Bubble-Temperature Measurements on *p*-Xylene with Methanol, Propan-1-ol, and Butan-1-ol at 95.1 kPa[†]

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Bubble temperatures at 95.1 kPa at nine liquid compositions, spaced evenly over the entire composition range, were measured for three binary systems—methanol (1) + *p*-xylene (2), propan-1-ol (1) + *p*-xylene (2), and butan-1-ol (1) + *p*-xylene (2)—using a Swietoslawski-type ebulliometer. The composition (x_1) vs temperature (*T*) data were found to be well-represented by the Wilson model.

Introduction

This investigation on the bubble-temperature measurements of the systems methanol (1) + *p*-xylene (2), propan-1-ol (1) + *p*-xylene (2), and butan-1-ol (1) + *p*-xylene (2) was taken up, in continuation of the work of Vijaya Kumar et al. (1996). The three systems were studied at 313.15 K by Oracz and Kolosinska (1987), while Chen et al. (1994) studied the propan-1-ol (1) + *p*-xylene (2) system at 433.2 K. Earlier studies at 101.32 kPa were conducted by Budantseva et al. (1975) for the methanol (1) + *p*-xylene (2) system and by Galska-Krajewska (1967) for the propan-1-ol (1) + *p*-xylene (2) and butan-1-ol (1) + *p*-xylene (2) systems.

Experimental Section

A Swietoslowski-type ebullimeter, very similar to the one described by Hala et al. (1958), was used for the experiments. The ebullimeter was connected to a vacuum pump and a nitrogen gas cylinder, with a closed end manometer in line, to enable the measurement and maintainance of the total pressure of the system to within ±0.1 kPa of the desired value, by adjusting the opening of the needle valve attached to the gas cylinder or the opening of the bypass line of the vacuum pump. The total pressure in the present set of experiments was maintained to within ±0.1 kPa, by frequently reading the mercury manometer and carrying out the required corrective adjustment. 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 for the measurement of temperature to an accuracy of ±0.1 K. The thermometer bulb is located at the point in a thermowell filled with mercury where the gas−liquid mixture impinges. The mixture samples to be studied are prepared by weighing the required amounts of the two pure liquids and stirring them well before charging them to the still. A Mettler balance, accurate to ±0.0001 g, was used to measure all the required weights. The heating rate was adjusted to yield the desired drop rate of about 30/min in accordance with the suggestion of Hala et al. (1958). The technique of subjecting the test mixture to the lowest pressure or highest temperature and reverting to atmospheric conditions was used to retain the consistency of composition throught the experiment. A gas chromatograph was used verify the composition, both at the beginning and end of each experiment. The equilibrium temperature was recorded after steady-state conditions judged by the constant temperature and uniform drop rate for at least 30 min.

Materials

Spectroscopic grade methanol procured from SD Fine Chemicals, Boisar, India, was distilled twice fractionally, after drying over silica gel. The middle fraction of the second distillation was collected and stored in an amber-colored bottle for use in the experiments.

Extrapure AR grade propan-1-ol supplied by Sisco Research Laboratories, Bombay, India, was distilled twice fractionally after storing over potassium carbonate overnight. The middle fraction of the second distillation was stored in an amber-colored bottle for use in the experiments.

AR grade butan-1-ol supplied by SD Fine Chemicals, Boisar, India, was dried over potassium carbonate and fractionally distilled twice. The middle fraction of the second distillation was stored in an amber-colored bottle for use in the experiments.

AR grade *p*-xylene supplied by E Merck, Darmstadt, FRG, was dried over phosphorus pentoxide and fractionally distilled twice. The middle fraction of the second distillation was stored in an amber-colored bottle for use in the experiments.

The purification of all the substances was carried out only a few hours before the phase-equilibrium experiments were started, and enough care was taken to prevent absorption of moisture, oxidation, etc.

On the basis of a comparison of the density and refractive-index data with the literature values presented in Table 1 as well as chromatographic studies, the purity of the substances used in the present set of experiments is estimated to be at least 99.8%.

Table 1. Comparison of the Density ρ and Refractive Index n_D of the Substances Used in the Present Work with Literature Data of Riddick et al. (1986)

substance	ρ (293.15 K)/kg. m^{-3}		n_D (293.15 K)	
	this work	lit.	this work	lit.
methanol	791.1	791.04	1.3287	1.328 40
propan-1-ol	804.1	803.61	1.3851	1.385 56
butan-1-ol	810.1	809.56	1.3992	1.399 29
p-xylene	861.1	860.98	1.4959	1.495 82

Table 2. Bubble-Temperature Measurements at 95.7 kPa

methanol (1) + p-xylene (2) system		propan-1-ol (1) + p-xylene (2) system		butan-1-ol (1) + p-xylene (2) system	
x_1	T/K	x_1	T/K	x_1	T/K
0.0000	409.2	0.0000	409.2	0.0000	409.2
0.1235	346.5	0.0996	380.5	0.1019	396.1
0.2228	340.8	0.1997	374.5	0.2010	391.0
0.3111	338.4	0.2969	372.4	0.2988	388.5
0.4237	337.7	0.3990	371.1	0.3898	387.2
0.5008	337.3	0.4969	370.2	0.5033	386.2
0.5889	337.0	0.5949	369.5	0.6059	385.8
0.6920	336.8	0.6954	368.9	0.7002	385.6
0.8052	336.5	0.7965	368.5	0.8030	385.7
0.8965	336.2	0.9018	368.3	0.9006	386.5
1.0000	336.4	1.0000	368.8	1.0000	389.2

Table 3. Antoine Constants Used in Equation 6

substance	A	B	C
methanol	16.5701	3626.55	−34.3
propan-1-ol	15.8357	3320.25	−74.3
butan-1-ol	15.1986	3137.02	−94.4
p-xylene	14.0789	3346.65	−57.8

Results and Discussion

The experimental composition (x_1) versus temperature (T) data summarized in Table 2 were fitted to the Wilson model in the form

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

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

where

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

$$\Lambda_{21} = (v_1^L/v_2^L)\exp[-(\lambda_{12} - \lambda_{22})/RT] \quad (4)$$

V_1^L and V_2^L are the pure liquid molar volumes, and $(\lambda_{12} - \lambda_{11})/R$ and $(\lambda_{12} - \lambda_{22})/R$ are the Wilson parameters with λ's as the energies of interaction between the molecules denoted by the subscripts.

The optimum Wilson parameters were obtained by minimizing the objective function defined as

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

The Nelder−Mead optimization technique described in detail by Kuester and Mize (1973) was used. Vapor pressures required in the calculations were computed from the Antoine constants noted in Table 3 for the equation in the form

$$\ln(P/kPa) = A - [B/(T/K) + C] \quad (6)$$

Table 4. Representation of the Bubble-Temperature Data by the Wilson Model

system	$[(\Lambda_{12} - \Lambda_{11})/R]/$ K	$[(\Lambda_{12} - \Lambda_{22})/R]/$ K	std. dev. in T/K
methanol (1) + p-xylene (2)	858.43	377.30	0.12
propan-1-ol (1) + p-xylene (2)	762.19	53.01	0.09
butan-1-ol (1) + p-xylene (2)	445.02	230.60	0.03

This equation when applied to the entire set of data in the range of interest from the TRC data source (1996) through the use of the evaluated set of constants presented in Table 3 gave an average absolute deviation of 0.5%. In the absence of experimental data, the pure liquid molar volumes were calculated from the Rackett equation of state (1970).

The results of the representation of the data by the Wilson model, summarized in Table 4, indicate that the model adequately represents the observed phase-equilibrium data.

A careful comparison of the literature phase-equilibrium data revealed that

(i) for the methanol (1) + p-xylene (2) system, the agreement with the isothermal data of Oracz and Kolasinska (1987) is poor with an average deviation of 1.3 kPa, while the agreement with the isobaric data of Budantseva et al. (1975) is satisfactory with a average deviation of 0.7 K,

(ii) for the propan-1-ol (1) + p-xylene (2) system, the agreement is poor with the data of Chen et al. (1994) with an average absolute deviation of 71 kPa for the 433.2 K isotherm and an average deviation of 1.6 K from the 101.32 kPa isobar given by Galska-Krajewska (1967), while the isothermal data of Oracz and Kolansinska (1987) are excellently represented with an average deviation of 0.02 kPa, and

(iii) for the butan-1-ol (1) + p-xylene (2) system, the agreement with the isobaric data of Galska-Krajewska is poor with an average absolute deviation of 1.6 K while the isothermal data of Oracz and Kolansinska (1987) are well-represented with an average deviation of 0.13 kPa.

The data and the representation presentation presented in this paper are within the accuracies of the measured variables noted and are expected to be useful for engineering design purposes.

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