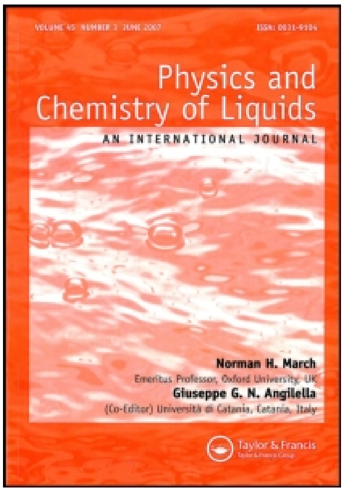

Physics and Chemistry of Liquids
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713646857

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To cite this Article Kumar, R. Vijaya , Rao, M. Anand , Rao, M. Venkateshwara and Prasad, D. H. L.(1996) 'Isobaric Vapour-Liquid Equilibria in the Allyl Alcohol 1,1,1-Trichloroethane System', Physics and Chemistry of Liquids, 32: 4, 233 — 237

To link to this Article: DOI: 10.1080/00319109608030538

URL: http://dx.doi.org/10.1080/00319109608030538

Phys. Chem. Liq., 1996, Vol. 32, pp. 233–237
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ISOBARIC VAPOUR-LIQUID EQUILIBRIA IN THE ALLYL ALCOHOL + 1,1,1-TRICHLOROETHANE SYSTEM

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(Received 3 March 1996)

Isobaric VLE are measured at 200, 500 and 705 mm Hg at ten compositions, spread evenly over the entire liquid mole fraction range, employing a Swietoslawski type ebulliometer. The bubble temperature (t)-liquid phase composition (x) data collected are found to be well represented by the Wilson model.

Keywords: Vapour-liquid equilibrium; allyl alcohol; 1, 1, 1-trichloroethane.

INTRODUCTION

In continuation of the investigators interest in the phase equilibria of the binary systems with an alcohol as one component and a chloroethane as the other [1–4], this study on the vapour-liquid equilibrium of allyl alcohol + 1, 1, 1-trichloroethane mixtures has been taken up. There is no published phase equilibrium information on this system. The bubble temperature (t)-composition (x) relations have been measured at 200, 500 and 705 mm Hg to study the effect of pressure on the phase equilibrium.

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EXPERIMENTAL

A Swietoslawski type ebulliometer, quite similar in design to the one described by Hala *et al.* [5] is used. A good vacuum pump connected through a mercury manometer in line facilitated the creation and maintenance of the chosen pressures to within ± 1 mm Hg. The bubble point temperatures are measured to an accuracy of ± 0.1°C, by means of a carefully calibrated mercury-1n-glass thermometer. The mixtures are prepared gravimetrically and placed in the ebulliometer. The heating rate is slowly adjusted to yield the desired condensate drop rate of about 30 per minute, following the recommendation of Hala *et al.* [5] The equilibrium value of the bubble point temperature is measured after maintaining the steady drop rate for sufficient length of time (at least 30 minutes) and the thermometer showed no change for at least 15 minutes.

MATERIALS

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

1,1,1-Trichloroethane of A R grade, procured from SD Fine-Chem. Ltd., Boisar (India) has been washed with concentrated hydrochloric acid, followed by 10% sodium chloride solution, dried over calcium chloride and finally distilled (fractionally) twice. The middle fraction of the second distillation is collected and stored in amber coloured bottles for use in the experimental work, after adding 0.5 g phenol as stabilizer.

A packed column of length equal to 30 theoretical plates is employed for the purification of both the pure liquids. Based on the comparison of the physical properties with the literature data [6, 7] presented in Table I, the substances used in this work are expected to be at least 99.8% pure.

TABLE I Comparison of the physical properties of pure liquids at 293.15 K with literature data from Mary Howe Grant [6, 7]

Substance	*Density g · ml^{-1}*	*Refractive-index*	*Reference*
Allyl alcohol	0.8523	1.4132	This work
	0.8520	1.4130	6
1,1,1-Trichloroethane	1.3250	1.4375	This work
	1.3249	1.4377	7

RESULTS AND DISCUSSION

The experimental *t*-*x* measurements are correlated using the Wilson [8] equation in the form

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

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

where

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

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

V_1^L and V_2^L are the 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 molecules 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

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

Nelder-Mead optimization technique, described in detail by Kuester and Mize [9] is used. Vapour pressures required in the computations are calculated from the Antoine constants give by Dean [10] and reproduced in Table II for ready reference. Liquid molar volumes are calculated from Yen and Woods [11] correlation. The values of the optimum Wilson parameters are noted along with the 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

TABLE II Antoine constants of the pure liquids used in this work

Substance	*A*	*B*	*C*
Allyl alcohol	7.34110	1271.47	188.000
1,1,1-Trichloroethane	6.86265	1182.53	222.894

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 azeotropic mixtures at different pressures as shown in Table IV is predicted based on the model calculations. Experimental investigations confirmed the formation of azeotropes under the conditions noted in the table. The data and the

TABLE III Vapour-liquid equilibria of Allyl alcohol(1) + 1,1,1-Trichloroethane system. Wilson parameters: $(\lambda_{12}-\lambda_{11})/R = 631.82$ K, $(\lambda_{12}-\lambda_{22})/R = 25.29$ K, standard deviation in temp. = 0.5 K

t, °C	x_1	y_1	γ_1	γ_2	G^E, $J\cdot mol^{-1}$
		Total Pressure = 200 mm Hg			
36.3	0.0000	0.0000	7.6209	1.0000	0
35.8	0.0564	0.0640	4.9587	1.0120	261
36.4	0.1533	0.1069	3.0193	1.0706	585
36.7	0.2409	0.1268	2.2330	1.1518	780
37.0	0.3851	0.1520	1.5991	1.3375	927
37.5	0.4121	0.1569	1.5250	1.3800	938
39.2	0.5371	0.1841	1.2786	1.6149	919
41.6	0.6667	0.2290	1.1296	1.9415	791
46.2	0.7832	0.3063	1.0515	2.3341	592
49.6	0.8729	0.4299	1.0171	2.7210	381
56.6	0.9485	0.6595	1.0028	3.1157	168
64.3	1.0000	1.0000	1.0000	3.4207	0
		Total Pressure = 500 mm Hg			
61.1	0.0000	0.0000	6.5289	1.0000	0
59.4	0.0564	0.0832	4.5259	1.0104	263
59.9	0.1533	0.1428	2.8896	1.0636	595
59.6	0.2409	0.1710	2.1733	1.1393	791
59.9	0.3851	0.2057	1.5809	1.3152	955
60.6	0.4121	0.2122	1.5098	1.3152	968
62.1	0.5371	0.2468	1.2718	1.5805	950
65.1	0.6667	0.3012	1.1267	1.8935	822
67.2	0.7832	0.3885	1.0503	2.2696	611
72.0	0.8729	0.5164	1.0167	2.6397	396
79.2	0.9458	0.7277	1.0027	3.0179	183
85.9	1.0000	1.0000	1.0000	3.3120	0
		Total Pressure = 705 mm Hg			
71.8	0.0000	0.0000	6.1541	1.0000	0
69.6	0.0564	0.0908	4.3652	1.0098	263
68.8	0.1533	0.1573	2.8382	1.0609	597
69.5	0.2409	0.1890	2.1544	1.1344	800
70.0	0.3851	0.2275	1.5731	1.3065	967
70.5	0.4121	0.2346	1.5034	1.3463	979
72.3	0.5371	0.2722	1.2689	1.5670	964
74.0	0.6667	0.3296	1.1254	1.8746	832
77.7	0.7832	0.4196	1.0498	2.2440	622
82.5	0.8729	0.5475	1.0165	2.6076	407
87.5	0.9484	0.7503	1.0027	2.9790	180
95.1	1.0000	1.0000	1.0000	3.2680	0

TABLE IV Azeotropic conditions

Pressure, mm Hg	*Temperature, °C*	*Mole fraction of Allyl alcohol*
200	36.3	0.0750
500	59.2	0.1250
705	69.0	0.1580

representation presented in the paper are therefore expected to be reliable with in the stated limits of the experimental error.

Acknowledgements

The authors place on record the help received from Mr. Y. V. L. Ravikumar on the computational aspects of the problem.

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