Vapor−Liquid Equilibria in Trichloroethylene + Ethanol, + Isopropanol, and + Isobutanol and in Tetrachloroethylene + Methanol at 95 kPa

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Boiling temperatures at 95 kPa, over the entire composition range, have been measured for the binary mixtures trichloroethylene with ethanol, isopropanol, and isobutanol, and tetrachloroethylene with methanol by using a Swietoslawski type ebulliometer. The liquid-phase composition versus temperature measurements are well represented by the Wilson model.

Introduction

This investigation on the vapor−liquid equilibria of the binary mixtures ethanol (1) + trichloroethylene (2), isopropanol (1) + trichloroethylene (2), trichloroethylene (1) + isobutanol (2), and methanol (1) + tetrachloroethylene (2) is in continuation of our systematic studies on the phase equilibria of binary mixtures containing aliphatic alcohols and chlorohydrocarbons.[1−3] The isopropanol (1) + trichloroethylene (2) system has been studied at 20 and 100 kPa by Aucejo *et al.*[4] and at 101.3 kPa by Subrahmanyeswara Rao and Subba Rao.[5] Subrahmanyeswara Rao and Subba Rao[5] also studied the trichloroethylene (1) + isobutanol (2) system at 101.3 kPa. Sagnes and Sanchez[6] measured the vapor−liquid equilibria of the methanol (1) + tetrachloroethylene (2) system at 101.3 kPa. The present measurements have been compared with the available literature data.

Experimental Section

Method. A Swietoslawski type ebulliometer, very similar to the one described by Hala et al.[7] is used for the present set of experiments. The experimental procedure and the details of the method adopted for the measurements have been described by Vijaya Kumar *et al.*[1] Briefly, the ebulliometer, which has provisions for boiling the liquid mixture vigorously and uniformly, condensing the vapor phase, and returning it to the boiling section, is connected to a vacuum pump and a dry nitrogen gas cylinder, with a closed end manometer in line, to enable the measurement and maintenance of the total pressure of the system at 95 kPa, by adjusting the needle valve attached to the gas cylinder/the opening of the bypass line of the vacuum pump. The total pressure of the system was maintained within ±0.1 kPa of the chosen value of 95 kPa, by frequently reading the levels of the mercury columns of the manometer and applying the needed corrective action. 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), was used to measure the equilibrium temperature to an accuracy of ±0.05 K. The thermometer was placed in a thermowell in the apparatus, the outer surface of which was constantly impinged by the equilibrium vapor−liquid mixture. The thermowell was filled with a small quantity of mercury to provide good thermal contact. The liquid mixtures for the study were prepared gravimetrically, by measuring the required masses of the two pure components, making use of a Mettler balance (accurate to 0.0001 g), and stirring them together in a round-bottomed vessel, before introduction into the ebulliometer. The heating rate was carefully controlled to produce the necessary condensate drop rate of 30 drops per minute, following the suggestion of Hala *et al.*,[7] by adjusting the energy supply to the heater. The mixture sample was subjected to the boiling temperature of the higher boiling component and reverted to the ambient conditions, several times, before starting the phase equilibrium experiment, to achieve and maintain constancy of composition. The values of the composition of the liquid phase at the beginning and the end of each experimental equilibrium measurement (determined chromatographically) were close to each other and were within ±0.0001 of the value reported.

Table 1. Comparison of the Density (*D*) and Refractive Index (n_D) at 293.15 K with Literature Data[8]

substance	D/kg·m^{-3} this work	D/kg·m^{-3} lit.	n_D this work	n_D lit.
methanol	791.1	791.04	1.3287	1.328 72
ethanol	789.0	789.03	1.3611	1.361 12
isopropanol	786.0	786.02	1.3775	1.377 49
isobutanol	802.0	802.04	1.3978	1.397 82
trichloroethylene	1462.0	1462.03	1.4765	1.476 49
tetrachloroethylene	1625.0	1625.02	1.5050	1.504 98

Materials. Spectroscopic grade methanol and ethanol procured from SD's Fine Chemicals, Boisar (India), were distilled twice, fractionally, after initial drying over silica gel. Extrapure AR grade isopropanol and AR grade isobutanol supplied by SISCO Research Laboratories, Mumbai (India), were distilled twice, fractionally, after drying over potassium carbonate. AR grade trichloroethylene supplied by E. Merck, Darmstadt (FRG), was dried over potassium carbonate and calcium chloride and fractionally distilled twice. AR grade tetrachloroethylene, supplied by SD's Fine Chemicals, Boisar (India), was fractionally distilled twice

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Table 2. Boiling Temperature Measurements at 95 kPa

ethanol (1) + trichloroethylene (2)		isopropanol (1) + trichloroethylene (2)		trichloroethylene (1) + isobutanol (2)		methanol (1) + tetrachloroethylene (2)	
x_1	T/K	x_1	T/K	x_1	T/K	x_1	T/K
0.0000	357.65	0.0000	357.65	0.0000	373.35	0.0000	391.75
0.1524	353.65	0.1509	348.55	0.1511	368.25	0.1403	337.55
0.2998	352.95	0.2973	346.95	0.2986	363.25	0.2950	336.45
0.4958	352.35	0.4450	346.55	0.4490	360.25	0.4544	336.15
0.5998	351.75	0.6014	346.75	0.5893	358.65	0.7509	335.45
0.7489	351.05	0.7472	347.65	0.7497	357.45	0.9004	335.15
0.9021	350.25	0.9014	350.35	0.9021	357.05	1.0000	336.05
1.0000	349.75	1.0000	353.85	1.0000	357.65		

Table 3. Antoine Constants Used in ln[P/kPa] = A − B/[(T/K) + C]

substance	A	B	C
methanol	16.5701	3626.55	−34.29
ethanol	16.8945	3803.98	−41.08
isopropanol	16.6755	3640.20	−53.54
isobutanol	14.8538	2874.72	−100.30
trichloroethylene	14.1655	3028.13	−43.20
tetrachloroethylene	14.1690	3259.29	−52.20

Table 4. Representation of the Boiling Temperature Measurements (in kelvin) by the Wilson Model

mixture	$[(\lambda_{12} - \lambda_{11})/R]$	$[(\lambda_{12} - \lambda_{22})/R]$	std dev
ethanol (1) + trichloroethylene (2)	1167.9	−373.0	0.04
isopropanol (1) + trichloroethylene (2)	477.1	122.6	0.04
trichloroethylene (1) + isobutanol (2)	201.2	266.8	0.05
methanol (1) + tetrachloroethylene (2)	898.9	562.2	0.05

after drying over anhydrous sodium sulfate. The purification of all the substances was carried out for only a few hours before the phase equilibrium experiments were commenced, and enough care was taken to avoid absorption of moisture, oxidation, and so forth during the intervening period. On the basis of a comparison of the density and refractive index data with the literature data given in ref 8, as shown in Table 1, the pure liquids used in the present work are estimated to be 99.9% pure.

Results and Discussion

The experimental composition (x_1) versus temperature (T) data, presented in Table 2, were fitted to the Wilson model. The optimum Wilson parameters are obtained by minimizing the objective function defined as

$$\varphi = [(P_{\mathrm{cal}}/P_{\mathrm{exp}}) - 1]^2 \tag{1}$$

The Nelder−Mead optimization technique, described in detail by Kuester and Mize,[9] was used. The vapor pressures needed in the computations were calculated from the Antoine equation with the constants collected from ref 10, are noted in Table 3 for ready reference. The molar volumes of the pure liquids were calculated from the liquid density data of the present work given in Table 1. The results of the representation of the data by the Wilson model are presented in Table 4. The Wilson parameters given in Table 4 were used to predict the vapor-phase compositions at the conditions of the available literature data. A summary of the comparisons, presented in Table 5, shows satisfactory agreement, generally within an average deviation of 0.01 units in y_1. The data and the representation given in the paper are expected to be useful for design purposes.

Table 5. Comparisons with Literature Phase Equilibrium Data

system	ref	avg abs dev in y_1
isopropanol (1) + trichloroethylene (2)	4	0.01
	5	0.03
trichloroethylene (1) + isobutanol (2)	5	0.01
methanol (1) + tetrachloroethylene (2)	6	0.01

Literature Cited

(1) Vijaya Kumar, R.; Anand Rao, M.; Venkateshwara Rao, M.; Ravikumar, Y. V. L.; Prasad, D. H. L. Bubble Temperature Measurements on 2-Propan-1-ol with 1,2-Dichloroethane, 1,1,1-Trichloroethane, 1,1,2,2-Tetrachloroethane. *J. Chem. Eng. Data* **1996**, *41*, 1020−1023.

(2) Vijaya Kumar, R.; Anand Rao, M.; Venkateshwara Rao, M.; Prasad, D. H. L. Isobaric Vapor- Liquid Equilibrium in Allyl alcohol + 1,1,2,2-Tetrachloroethylene System. *Physics Chem. Liq.* **1997**, *35*, 81−85.

(3) Vittal Prasad, T. E.; Kumari Vallabhaneni, G.; Krishna Sameera, M.; Praveena Bose, V.; Prasad, D. H. L. Bubble Temperature Measurements on *p*-Xylene with Methanol, Propan-1-ol and Butan-1-ol at 95.1 kPa. *J. Chem. Eng. Data* **1998**, *43*, 555−557.

(4) Aucejo, A.; Gonzalez-Alfaro, V.; Morton, J. B.; Vazqez, M. I. Isobaric Vapor-Liquid Equilibria of Trichloroethylene with 1-Propanol and 2-Propanol at 20 and 100 kPa. *J. Chem. Eng. Data* **1995**, *40*, 332−335.

(5) Subrahmanyeswara Rao, D.; Subba Rao, B. V. Studies in Vapour-Liquid Equilibria for the Systems Isopropanol − Trichloroethylene and Trichloroethylene − Isobutanol. *Indian J. Technol.* **1973**, *11*, 91−94.

(6) Sagnes, M.; Sanchez, V. Vapor-Liquid Equilibria for Fourteen Systems Consisting of Chlorinated Hydrocarbons and Alcohols. *J. Chem. Eng. Data* **1971**, *16*, 351−354.

(7) Hala, E.; Pick, J.; Fried, V.; Villim, O. *Vapor-Liquid Equilibrium*; Pergamon: Oxford, U.K.; p 958.

(8) Riddick, J. A.; Bunger, W. S.; Sakno, T. K. *Organic Solvents—Physical Properties and Methods of Purification*, 4th ed.; Wiley: New York, 1986.

(9) Kuester, R. T.; Mize, J. H. *Optimization Techniques with Fortran*; McGraw-Hill: New York, 1973.

(10) Reid, R. C.; Prausnitz, J. M.; Sherwood, T. K. *The Properties of Gases and Liquids*, 3rd ed.; McGraw-Hill: New York, 1977.

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