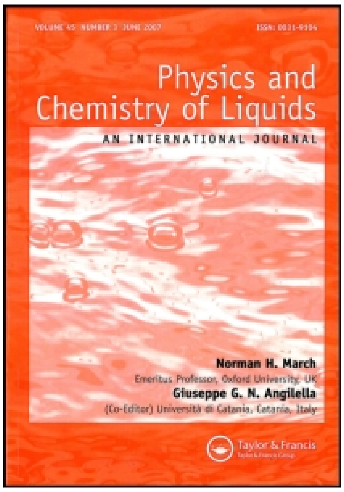

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ISOBARIC VAPOUR-LIQUID EQUILIBRIA IN THE ALLYL ALCOHOL + 1, 1, 2, 2 - TETRACHLOROETHANE SYSTEM

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Isobaric VLE are measured at 200, 500 and 706 mm Hg for ten liquid phase compositions spread evenly over the entire mole fraction range using a Swietoslawski type ebullimeter. The bubble temperature (t) - liquid phase mole fraction(x) data collected are found to be well represented by the Wilson model.

Keywords: Vapour-liquid equilibrium; bubble point; allyl alcohol

1. INTRODUCTION

In continuation of the interest in the phase equilibria of binary mixtures with an alcohol as one component and a chloroethane as the other [1 – 5], this study on the vapour-liquid equilibira of allyl alcohol + 1,1,2,2-tetrachloroethane mixtures has been taken up. There is no published information on the phase equilibrium of this system. The bubble temperature(t) - liquid phase composition(x) measurements have been carried out at 200, 500 and 706 mm Hg, to study the effect of pressure on phase equilibrium.

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2. EXPERIMENTAL

A Swietoslawski type ebulliometer, quite similar to the one described by Hala *et al.* [6], is used for the experiments. A good vacuum pump, connected through a mercury manometer in line facilitated the creation and maintenance of the chosen pressures to with in ± 1 mm Hg. The bubble-point temperatures are measured to an accuracy of ± 0.1°C by means of a carefully calibrated mercury-in-glass thermometer. The mixtures are prepared gravimetrically and placed in the ebulliometer. The heating rate is adjusted to yield the desired condensate drop rate of about 30 per minute, following the recommendation of Hala *et al.* [6]. The equilibrium values of the bubble point temperature are measured after maintaining the steady drop rate for sufficient length of time (at least 30 minutes) and the thermometer showed no change in temperature for at least 15 minutes.

3. MATERIALS

Allyl alcohol (2-Propen-1-ol) of AR grade procured from SD Fine-Chem. Ltd., Boisar(India), has been fractionally distilled twice and the middle fraction of the second distillation is collected for use in the experiments.

1,1,2,2-Tetrachloroethane of AR grade procured from SD Fine Chem. Ltd., Boisar(India), is shaken with concentrated sulphuric acid for 10 minutes at 80 to 90°C. The discoloured acid is removed and the acid washing repeated several times till discolouration of the acid stops occuring. 1,1,2,2-Tetrachloroethane, after the treatment is washed with distilled water thrice and steam distilled. After drying over potassium carbonate the sample is fractionally distilled twice. During the fractionation, 0.5 g phenol is added as the stabilizer. The middle fraction of the second distillation is stored in amber coloured bottles for use in the experiments.

A packed column of length equal to 30 theoretical plates is employed for the final stage of purification of both the substances. Based on the comparison of the physical properties of the pure liquids with literature data [7,8] presented in Table I, the substances used in the present set of experiments are expected to be at least 99.8% pure.

TABLE I Comparison of the Physical Properties of the Pure Liquids at 293.15 K with Literature Data

Substance	*Density g/ml*	*Refractive index*	*Reference*
Allyl alcohol	0.8523	1.4132	This work
	0.8520	1.4130	7
1,1,2,2-Tetra-chloroethane	1.5933	1.4944	This work
	1.5930	1.4942	8

4. RESULTS AND DISCUSSION

The experimental bubble point temperature(t) - mole fraction of the liquid phase(x) measurements are correlated using the Wilson [9] equation in the form :

$$\ln \gamma_1 = -\ln(x_1 + \Lambda_{12}x_2) + \frac{\Lambda_{12}}{(x_1 + \Lambda_{12}x_2)} - \frac{\Lambda_{21}}{(x_2 + \Lambda_{21}x_1)} \tag{1}$$

$$\ln \gamma_2 = -\ln(x_2 + \Lambda_{21}x_1) + \frac{\Lambda_{21}}{(x_2 + \Lambda_{21}x_1)} - \frac{\Lambda_{12}}{(x_1 + \Lambda_{12}x_2)} \tag{2}$$

where

$$\Lambda_{12} = (V_2^L/V_1^L) \exp - (\lambda_{12} - \lambda_{11})/\mathrm{RT} \tag{3}$$

$$\Lambda_{21} = (V_1//V_2) \exp - (\lambda_{12} - \lambda_{22})/\mathrm{RT} \tag{4}$$

V^L_1 and V^L_2 are liquid molar volumes, and $(\lambda_{12} - \lambda_{11})/R$ $(\lambda_{12} - \lambda_{22})/R$ are the Wilson parameters. λ's are the energies of interaction between the moelcules designated by the subscripts. The optimum Wilson parameters $(\lambda_{12} - \lambda_{11})/R$ and $(\lambda_{12} - \lambda_{22})/R$ are obtained by minimizing the objective function ϕ defined as :

$$\phi = \sum |[(P_{\mathrm{cal}}/P_{\mathrm{expt}}) - 1]|^2 \tag{5}$$

Nelder-Mead optimization technique described in Kuester and Mize [10] is used. Vapour pressures required in the computations are

TABLE II Antoine Constants of the Pure Liquids

Substance	*A*	*B*	*C*
Allyl alcohol	7.34110	1271.47	188.00
1,1,2,2-Tetrachloro-ethane	7.00460	1444.30	205.10

TABLE III Vapour-liquid Equilibria of Allyl alcohol(1) + 1,1,2,2-Tetracholoroethane(2) System Wilson Parameters : $(\lambda_{12} - \lambda_{11})/R = 528.52°K (\lambda_{12} - \lambda_{22})/R = -96.84°K$, Std. Dev in T = 0.5°K

t,°C	x_1	y_1	γ_1	γ_2	$G^E/J/mol$
		Total Pressure = 200 mm Hq			
102.0	0.0000	0.0000	3.1291	1.0000	0
88.0	0.0636	0.4407	2.6150	1.0071	203
78.6	0.1773	0.6428	1.9492	1.0506	465
76.4	0.2420	0.6926	1.7063	1.0894	564
73.4	0.3397	0.7434	1.4533	1.1647	656
71.5	0.4454	0.7850	1.2763	1.2678	687
70.7	0.5478	0.8209	1.1638	1.3897	663
69.4	0.6517	0.8569	1.0884	1.5376	584
68.0	0.7356	0.8871	1.0478	1.6768	485
67.0	0.8520	0.9327	1.0139	1.9038	302
65.9	0.9453	0.9736	1.0018	2.1186	121
64.4	1.0000	1.0000	1.0000	2.2601	0
		Total Pressure = 500 mm Hq			
130.3	0.0000	0.0000	2.8851	1.0000	0
114.8	0.0636	0.4212	2.4720	1.0062	204
102.7	0.1773	0.6343	1.8962	1.0457	469
100.8	0.2420	0.6878	1.6751	1.0817	573
96.7	0.3397	0.7419	1.4390	1.1524	668
94.4	0.4454	0.7854	1.2702	1.2504	704
93.2	0.5478	0.8222	1.1612	1.3672	680
90.4	0.6517	0.8584	1.0875	1.5098	599
90.0	0.7356	0.8886	1.0475	1.6448	500
88.5	0.8520	0.9338	1.0139	1.8658	313
86.8	0.9453	0.9741	1.0018	2.0760	125
86.0	1.0000	1.0000	1.0000	2.2149	0
		Total Pressure = 706 mm Hq			
142.4	0.0000	0.0000	2.7965	1.0000	0
127.1	0.0636	0.4122	2.4184	1.0059	208
113.6	0.1773	0.6298	1.8753	1.0437	472
111.0	0.2420	0.6850	1.6626	1.0786	577
107.0	0.3397	0.7406	1.4331	1.1475	674
104.7	0.4454	0.7850	1.2675	1.2434	713
102.3	0.5478	0.8223	1.1601	1.3581	686
100.7	0.6517	0.8588	1.0870	1.4984	607
99.0	0.7356	0.8890	1.0473	1.6314	506
97.7	0.8520	0.9341	1.0139	1.8497	317
95.8	0.9453	0.9743	1.0018	2.0575	126
95.2	1.0000	1.0000	1.0000	2.1951	0

calculated from the Antoine constants given by Riddick *et al.* [11] and reproduced in Table II for ready reference. Liquid molar volumes are calculated from Yen and Woods [12] correlation. The values of the optimum Wilson parameters are noted along with detailed information on the observed bubble point temperature (t), the mole fraction of allyl alcohol in the liquid phase (x_1), and the calculated values of mole fraction of allyl alcohol in the vapour phase (y_1), the liquid phase activity coefficients (γ_1 and γ_2) and the excess Gibbs free energy G^E in Table III. Formation of azeotropic mixtures has not been observed in contrast to the case of allyl alcohol + 1, 2-dichloroethane and allyl alcohol + 1,1,1-trichloroethane systems.

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