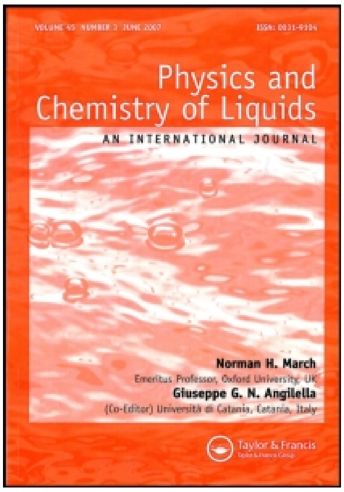

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ISOBARIC VAPOUR-LIQUID EQUILIBRIA IN THE BINARY SYSTEMS FORMER BY p-XYLENE WITH 1,2-DICHLOROETHANE, 1,1,1-TRICHLOROETHANE AND 1,1,2,2-TETRACHLOROETHANE AT 66.5 kPa+

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Isobaric Vapour-Liquid equilibria of p-xylene + 1,2-dichloroethane, p-xylene + 1,1,1-trichloroethane and p-xylene + 1,1,2,2,-tetrachloroethane, binary mixtures measured at 66.5 kPa are reported. Activity coefficients are evaluated and correlated.

KEY WORDS: Vapour-liquid equilibria, p-xylene, 1,2,-dichloroethane, 1,1,1,-trichloroethane, 1,1,2,2-tetrachloroethane.

INTRODUCTION

This paper presents vapour-liquid equilibrium data on three binary systems: p-xylene + 1,2-dichloroethane, p-xylene + 1,1,1-trichloroethane and p-xylene + 1, 1,2,2 + tetrachloroethane, at 66.5 kPa, in continuation of the investigators interest in a systematic study of the thermalphysical properties of liquid mixtures containing an alkylbnzene and a chloroethane[1–4]. Bhushankumar and Raju[5] studied the phase equilibria of the p-xylene + 1,2-dichloroethane system at 97.8 kPa, while Venkateswara Roa and Vishwanath[1–3] studied all the three systems at 91.1 kPa This investigation is taken up to study the change in the phase equilibrium of the three systems at the sub-atmospheric pressure of 66.5 kPa.

EXPERIMENTAL

A recirculation type still, similar to the one described by Dvorak and Boublik[6], has been used for the experiments. The temperatures were measured to an accuracy of

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± 0.05 K, by means of carefully calibrated mercury-in-glass thermometers. The system pressure was maintained at the constant value of 66.5 ± 0.0665 kPa by means of a model #7 cartesan monostat, procured from Emil. Greiner Co., New York. The equilibrium conditions were attained in 1 hr time. An additional 30 min. was allowed before the collection of the equilibrium liquid and vapour samples for analysis. The constancy of the composition was established from three sets of samples collected at 15 min. intervals.

Based on the comparison of the physical properties of the pure liquids reported in Table 1, the pure compounds were expected to be at least 99.5% pure. The compositions of the liquid and vapour samples at equilibrium were calculated from the measured value of refractive-index/density and Eqn. (1) developed from the mole fraction of p-xylene and the corresponding refractive-index/density, and the coefficients given in Table 2. The characteristic property used was the refractive index at 293.15 K for p-xylene + 1,2-dichloroethane and p-xylene + 1,1,1-trichloroethane systems and density at 313.15 K in the case of p-xylene + 1,1,2,2-tetrachloroethane system.

$$F = 1.0000 + BE + CE^2 + DE^3 \qquad (1)$$

where F = the molefraction of p-xylene and

$$E = \frac{(n - n_1)}{(n_2 - n_1)} \qquad (2)$$

Table 1 Comparison of the physical properties of pure liquids with literature[7] data at 293.15 K.

Component	*Refractive-index*		*Density* ($g \cdot ml^{-1}$)	
	This work	*Literature*	*This work*	*Literature*
p-xylene	1.4960	1.4958	0.8560	0.8611
1,2-Dichloroethane	1.4450	1.4447	1.2526	1.2531
1,1,1-Trichloroethane	1.4375	1.4379	1.3384	1.3890
1,1,2,2-Tetrachloroethane	1.4950	1.4949	1.5950	1.5953

Table 2 Coefficients of the composition-characteristic property relation, Eqn. (1).

Mixture	*No. of data points*	*B*	*C*	*D*	*PADD*
p-xylene + 1,2-Dichloroethane	12	− 1.2533	0.2159	0.0374	0.23
p-xylene + 1,1,1,-Trichloroethane	12	− 1.0556	− 0.0468	0.1024	0.20
p-xylene + 1,1,2,2-Tetrachloroethane	12	− 1.2157	0.3508	− 0.1351	0.12

in which
n = refractive index of the mixture, n_1, n_2 = refractive indices of pure liquids, for p-xylene + 1,2-dichloroethane, and p-xylene + 1,1,1-trichloroethane systems. In the case of p-xylene + 1,1,2,2-tetrachloroethane system.

$$E = \frac{(\rho - \rho_1)}{(\rho_2 - \rho_1)} \tag{3}$$

where ρ = the density of the mixture, and ρ_1, ρ_2 = densities of the pure components. The percent average absolute deviation (PAAD) is represented as:

$$\mathrm{PAAD} = \frac{\sum[|(F_{\mathrm{expt}} - R_{\mathrm{cal}})|]}{[F_{\mathrm{expt}}]} \frac{100}{N} \tag{4}$$

where N = the number of synthetic samples studied for each system (12 in this work). Table 2 shows the coefficients of Eqn. (1) for the three systems, together with the PAAD for the synthetic sample data.

RESULTS

The phase equilibrium data are presented in Tables 3–5. The liquid phase activity coefficients (γ_1 and γ_2) are calculated from

$$\gamma_1 = \frac{z_1 y_1 p}{x_1 p_1^0} \tag{5}$$

and

$$\gamma_2 = \frac{z_2 y_2 p}{x_2 p_2^0} \tag{6}$$

The pure component vapour pressures (p_1^0 and p_2^0) at each temperature are calculated from the Antoine equation

$$\ln p^0 = \frac{A - B}{(T + C)} \tag{7}$$

where p^0 is the vapour pressure in kPa and T is the absolute temperature in K using the values of A, B and C given in Table 6. The vapour pressure data on the pure substances including the boiling point observations of the pure liquids at 66.5 kPa are represented by the Antoine equation to within ±0.1 kPa. The calculated values of vapour pressure at different temperatures are shown in the columns headed p_1^0 and p_2^0 in Tables 3–5.

Table 3 Vapour-liquid equilibrium data of p-xylene(1) + 1,2-dichloroethane(2) system at 66.5 kPa.

Temperature (*K*)	x_1	y_1	B_{11} ($ml \cdot mol^{-1}$)	B_{22} ($ml \cdot mol^{-1}$)	v_1^L ($ml \cdot mol^{-1}$)	v_2^L ($ml \cdot mol^{-1}$)	p_1^0 (kPa)	p_2^0 (kPa)	z_1	z_2	γ_1	γ_2
396.50	1.0000	1.0000	−1597	−667	135.5	82.6	66.51	306.89	–	–	–	–
392.15	0.9625	0.8505	−1644	−695	134.7	82.4	58.54	275.06	0.996	1.051	0.9998	1.0130
387.75	0.9212	0.7161	−1700	−713	134.0	82.3	51.23	245.77	0.991	1.045	1.0000	1.0187
379.85	0.8290	0.5050	−1810	−747	132.7	81.3	39.92	199.30	0.984	1.035	0.9985	0.9969
374.35	0.7590	0.3890	−1894	−771	131.9	80.7	33.37	170.97	0.978	1.029	0.9989	1.0147
370.55	0.7050	0.3205	−1957	−788	131.3	80.2	29.29	153.24	0.975	1.025	1.0063	1.0246
361.65	0.5450	0.1810	−2188	−828	130.0	79.3	21.39	117.82	0.967	1.015	0.9984	1.0312
356.75	0.4250	0.1190	−2215	−851	129.3	78.7	17.91	101.08	0.962	1.011	1.0001	1.0191
353.15	0.3100	0.0759	−2292	−867	128.8	78.4	15.61	90.31	0.959	1.007	1.0003	0.9931
348.15	0.1690	0.0350	−2407	−890	128.1	77.8	12.81	76.75	0.954	1.003	1.0257	1.0225
347.55	0.1300	0.0260	−2421	−893	128.0	77.7	12.52	75.09	0.953	1.003	1.0124	0.9944
346.75	0.1140	0.0227	−2440	−896	127.9	77.6	12.15	73.23	0.953	1.002	1.0157	1.0042
345.95	0.0600	0.0113	−2460	−900	127.8	77.5	11.75	71.20	0.953	1.002	1.0158	1.0070
343.90	0.0000	0.0000	−2510	−910	127.6	77.3	10.80	66.46	–	–	–	–

Table 4 Vapour-liquid equilibrium data of p-xylene(1) + 1, 1, 1-trichloroethane(2) system at 66.5 kPa.

Temperature (K)	x_1	y_1	B_{11} ($ml \cdot mol^{-1}$)	B_{22} ($ml \cdot mol^{-1}$)	v_1^L ($ml \cdot mol^{-1}$)	v_2^L ($ml \cdot mol^{-1}$)	p_1^0 (kPa)	p_2^0 (kPa)	z_1	z_2	γ_1	γ_2
396.50	1.0000	1.0000	−1771	−840	134.4	118.2	66.51	328.00	-	-	-	-
384.55	0.9190	0.6505	−1743	−907	133.5	116.0	46.34	287.03	0.988	1.073	1.0036	1.0726
376.75	0.8370	0.4625	−1857	−951	132.2	114.7	36.05	235.92	0.981	1.059	0.9999	0.8012
373.95	0.8090	0.4102	−1900	−967	131.8	114.3	32.93	219.33	0.978	1.054	1.0014	0.9868
367.75	0.7050	0.2910	−2004	−1003	130.9	113.0	26.58	185.40	0.972	1.044	1.0038	0.8999
356.55	0.5520	0.1550	−2218	−1070	129.3	111.5	17.73	134.69	0.962	1.027	1.0132	0.9564
353.15	0.4300	0.1092	−2291	−1091	128.8	111.0	15.61	121.28	0.930	1.023	1.0061	0.8730
348.35	0.3700	0.0715	−2406	−1121	128.2	110.2	12.94	105.26	1.011	1.016	1.0040	0.9460
345.55	0.2600	0.0450	−2475	−1138	127.7	109.8	11.55	96.51	1.006	1.013	1.0025	0.9008
343.05	0.2400	0.0375	−2534	−1152	127.4	109.5	10.44	89.22	1.006	1.009	1.0012	0.9528
334.30	0.0000	0.0000	−2742	−1199	126.3	107.5	7.21	66.48	-	-	-	-

Table 5 Vapour-liquid equilibrium data of p-xylene (1) + 1,1,2,2-tetrachloroethane(2) system at 66.5 kPa.

Temperature (*K*)	x_1	y_1	B_{11} ($ml\cdot mol^{-1}$)	B_{22} ($ml\cdot mol^{-1}$)	v_1^L ($ml\cdot mol^{-1}$)	v_2^L ($ml\cdot mol^{-1}$)	p_1^0 (*kPa*)	p_2^0 (*kPa*)	z_1	z_2	γ_1	γ_2
396.50	1.0000	1.0000	− 1585	− 1360	136.6	118.5	66.51	53.16	–	–	–	–
397.65	0.8300	0.8572	− 1577	− 1355	136.5	118.4	68.77	54.98	1.001	0.995	0.9997	1.0150
398.35	0.7100	0.7460	− 1569	− 1351	136.5	118.3	70.18	56.95	1.002	0.995	0.9976	1.0217
399.55	0.5590	0.6075	− 1555	− 1344	136.2	118.1	72.80	58.23	1.003	0.993	0.9957	1.0124
399.75	0.5419	0.5880	− 1553	− 1343	136.2	118.1	73.11	58.62	1.003	0.997	0.9899	1.0172
400.25	0.4467	0.4960	− 1548	− 1340	136.1	118.0	74.28	59.42	1.004	0.997	0.9980	1.0155
400.65	0.3950	0.4402	− 1539	− 1335	137.0	117.9	75.03	60.23	1.005	0.997	0.9927	1.0185
401.35	0.3250	0.3725	− 1535	− 1333	135.9	117.9	76.55	61.46	1.005	0.998	1.0007	1.0018
402.65	0.2110	0.2022	− 1521	− 1325	135.7	117.7	79.42	63.78	1.006	0.999	1.0052	1.0490
403.05	0.1430	0.1721	− 1517	− 1322	135.6	117.6	80.22	64.65	1.007	0.999	1.0046	0.9887
404.10	0.0000	0.0000	− 1526	− 1330	135.5	117.5	82.67	66.64	–	–	–	–

Table 6 Antoine constants of the pure liquids of this study, used in connection with Eqn. (7).

Substance	*A*	*B*	*C*
p-xylene	14.0618	3347.25	−57.84
1,2-Dichloroethane	14.5305	3128.63	−41.15
1,1,1,-Trichloroethane	13.9904	2802.75	−48.15
1,1,2,2-Tetrachloro-ethane	14.0653	3374.13	−62.15

The vapour phase imperfection coefficients z_1 and z_2 calculated from

$$z_1 = \exp[\{(p - p^0{}_1)(B_{11} - V_1{}^L) + p y_2{}^2 \delta_{12}\}/\mathrm{RT}] \tag{8}$$

$$z_2 = \exp[\{(p - p^0{}_2)(B_{22} - V_2{}^L) + p y_1{}^2 \delta_{12}\}/\mathrm{RT}] \tag{9}$$

with

$$\delta_{12} = 2B_{12} - B_{11} - B_{22} \tag{10}$$

are also recorded in Tables 3–5. The pure component second virial coefficients for p-xylene are calculated from Tsonopoulos equation[8], while for 1,2-dichloroethane, 1,1,1-trichlorethane, they are interpolated from the data given by Dymond and Smith[9] and Bohmhammd and Manchen[10]. The second Virial Coefficients of 1,1,2, 2-tetrachloroethane are calculated from the generalized equation

$$B/V_c = 25.208 - 192.116 T_R - 417.455 T_R^2 - 368.78 T_R^3 + 116.82 T_R^4 \tag{11}$$

developed on the basis of the available literature data on ethylchloride, 1,2-dichloroethane and 1,1,1-trichloroethane. All the numerical values of pure component second virial coefficients are noted in Tables 3–5. Cross-second virial coefficients (B_{12}) are calculated from the Pitzer and curl[11] type generalization described by Van Ness and Abbott[12]. The correlation of Yen and Woods[13] gave the values of molar volumes of the pure components given in Table 3–5. The critical properties and the other data needed in the calculations are collected from Reid *et al.*[14].

THERMODYNAMIC CONSISTENCY

To test the thermodynamic consistency, the practical procedure described by Fredenslund *et al.*[15] based on the ideas originaly proposed by Van Vess *et al.*,[16] and Abbott and Van Ness[17] is used. The excess Gibbs free energy G^E is related to liquid composition in the form:

$$(G^E/\mathrm{RT}) = x_1 \ln \tau_1 + x_2 \ln \tau_2 = g = x_1(1 - x_1)\sum a_k L_k(x_1) \tag{12}$$

where $L_k(x_1)$ represents the Legendre function given by

$$L_k(x_1) = (2k-1)(2x_1-1)L_{k-1}(x_1) - (K-1)L_{k-2}(x_1)/k \qquad (13)$$

with $k = 0, 1, 2 \ldots n$. The set of systems studied in this work could be represented to good accuracy by the first order Legendre polynomials with the coefficients A_0 and A_1 given in Table 7. The coefficients are used to calculate the activity coefficient γ_1 through the equation

$$\ln\gamma_1 = g + (1-x_1)(dg/dx_1) \qquad (14)$$

Values of y_1, calculated from Eqn. (5) after substituting the other variables, compared with the measured values of y_1, with an average absolute departure of less than 0.01 units as shown in Table 7, indicating that the data are thermodynamically consistent.

The activity coefficient data are fitted to the Van Laar model:

$$g = A^1 x_1 x_2 \; [x_1(A^1/B^1) + x_2] \qquad (15)$$

and the Wilson model:

$$g = -x_1 \ln(x_1 + A_{12}x_2) - x_2 \ln(x_2 + A_{21}x_1) \qquad (16)$$

DISCUSSION

The results shown in Table 8 indicate that both the Van Laar and Wilson models adequately represent the phase equilibrium data. The general pattern of the phase diagrams (not shown in this paper) are comparable to the literature data[1-3,5]. The lowering of the total pressure from about 91.1 kPa to 66.5 kPa has reduced the boiling temperatures of the mixtures by about 5–10 K and some what broadened

Table 7 Coefficients of the Legendre polynomial and average departure in the calculation of y_1.

Mixture	*Coefficients of Legendre polynomial*	*No. of observations*	*Average absolute deviation in y_1*
p-xylene + 1,2-dichloroethane	$A_0 = 0.0450$ $A_1 = 0.0365$	12	0.001
p-xylene + 1,1,1, 1-trichloroethane	$A_0 = -0.1775$ $A_1 = 0.2020$	9	0.003
p-xylene + 1,12,2-trichloroethane	$A_0 = 0.0250$ $A_1 = 0.0380$	9	0.002

Table 8 Constants of the Van Laar and Wilson equations.

System	*Model constants*	*PAAD in* τ_1^a
p-xylene + 1,2-dichloroethane	Van Laan: $A^1 = 0.0815$	0.24
	$B^1 = 0.0085$	
	Wilson: $A_{12} = 0.4561$	1.00
	$A_{21} = 1.7081$	
p-xylene + 1,1,1-trichlorethane	Van Laan: $A^1 = 0.3795$	0.75
	$B^1 = 0.0245$	
	Wilson: $A_{12} = 0.2132$	1.21
	$A_{21} = 2.1432$	
p-xylene + 1,1,2,2-dichloroethane	Van Laan: $A^1 = 0.0630$	0.71
	$B^1 = 0.0130$	
	Wilson: $A_{12} = 0.5150$	0.85
	$A_{21} = 1.6005$	

PAAD in $\tau_1 = [|(\tau_1\text{expt} - \tau_1\text{cal})/\tau_1\text{exp}|] \times 100/N$ where N is the number of observations.

the phase diagram. The activity coefficients are near unity and there is no clear trend with composition, probably due to fluctuations in the total pressure.

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