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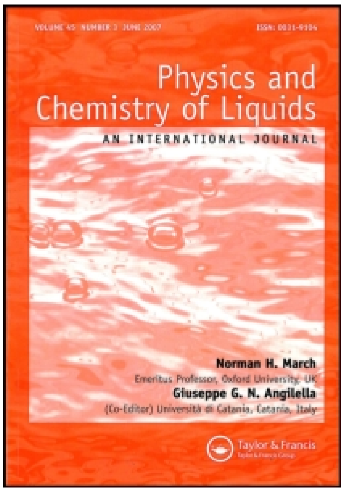

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Activity Coefficient and Excess Gibbs Free Energies of Propargyl Alcohol with Trichloroethylene

R. Vijaya Kumar[a]; M. Anand Rao[a]; M. Venkateshwara Rao[b]; D. H. L. Prasad[c]
[a] Department of Chemistry, Osmania University, [b] College of Technology, Osmania University, [c] Indian Institute of Chemical Technology, Hyderabad, India

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ACTIVITY COEFFICIENT AND EXCESS GIBBS FREE ENERGIES OF PROPARGYL ALCOHOL WITH TRICHLOROETHYLENE

R. VIJAYA KUMAR[a], M. ANAND RAO[a],
M. VENKATESHWARA RAO[b] and D. H. L. PRASAD[c,*]

[a] *Department of Chemistry, Osmania University;*
[b] *College of Technology, Osmania University;*
[c] *Indian Institute of Chemical Technology, Hyderabad-500 007 (India)*

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Isobaric vapour-liquid equilibrium data are measured at 200, 500 and 707 mm Hg at ten compositions spread evenly over the entire liquid mole fraction range, employing a Swietoslawski type ebulliometer. The liquid phase composition *vs.* bubble temperature ($x-t$) data are found to be well represented by 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

INTRODUCTION

In continuation of the investigators interest in the phase equilibria of binary mixtures with an alcohol as one component and a chlorohydrocarbon as the other [1–5], this study on the vapour-liquid equilibrium of propargyl alcohol(1) + trichloroethylene(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, 500 and 707 mm Hg, to study the effect of pressure on the phase equilibrium.

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*Corresponding author.

EXPERIMENTAL

A Swietoslawski type ebulliometer very similar to the one described by Hala *et al.* [6] is used. Connection of the ebulliometer to a good vacuum system, through a mercury manometer in line, facilitated the creation and maintenance of the chosen pressure with in ± 1 mm Hg. The equilibrium 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 as suggested by Hala *et al.* [6]. The equilibrium temperature is measured after maintaining a steady drop rate for at least 30 minutes and the thermometer showed no change in the reading for at least 15 minutes.

MATERIALS

Propargyl alcohol (2-Propyn-1-ol) procured from Fluka Company (Switzerland), certified to be greater than 99% pure, is fractionally distilled twice after adding 0.25–0.50% aqueous hydrogen chloride to prevent decomposition during distillation. The middle fraction of the second distillation is used for the experimental studies.

Spectroscopic grade trichloroethylene procured from S D Fine-Chem. Ltd., Boisar (India) has been steam distilled from 10% calcium hydroxide slurry. The organic phase is collected at −30 to −50°C and ice removed by filtration. The filtrate is fractionally distilled twice. 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 used for the purification of both the substances. Based on a comparison of the physical properties with literature [7, 8] data presented in Table I, the substances are expected to be at least 99.8% pure.

RESULTS AND DISCUSSION

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

TABLE I Comparison of physical properties of pure liquids at 298.15 K with literature data

Substance	*Density (g/ml)*	*Refractive index*	*Reference*
Propagyl alcohol	0.9481	1.4312	This work
	0.9480	1.4310	[7]
Trichloroethylene	1.4639	1.4781	This work
	1.4640	1.4782	[8]

form:

$$\ln\gamma_1 = -\ln(X_1 + \Lambda_{12}X_{12}) + X_2\left[\frac{\Lambda_{12}}{X_1 + \Lambda_{12}X_2} - \frac{\Lambda_{21}}{X_2 + \Lambda_{21}X_1}\right] \quad (1)$$

and

$$\ln\gamma_2 = -\ln(X_1 + \Lambda_{21}X_1) + X_1\left[\frac{\Lambda_{21}}{X_2 + \Lambda_{21}X_1} - \frac{\Lambda_{12}}{X_1 + \Lambda_{12}X_2}\right] \quad (2)$$

where

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

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

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

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

Nelder-Mead optimization technique described in detail in Kuester and Mize [10] is used. Vapour pressures required are calculated from the Antoine constants given in 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 also noted along with the detailed information on the

TABLE II Antoine constants of the pure liquids

Substance	*A*	*B*	*C*
Propargyl alcohol	8.65600	2226.40	273.20
Trichloroethylene	7.02808	1315.04	230.00

TABLE III Vapour liquid equilibrium of propargyl alcohol(1) + trichloroethylene (2) system Wilson Parameters: $(\lambda_{12}-\lambda_{11})/R = 854.24\,K$; $(\lambda_{12}-\lambda_{22})/R = 215.56\,K$; stand and deviation = 0.5 K

$t/°C$	x_1	y_1	γ_1	γ_2	$G^E/\ J/mol$
		Total Pressure = 200 mm Hg			
48.2	0.0000	0.0000	18.4873	1.0000	0
45.8	0.0633	0.1239	8.2244	1.0247	414
46.3	0.1629	0.1579	4.1233	1.1150	855
45.6	0.2592	0.1687	2.7595	1.2399	1119
46.7	0.3708	0.1771	2.0032	1.4343	1289
46.5	0.4914	0.1869	1.5648	1.7279	1324
47.3	0.5473	0.1928	1.4286	1.9060	1298
48.4	0.6866	0.2164	1.1953	2.5366	1107
49.5	0.7594	0.2398	1.1153	3.0333	939
53.6	0.8500	0.2987	1.0460	3.9303	662
60.9	0.9382	0.4724	1.0082	5.2828	306
77.1	1.0000	1.0000	1.0000	6.5705	0
		Total Pressure = 500 mm Hg			
73.8	0.0000	0.0000	14.9412	1.0000	0
69.9	0.0633	0.1426	7.5224	1.0214	421
69.3	0.1629	0.1888	3.9633	1.1052	885
69.3	0.2592	0.2044	2.6903	1.2243	1157
70.3	0.3708	0.2161	1.9695	1.4116	1336
69.9	0.4914	0.2290	1.5458	1.6947	1376
70.3	0.5473	0.2365	1.4137	1.8662	1355
71.9	0.6866	0.2660	1.1875	2.4690	1151
73.6	0.7594	0.2944	1.1102	2.9388	977
77.2	0.8500	0.3632	1.0436	3.7754	686
85.3	0.9382	0.5485	1.0072	5.0115	318
100.5	1.0000	1.0000	1.0000	6.1854	0
		Total Pressure = 707 mm Hg			
84.7	0.0000	0.0000	13.7651	1.0000	0
80.3	0.0633	0.1505	7.2520	1.0202	424
80.0	0.1629	0.2023	3.8980	1.1013	913
79.6	0.2592	0.2201	2.6626	1.2180	1364
80.8	0.3708	0.2333	1.9556	1.4023	1359
79.7	0.4014	0.2477	1.5380	1.6813	1339
81.8	0.5473	0.2559	1.4077	1.8510	1374
82.0	0.6866	0.2879	1.1844	2.4422	1169
84.6	0.7594	0.3182	1.1082	2.9017	988
87.9	0.8500	0.3907	1.0427	3.7158	698
96.5	0.9382	0.5783	1.0074	4.9094	323
100.0	1.0000	1.0000	1.0000	6.0404	0

TABLE IV Azeotropic conditions

Pressure/mm Hg	*Temperature/° C*	*Mole fraction Propargyl alcohol*
200	45.8	0.1575
500	67.2	0.1923
707	80.0	0.2150

observed bubble point temperature (t), mole fraction of the propargyl alcohol in the liquid phase (x_1) and the calculated values of: mole fraction of propargyl 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 as shown in Table IV, is predicted based on the model. Experimental investigation confirmed the formation of azeotropes under the conditions noted in the table. The data and the representation presented in the paper are therefore expected to be reliable within the stated limits of experimental error.

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