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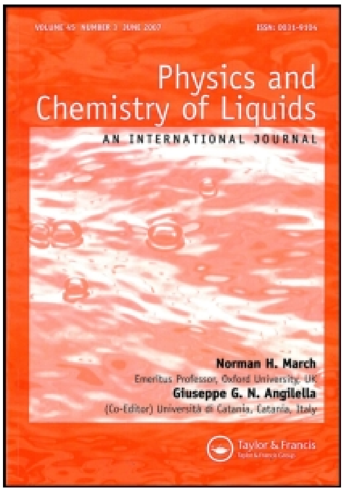

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Activity Coefficient and Excess GIBBS Free Energy of Allyl Alcohol with Tetrachloroethylene

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ACTIVITY COEFFICIENT AND EXCESS GIBBS FREE ENERGY OF ALLYL ALCOHOL WITH TETRACHLOROETHYLENE

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Isobaric vapour-liquid equilibrium data are measured at 200, 500 and 705 mm Hg at ten compositions, spread evenly, over the entire mole fraction range. The composition vs. boiling point (*x-t*) data are found to be well represented by the Wilson model. The optimum Wilson parameters are used to calculate the vapour phase compositions, activity coefficients and the excess Gibbs free energies.

Keywords: Vapour-liquid equilibrium; activity coefficient; excess Gibbs free energy; allyl alcohol; tetrachloroethylene

1. INTRODUCTION

In continuation of our interest in the phase equilibria of binary mixtures with an alcohol as one component and a chlorohydrocarbon as the other [1–6], this study on the vapour-liquid equilibrium of allyl alcohol(1) + tetrachloroethylene(2) mixtures has been taken up. There is no published information on the phase equilibrium of this system. The composition(x) - bubble temperature(t) relations have been measured at 200, 300 and 705 mm Hg, to study the effect of pressure on the phase equilibrium.

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2. EXPERIMENTAL

A Swietoslawski type ebulliometer, very similar in design to the one described by Hala *et al.* [7], is used. Connection of the ebulliometer, to a good vacuum system through a mercury column, facilitated the creation and maintenance of the chosen pressure to with in ± 1 mm Hg. The equilibrium temperatures are measured to an accuracy of ± 0.1°C, by means of carefully calibrated mercury-in-glass thermometers. The mixtures are prepared gravimetrically and placed in the ebuliiometer. The heating rate is adjusted to yield a condensate drop rate of about 30 per minute based on the recommendation of Hala *et al.* [7] The equilibrium temperature is measured after maintaining the steady drop rate for sufficient length of time (at least 30 minutes), and the thermometer showed no change in the temperature for at least 15 minutes.

3. MATERIALS

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

Tetrachloroethylene of spectroscopic grade, procured from S D Fine-Chem. Ltd., Boisar (India), is dried over sodium sulphate and fractionally distilled twice. The middle fraction of the second distillation is collected for use in the experiments.

A packed column of length equal to 30 theoretical plates is employed for the purification of both the substances. Based on the comparison of the physical properties with literature [8, 9] data, presented in Table I, the substances are expected to be at least 99.8% pure.

4. RESULTS AND DISCUSSION

The experimental (x-t) measurements are correlated using the Wilson [10] equation in the form

TABLE I Physical Properties of the Pure Liquid at 293.15 K

Substance	*Density (g/ml)*	*Refractive index*	*Reference*
Allyl alcohol	0.8523	1.41320	This work
	0.8520	1.41300	8
Tetrachloroethylene	1.6225	1.50550	This work
	1.6226	1.50547	9

$$\ln \gamma_1 = -\ln[x_1 + \Lambda_{12}x_2] + x_2\left[\frac{\Lambda_{12}}{x_1 + \Lambda_{12}x_2} - \frac{\Lambda_{21}}{x_2 + \Lambda_{21}x_1}\right] \quad (1)$$

$$\ln \gamma_2 = -\ln[x_2 + \Lambda_{21}x_1] + x_1\left[\frac{\Lambda_{21}}{x_2 + \Lambda_{21}x_1} - \frac{\Lambda_{12}}{x_1 + \Lambda_{12}x_2}\right] \quad (2)$$

where

$$\Lambda_{12} = (V_1^L/V_2^L)\exp\left[-(\lambda_{12} - \lambda_{11})/RT\right] \quad (3)$$

and

$$\Lambda_{21} = (V_2^L/V_1^L)\exp\left[-(\lambda_{12} - \lambda_{22})/RT\right] \quad (4)$$

V_1^L and V_2^L are liquid molar volumes and $(\lambda_{12}-\lambda_{11})$ and $(\lambda_{12}-\lambda_{22})$ are the Wilson parameters. λ's are the energies of interaction between the molecules designated by the subscripts. The optimum Wilson parameters are obtained by minimizing the objective function, ϕ defined as

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

Nelder-Mead optimization technique described in detail in Kuester and Mize [11] is used. Vapour pressures are calculated from the Antoine constants given by Dean [12] and reproduced in Table II, for ready reference. Liquid molar volumes are calculated from the Yen and Woods [13] correlation. The values of the optimum Wilson parameters are also noted along with the detailed information on the

TABLE II Antoine Constants of the Pure Liquids used in This work

Substance	*A*	*B*	*C*
Allyl alcohol	7.34110	1271.47	189.00
Tetrachloroethylene	6.97680	1386.90	217.52

TABLE III Vapour-Liquid Equilibrium of Allyl alcohol (1) + Tetrachloroethylene (2) system
Wilson Parameters: $(\lambda_{12}\text{-}\lambda_{11})/R = 1298.75$ K; $(\lambda_{12}\text{-}\lambda_{22})/R = 102.60$ K; Standard Deviation in Temperature = 0.3 K

$t(°c)$	x_1	y_1	γ_1	γ_2	G^E (*J/mol*)
		Total Pressure = 200 mm Hg			
79.1	0.0000	0.0000	44.3873	1.0000	0
60.4	0.0752	0.5116	7.9573	1.0560	572
61.2	0.1603	0.5275	3.9388	1.1548	947
60.5	0.2422	0.5369	2.6853	1.2698	1166
59.8	0.3374	0.5485	1.9935	1.4322	1303
59.6	0.4520	0.5665	1.5557	1.6816	1341
59.6	0.5434	0.5860	1.3471	1.9388	1284
59.3	0.6577	0.6212	1.1794	2.3668	1115
59.9	0.7541	0.6669	1.0891	2.8640	895
60.5	0.8551	0.7450	1.0306	3.5933	586
62.7	0.9526	0.8842	1.0033	4.6172	211
64.3	1.0000	1.0000	1.0000	5.2829	0
		Total Pressure = 500 mm Hg			
106.7	0.0000	0.0000	33.7880	1.0000	0
84.4	0.0752	0.5332	7.7888	1.0505	595
83.8	0.1603	0.5540	3.8932	1.1466	988
83.0	0.2422	0.5647	2.6594	1.2596	1219
82.1	0.3374	0.5772	1.9770	1.4194	1365
81.5	0.4520	0.5958	1.5453	1.6645	1403
81.5	0.5434	0.6157	1.3998	1.9183	1354
81.5	0.6577	0.6508	1.1751	2.3331	1168
81.9	0.7541	0.6956	1.0867	2.8139	936
82.2	0.8551	0.7703	1.0296	3.5125	611
83.7	0.9526	0.8985	1.0032	4.4807	220
85.9	1.0000	1.0000	1.0000	5.1027	0
		Total Pressure = 705 mm Hg			
118.4	0.0000	0.0000	30.5488	1.0000	0
93.9	0.0752	0.5392	7.7334	1.0480	602
92.6	0.1603	0.5626	3.8783	1.1428	1002
92.4	0.2422	0.5739	2.6503	1.2549	1241
92.9	0.3374	0.5868	1.9708	1.4136	1391
91.1	0.4520	0.6038	1.5694	1.6328	1431
90.8	0.5434	0.6257	1.3371	1.9064	1369
90.7	0.6577	0.6609	1.1734	2.3187	1189
91.0	0.7541	0.7054	1.0858	2.7928	953
91.6	0.8551	0.7788	1.0293	3.4789	623
92.9	0.9526	0.9027	1.0031	4.4246	232
95.0	1.0000	1.0000	1.0000	5.0291	0

TABLE IV Azeotropic Conditions

Pressure (mm Hg)	*Temperature (°C)*	*Mole Fraction of Allyl alcohol*
200	59.5	0.6025
500	81.1	0.6440
705	90.9	0.6652

observed bubble point temperature (t), mole fraction of the allyl alcohol in the liquid phase (x_1), and the calculated values of the mole fraction of the 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. The prospect of formation of azeotropes at the different pressures as shown in Table IV, is predicted from the model. Experimental investigations confirmed the formation of azeotropes under the conditions noted in the table, indicating that the data and the representation presented in this paper are reliable with in the stated limits of experimental errors.

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