Bubble Temperature Measurements on 2-Propyn-1-ol with 1,2-Dichloroethane, 1,1,1-Trichloroethane, and 1,1,2,2-Tetrachloroethane[†]

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Bubble temperatures at 26.6, 66.5, and 93.8 kPa at ten liquid phase compositions spread evenly over the entire composition range are measured for the three binary systems noted in the title, using a Swietoslawski type ebulliometer. The temperature (T)−composition (x) data are found to be well represented by the Wilson model. The calculated values of the vapor phase composition and the liquid phase activity coefficients are also presented.

Introduction

In continuation of the investigators studies on the phase equilibria of binary mixtures with an alcohol as one component and a chloroethane as the other, Kiran Kumar et al. (1991), Lakshman et al. (1991), and Srinivas et al. (1991), this study on the bubble temperature measurements of 2-propyn-1-ol (1) + 1,2-dichloroethane (2), 2-propyn-1-ol (1) + 1,1,1-trichloroethane (2), and 2-propyn-1-ol (1) + 1,1,2,2-tetrachloroethane (2) binary mixtures is undertaken. There is no published phase equilibrium information on these systems. The equilibrium temperature (T)−composition (x) relations have been studied at 26.6, 66.5, and 93.8 kPa.

Experimental Section

A Swietoslawski type ebulliometer, very similar to the one described by Hala et al. (1958) is used for the experiments. The ebulliometer is connected to a vacuum pump capable of producing good vacuum (better than 0.05 kPa) within a few minutes, through a closed-end mercury manometer and a large buffer vessel. This arrangement provided for the maintenance and measurement of the needed subatmospheric pressures by means of two Teflon needle valves in line. The accuracy of pressure measurement is believed to be better than 0.133 kPa. A mercury-in-glass thermometer, calibrated by means of point to point comparison with a platinum resistance thermometer certified by the National Institute of Standards and Technology (Boulder, CO), has been used to measure the equilibrium temperature of the gas−liquid mixture, impinging on the thermo-well (filled with mercury) due to the Cottrell effect, to within ±0.1 K. The mixture samples to be studied are prepared by weighing the desired amounts of the two components and stirring well before charging into the ebulliometer. A Mettler balance accurate to 0.0001 g is used for measuring all the weights. The heating rate is adjusted to yield the desired condensate drop rate of about 30 per minute, in accordance with the suggestion of Hala et al. (1958). The method suggested by Hala et al., in combination with the technique of subjecting the test sample several times to the lowest pressure to be studied and reverting to atmopsheric pressure, has provided for the constancy of composition during the experiments. A gas chromatograph is used to verify the composition at the beginning and end of each experiment. The equilibrium temperature is measured after maintaining the steady state conditions recorded by the steady drop rate and constancy of equilibrium temperature for at least 30 min.

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

AR grade 1,2-dichloroethane procured from BDH, Bombay (India), is further purified by washing with dilute potassium hydroxide solution and water, dried over phosphorus pentoxide, and fractionally distilled twice. The middle fraction of the second distillation is stored in amber-colored bottles for use in the experiments.

AR grade 1,1,1-Tetrachloroethane procured from SD Fine-Chemicals, Boisar (India), is washed with concentrated hydrochloric acid, followed by washing with 10% sodium chloride solution and drying over calcium chloride. Phenol (0.5 g) is added before subjecting the samples to fractional distillation. The middle fraction of the second distillation is stored in amber-colored bottles for use in the experiments.

AR grade 1,1,2,2-tetrachloroethane procured from SD Fine-Chemicals, Boisar (India), is shaken with concentrated sulfuric acid for 10 min at 355 K. The discolored acid is removed and the acid washing repeated several times till the acid discoloration stops. The product is then washed with water, steam distilled, again washed with water, dried over potassium carbonate, and fractionally

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[†] IICT Communication No. 3643.

S0021-9568(96)00015-5 CCC: $12.00

Table 1. Comparison of Refractive Index and Density of the Pure Liquids with Literature Data at 298.15 K

substance	n_D		δ/kg·m^{-3}	
2-propyn-1-ol	this work	1.4302	this work	945.1
	Rogers & Panish (1955)	1.4300	Rogers & Panish (1955)	945.0
1,2-dichloroethane	this work	1.4420	this work	1246.4
	Bigg et al. (1964)	1.4421	Bigg et al. (1964)	1246.37
1,1,1-trichloroethane	this work	1.4360	this work	1330.0
	Mansson et al. (1971)	1.4359	Mansson et al. (1971)	1329.9
1,1,2,2-tetrachloroethane	this work	1.4915	this work	1586.7
	Mumford & Phillips (1950)	1.4914	Mumford & Phillips (1950)	1586.66

Table 2. Antoine Constants of the Pure Liquids used in Equation 5

substance	*A*	*B*	*C*	ref
2-propyn-1-ol	7.781	2226.4	0	Antara Chemicals Division (1957)
1,2-dichloroethane	6.283 56	1341.370	−43.100	Dreisbach & Martin (1949)
1,1,1-trichloroethane	5.987 55	1182.527	−50.256	Ambrose et al. (1973)
1,1,2,2-tetrachloroethane	6.129 5	1444.3	−68.050	Patel et al. (1979)

Table 3. Vapor−Liquid Equilibrium of 2-Propyn-1-ol (1) + 1,2-Dichloroethane (2) System [Wilson Constants: $(\lambda_{21} - \lambda_{11})/R = 609.21$ K; $(\lambda_{21} - \lambda_{22})/R = -72.57$ K; Std Dev (*e*) = 0.3 K]

Total Pressure = 26.6 kPa				
0.000	319.25	0.000	5.359	1.000
0.050	319.45	0.046	3.785	1.009
0.143	319.85	0.086	2.441	1.055
0.245	321.15	0.112	1.806	1.133
0.322	321.05	0.129	1.538	1.206
0.477	322.65	0.169	1.242	1.386
0.526	323.85	0.193	1.166	1.480
0.621	325.45	0.226	1.106	1.592
0.753	329.95	0.319	1.040	1.816
0.818	333.65	0.395	1.021	1.939
0.938	342.45	0.676	1.002	2.196
1.000	350.25	1.000	1.000	2.343
Total Pressure = 66.5 kPa				
0.000	349.85	0.000	4.745	1.000
0.050	343.85	0.053	3.517	1.007
0.143	343.85	0.103	2.367	1.050
0.245	344.65	0.136	1.783	1.132
0.322	344.65	0.158	1.528	1.192
0.477	346.75	0.207	1.241	1.365
0.526	348.05	0.235	1.165	1.457
0.621	350.35	0.272	1.106	1.566
0.753	354.75	0.375	1.040	1.787
0.818	357.55	0.454	1.021	1.909
0.938	366.55	0.725	1.002	2.165
1.000	373.65	1.000	1.000	2.311
Total Pressure = 93.8 kPa				
0.000	354.35	0.000	4.529	1.000
0.050	353.75	0.056	3.415	1.007
0.143	354.05	0.111	2.336	1.048
0.245	355.05	0.147	1.773	1.118
0.322	355.25	0.171	1.524	1.187
0.477	356.95	0.223	1.240	1.357
0.526	358.05	0.253	1.165	1.448
0.621	360.95	0.293	1.106	1.556
0.753	364.25	0.398	1.040	1.776
0.818	367.75	0.478	1.021	1.897
0.938	376.75	0.743	1.002	2.152
1.000	383.35	1.000	1.000	2.298

Table 4. Vapor−Liquid Equilibrium of 2-Propyn-1-ol (1) + 1,1,1-Trichloroethane (2) System [Wilson Parameters: $(\lambda_{12} - \lambda_{11})/R = 758.83$ K; $(\lambda_{12} - \lambda_{22})/R = 171.41$ K; Std Dev (*e*) = 0.5 K]

Total Pressure = 26.6 kPa				
0.000	309.45	0.000	13.274	1.000
0.059	309.25	0.062	7.348	1.017
0.162	309.55	0.091	3.941	1.096
0.267	310.15	0.103	2.631	1.221
0.356	310.25	0.109	2.055	1.365
0.478	310.95	0.117	1.596	1.634
0.563	310.35	0.124	1.392	1.894
0.637	311.55	0.132	1.264	2.188
0.740	313.35	0.152	1.134	2.770
0.848	318.15	0.204	1.047	3.749
0.951	331.05	0.418	1.005	5.269
1.000	350.25	1.000	1.000	6.201
Total Pressure = 66.5 kPa				
0.000	334.25	0.000	10.899	1.000
0.059	333.35	0.075	6.614	1.015
0.162	333.45	0.116	3.753	1.086
0.267	333.65	0.133	2.558	1.204
0.356	334.15	0.142	2.015	1.341
0.478	335.65	0.153	1.575	1.598
0.563	334.45	0.163	1.379	1.847
0.637	335.35	0.175	1.254	2.127
0.740	338.75	0.202	1.129	2.678
0.848	343.05	0.268	1.045	3.593
0.951	357.15	0.508	1.005	4.986
1.000	373.05	1.000	1.000	5.858
Total Pressure = 93.8 kPa				
0.000	344.95	0.000	10.098	1.000
0.059	343.45	0.080	6.337	1.014
0.162	343.75	0.127	3.676	1.083
0.267	344.05	0.147	2.528	1.198
0.356	344.55	0.157	1.999	1.331
0.478	346.05	0.171	1.567	1.584
0.563	345.05	0.182	1.373	1.828
0.637	346.05	0.195	1.250	2.102
0.740	349.55	0.225	1.127	2.642
0.848	354.05	0.297	1.044	3.532
0.951	368.45	0.545	1.005	4.881
1.000	383.35	1.000	1.000	5.729

distilled twice. The middle fraction of the second distillation is stored in amber-colored bottles for use in the experiments.

A packed column of height equivalent to 30 theoretical plates is employed for the purification of all the substances. Among the other tests, measurements on density and refractive index for sodium-D light are used to establish the purity of the substances used. Measurements on the density at 298.15 K are carried out by means of a pycnometer calibrated using demineralized and deionized water and a thermostat maintaining the temperature to within ±0.05 K. An Abbe refractometer, thermostated to within ±0.05 K, in conjunction with a sodium-D light source is used for the measurement of the refractive index. On the basis of a comparison of the density and refractive index at 298.15 K presented in Table 1, the substances used in the present set of experiments are expected to be at least 99.8% pure.

Results and Discussion

The experimental temperature (T)−composition (x) measurements are fitted to the Wilson (1964) model in the form

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

Table 5. Vapor–Liquid Equilibruim of 2-Propyn-1-ol (1) + 1,1,2,2-Tetrachloroethane (2) System [Wilson Parameters: $(\lambda_{12} - \lambda_{11})/R = 531.31$ K; $(\lambda_{12} - \lambda_{22})/R = 89.30$ K; Std Dev (e) = 0.3 K]

		Total Pressure = 26.6 kPa		
0.000	395.05	0.000	4.083	1.000
0.100	360.35	0.467	3.111	1.017
0.187	355.45	0.582	2.483	1.058
0.277	353.95	0.641	2.034	1.126
0.351	351.65	0.673	1.764	1.203
0.437	350.75	0.7 0	1.535	1.317
0.541	350.05	0.730	1.333	1.509
0.663	349.75	0.766	1.174	1.832
0.761	349.55	0.802	1.087	2.216
0.880	349.75	0.869	1.023	2.937
0.982	350.65	0.972	1.001	3.951
1.000	350.25	1.000	1.000	4.198
		Total Pressure = 66.5 kPa		
0.000	403.45	0.000	3.687	1.000
0.100	387.05	0.456	2.912	1.015
0.187	381.35	0.577	2.374	1.053
0.277	378.35	0.640	1.972	1.115
0.351	376.35	0.674	1.725	1.186
0.437	375.95	0.704	1.511	1.294
0.541	374.55	0.735	1.320	1.474
0.663	373.65	0.772	1.167	1.778
0.761	373.35	0.809	1.084	2.136
0.880	374.25	0.876	1.022	2.806
0.982	373.35	0.974	1.001	3.736
1.000	373.65	1.000	1.000	3.960
		Total Pressure = 93.8 kPa		
0.000	415.65	0.000	3.547	1.000
0.100	397.75	0.453	2.839	1.014
0.187	392.15	0.576	2.333	1.050
0.277	389.35	0.641	1.949	1.110
0.351	386.85	0.676	1.709	1.180
0.437	385.15	0.707	1.502	1.285
0.541	384.65	0.739	1.315	1.460
0.663	383.75	0.776	1.165	1.756
0.761	383.35	0.813	1.083	2.106
0.880	383.25	0.879	1.022	2.756
0.982	383.15	0.975	1.001	3.653
1.000	383.35	1.000	1.000	3.869

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

where

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

and

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

V_1^L and V_2^L are the pure 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 denoted 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

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

The Nelder–Mead optimization technique described in detail by Kuester and Mize (1973) is used. Vapor pressures required in the calculations are computed from the Antoine constants collected from the literature for the equation in the form

$$\log(P/\text{kPa}) = A - B/[(T/\text{K}) + C] \quad (6)$$

Table 6. Azeotropic Conditions

P/kPa	mole fraction of 2-propyn-1-ol	T/K
	2-Propyn-1-ol (1) + 1,2-Dichloroethane (2) System	
26.6	0.048	319.35
66.5	0.051	340.65
93.8	0.053	350.85
	2-Propyn-1-ol (1) + 1,1,1-Trichloroethane (2) System	
26.6	0.055	309.35
66.5	0.077	332.65
93.8	0.103	343.55
	2-Propyn-1-ol (1) + 1,1,2,2-Tetrachloroethane (2) System	
22.6	0.850	349.45
66.5	0.875	373.35
93.8	0.893	383.15

The set of constants reproduced in Table 2, for ready reference, represent the pure liquid boiling temperature data at the three pressures studied in this work with an overall average absolute deviation of 0.25%. Liquid molar volumes are calculated from the Yen and Woods (1966) correlation. Critical properties and the other input data required for the estimation method are collected from Reid et al. (1987). The values of the optimum Wilson parameters are also noted along with the detailed information on the observed bubble temperature (T), the mole fraction of 2-propyl-1-ol (x_1) in the liquid phase, the calculated values of mole fraction of 2-propyn-1-ol in the vapor phase (y_1) and the liquid phase activity coefficients γ_1 and γ_2 in Tables 3–5.

The prospect of formation of azeotropic mixtures at the different pressures under the temperature and composition conditions noted in Table 6 is predicted on the basis of the model. Experimental investigations confirmed the formation of azeotropic mixture under the conditions noted in Table 6. The data and the representation presented in the paper are therefore expected to be reliable within the stated limits of the experimental error.

Acknowledgment

The authors are grateful to Dr. A. Rajiah for his valuable suggestions and encouragement.

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Received for review January 16, 1996. Accepted May 10, 1996.⊗

JE9600156

⊗ Abstract published in *Advance ACS Abstracts,* July 1, 1996.