobenzene(1)–nitrobenzene(2) $t - x$ data at 200 mm Hg

x_1	t_{expt} °C	t_{cal} using Wilson equation °C	t_{ideal} °C	$t_{\text{expt}} - t_{\text{cal}}$ °C
0.1052	156.5	156.3	156.6	0.2
0.1052	156.7	156.3	156.6	0.4
0.3133	149.3	148.3	149.3	1.0
0.3133	149.3	148.3	149.3	1.0
0.3886	145.7	145.7	147.6	0.0
0.3886	145.9	145.7	147.0	0.2
0.4479	143.6	143.7	145.3	−0.1
0.4479	143.8	143.7	145.3	0.1
0.5307	141.2	141.1	143.0	0.2
0.6531	137.8	137.7	139.9	0.1
0.6531	137.6	137.7	139.9	−0.1
0.6816	137.0	137.0	139.2	0.0
0.6816	136.9	137.0	139.2	−0.1
0.7111	136.0	136.2	138.5	−0.1
0.8603	133.4	133.3	135.2	0.1
0.8603	133.5	133.3	135.2	0.2

TABLE VII

1,2-dichlorobenzene(1)–nitrobenzene(2) $t - x$ data at 700 mm Hg

x_1	t_{expt} °C	t_{cal} using Wilson equation °C	t_{ideal} °C	$t_{\text{expt}} - t_{\text{cal}}$ °C
0.1052	202.5	202.4	202.7	0.1
0.1052	202.3	202.4	202.7	−0.1
0.3133	194.9	194.3	195.2	0.6
0.3133	195.1	194.3	195.2	0.8
0.3886	191.5	191.6	192.7	−0.1
0.3886	191.5	191.6	192.7	−0.1
0.4479	189.5	189.5	190.9	0.0
0.4479	189.5	189.5	190.9	0.0
0.5307	186.9	186.8	188.5	0.1
0.5307	187.1	186.8	188.5	0.3
0.6531	183.0	183.2	185.1	0.2
0.6531	183.1	183.2	185.1	−0.1
0.6816	182.5	182.5	184.3	0.0
0.6816	182.6	182.5	184.3	0.1

TABLE VIII

Vapour compositions, activity coefficients and excess gibbs free energies for the system chlorobenzene(1)–nitrobenzene(2) at 200 mm Hg

x_1	y_{cal}	t_{cal} using Wilson equation °C	υ_1	υ_2	G^E J mole^{-1}
0.05	0.3389	149.3	1.1463	1.0011	27
0.10	0.5298	140.7	1.1084	1.0030	45
0.15	0.6490	133.9	1.0991	1.0075	58
0.20	0.7294	128.3	1.0568	1.0118	66
0.25	0.7868	123.5	1.0400	1.0163	70
0.30	0.8296	119.4	1.0275	1.0207	71
0.35	0.8625	115.7	1.0183	1.0247	69
0.40	0.8885	112.5	1.0116	1.0283	66
0.45	0.9093	109.5	1.0068	1.0313	61
0.50	0.9262	106.8	1.0036	1.0337	56
0.55	0.9402	104.3	1.0015	1.0355	50
0.60	0.9518	102.0	1.0002	1.0367	44
0.65	0.9616	99.8	0.9995	1.0372	37
0.70	0.9699	99.9	0.9992	1.0370	31
0.75	0.9769	96.0	0.9992	1.0363	25
0.80	0.9830	94.3	0.9993	1.0350	19
0.85	0.9882	92.6	0.9996	1.0331	13
0.90	0.9927	91.1	0.9998	1.0307	8
0.95	0.9966	89.6	0.9999	1.0279	4

TABLE IX

Vapour compositions, activity coefficients and excess gibbs free energies for the system chlorobenzene(1)–nitrobenzene(2) at 700 mm Hg

x	y_{cal}	t_{cal} using Wilson equation °C	υ_1	υ_2	G^E J mole^{-1}
0.05	0.2820	195.6	1.2500	1.0009	45
0.10	0.4616	186.6	1.2171	1.0034	84
0.15	0.5824	179.2	1.1868	1.0076	116
0.20	0.6677	173.0	1.1595	1.0132	143
0.25	0.7305	167.8	1.1349	1.0202	165
0.30	0.7785	163.3	1.1132	1.0284	181
0.35	0.8162	159.3	1.0940	1.0378	192
0.40	0.8466	155.7	1.0771	1.0482	199
0.45	0.8716	152.5	1.0625	1.0596	201
0.50	0.8926	149.6	1.0498	1.0719	209
0.55	0.9104	146.9	1.0390	1.0851	194
0.60	0.9258	144.4	1.0297	1.0990	185
0.65	0.9392	142.1	1.0220	1.1136	172
0.70	0.9510	139.9	1.0157	1.1289	156
0.75	0.9615	137.8	1.0105	1.4448	137
0.80	0.9708	135.8	1.0065	1.1613	115
0.85	0.9792	134.0	1.0036	1.1784	90
0.90	0.9868	132.2	1.0015	1.1959	62
0.95	0.9937	130.4	1.0004	1.2139	33

TABLE X

Vapour compositions, activity coefficients and excess gibbs free energies for the system 1,2-dichlorobenzene(1)-nitrobenzene(2) at 200 mm Hg

x	y_{cal}	t_{cal} using Wilson equation	v_1	v_2	G^E J mole^{-1}
0.05	0.1125	158.6	1.6345	0.9997	5
0.10	0.2134	156.5	1.0410	0.9989	10
0.15	0.3043	154.5	1.0476	0.9974	16
0.20	0.3863	152.5	1.0543	0.9953	23
0.25	0.4603	150.6	1.0611	0.9924	31
0.30	0.5272	148.8	1.0677	0.9888	40
0.35	0.5877	147.0	1.0742	0.9844	50
0.40	0.6422	145.3	1.0802	0.9793	61
0.45	0.6915	143.7	1.0857	0.9737	75
0.50	0.7358	142.1	1.0904	0.9677	89
0.55	0.7756	140.6	1.0940	0.9617	105
0.60	0.8113	139.1	1.0962	0.9563	123
0.65	0.8430	137.8	1.0965	0.9533	141
0.70	0.8712	136.5	1.0943	0.9543	161
0.75	0.8959	135.3	1.0891	0.9637	179
0.80	0.9176	134.3	1.0798	0.9897	194
0.85	0.9363	133.5	1.0658	1.0511	201
0.90	0.9527	132.8	1.0460	1.2000	191
0.95	0.9680	132.4	1.0208	1.6467	144

TABLE XI

Vapour compositions, activity coefficients and excess gibbs free energies for the system 1,2-dichlorobenzene(1)-nitrobenzene(2) at 700 mm Hg

x	y_{cal}	t_{cal} using Wilson equation °C	v_1	v_2	G^E J mole^{-1}
0.05	0.0994	204.8	1.0323	0.9998	5
0.10	0.1905	202.6	1.0370	0.9992	11
0.15	0.2742	200.6	1.0416	0.9982	17
0.20	0.3512	198.6	1.0461	0.9967	24
0.25	0.4219	196.6	1.0504	0.9948	32
0.30	0.4869	194.7	1.0545	0.9925	40
0.35	0.5466	192.9	1.0582	0.9898	49
0.40	0.6014	191.2	1.0614	0.9869	59
0.45	0.6516	189.5	1.0639	0.9838	73
0.50	0.6976	187.6	1.0656	0.9810	84
0.55	0.7396	186.2	1.0662	0.9787	97
0.60	0.7779	184.7	1.0656	0.9978	110
0.65	0.8127	183.3	1.0635	0.9992	119
0.70	0.8442	182.0	1.0595	6.9852	131
0.75	0.8728	180.8	1.0533	0.9986	140
0.80	0.8986	179.7	1.0449	1.0253	145
0.85	0.9223	178.7	1.0339	1.0764	142
0.90	0.9447	177.9	1.0209	1.1765	126
0.95	0.9679	177.2	1.0076	1.3896	85

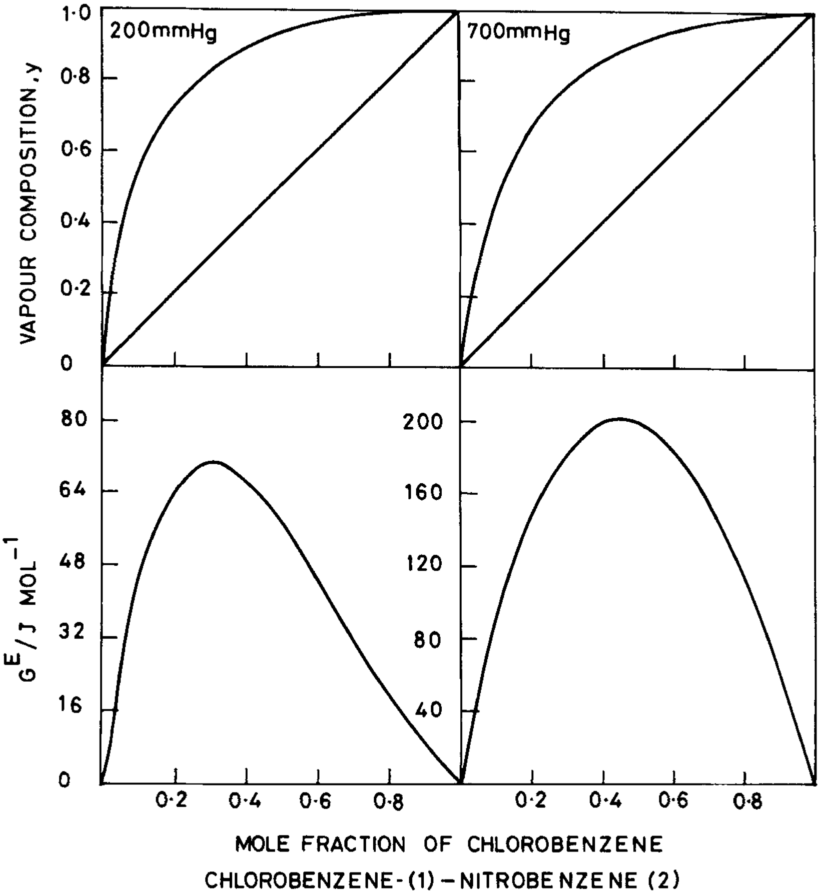

FIGURE 1 Vapour composition and G^E versus mole fraction of chlorobenzene.

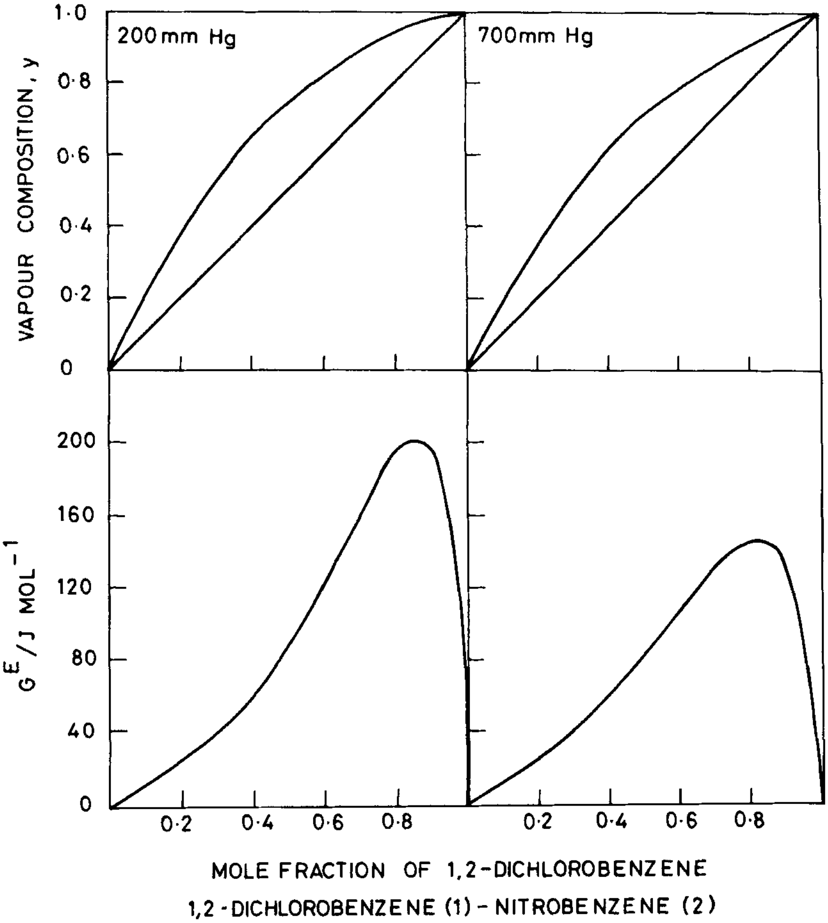

FIGURE 2 Vapour composition and G^E versus mole fractions of 1,2-dichlorobenzene.

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