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Bubble points of some binary mixtures formed by *o*-cresol at 95.75 kPa

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Abstract

Bubble points at 95.75 kPa, over the entire composition range were measured for the binary mixtures formed by *o*-cresol with 1,2-dichloroethane, 1,1,2,2-tetrachloroethane, trichloroethylene, tetrachloroethylene, *o*-, *m*-, *p*-xylenes and *n*-heptane, making use of a Swietoslawski type ebulliometer. The liquid phase composition versus temperature measurements was found to be well represented by the Wilson model.

Keywords: Bubble points; *o*-Cresol; Chloethanes; Chloroethylenes; Xylenes; *n*-Heptane

1. Introduction

o-Cresol has been used in the manufacture of phenolic resins and in small proportion in the preparation of epoxy resins, besides application in the manufacture of 4,4-dinitro-2-methyl-phenol (frequently used as a herbicide and polymerization inhibitor). Uses of the other compounds forming the binary mixtures—xylenes, *n*-heptane, chloroethanes and chloroethylenes as industrial solvents and otherwise have been well known. Bubble temperature measurements, the vapor–liquid equilibria and other derived information find use in the design and operation of conventional separation processes involving the compounds.

This investigation leading to the vapor–liquid equilibria of the binary mixtures formed by *o*-cresol with the chloroethanes, chloroethylenes, xylenes and *n*-heptane has been taken up in continuation of our recent systematic studies leading to the phase equilibria of the binary mixtures formed by alcohols, hydrocarbons and halohydrocarbons [1,2]. There were no published vapor–liquid equilibrium data on the systems chosen for the present study.

2. Experimental

2.1. Method

A Swietoslawski type ebulliometer, very similar to the one described by Hala et al. [3] and mentioned in some detail in our earlier publication [1] was used in the present work. The ebulliometer was 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 95.75 kPa, by adjusting the opening of the needle valve attached to the gas cylinder or the opening of the by pass line of the vacuum pump. The total pressure in this set of experiments was maintained within ±0.05 kPa of the chosen value, by frequently reading the mercury columns of the manometer and applying the 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, USA) was used to measure the equilibrium temperature to an accuracy of ±0.05 K.

The thermometer was placed in a thermowell (in the apparatus) whose outer surface was constantly impinged by equlilbrium vapor–liquid mixture. The thermowell had a small quantity of mercury to provide for good contact. The mixtures to be studied are prepared gravimetrically, by weighing the

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required components making use of a Mettler balance accurate to 0.00001 g, and were stirred well before being introduced to the apparatus. For accuracy, the exact liquid phase compositions (recorded in Table 2) were determined by gas chromatography. The heating rate was maintained at a level capable of producing a liquid condensate drop rate of 30 drops min^{-1}, in accordance with the suggestion of Hala et al. [3], by carefully adjusting the energy supply to the heater. Constancy of the liquid phase composition was achieved and maintained by subjecting the test sample to the highest temperature, proposed to be studied and reverting to the ambient conditions several times, before starting the actual experiment. Gas chromatograph was also used to verify the constancy of the composition of the sample at the beginning and end of each phase equilibrium measurement. Equilibrium temperature was recorded, after the steady state conditions (judged by the maintenance of a constant temperature and uniform boiling rate indicated by the maintenance of the chosen liquid drop rate of 30 min^{-1}) were observed for at least 30 min.

2.2. Materials

Synthesis grade *o*-cresol (E. Merck, Mumbai, India) was dried over anhydrous calcium hydroxide and stored over molecular sieves for 2 days and fractionally distilled. AR grade 1,2-dichloroethane (BDH Chemicals, Mumbai, India) was further purified by washing with dilute potassium hydroxide solution and water, drying over phosphorous pentoxide and fractional distillation. AR grade 1,1,2,2-tetrachloroethane (SD's Fine Chemicals, Boisar, India) was shaken with concentrated sulfuric acid for 10 min at 355 K. Discolored acid was removed and the acid washing repeated several times until the acid discoloration stops. The product was then washed with water, dried over potassium carbonate and fractionally distilled.

Spectroscopic grade trichloroethylene (SD's Fine Chemicals) was steam distilled from 10% calcium hydroxide slurry. The organic phase was collected at 243–223 K and the ice removed by filtration. The filtrate was subjected to fractional distillation. AR grade tetrachloroethylene (SD's Fine Chemicals) was distilled twice fractionally after drying over anhydrous sodium sulfate.

Pure *o*-xylene (99%) (Lancaster, Lancashire, UK) was dried over calcium chloride and silica gel and fractionally distilled. *m*- and *p*-Xylenes synthesis grade (E. Merck) were purified by drying over molecular sieves and repeated fractional distillation. ExcelaR grade *n*-heptane (Qualigenes Fine Chemical, Mumbai, India) was stored over sodium for a week and fractionally distilled.

The purification of all the liquids was carried out only a few hours before the start of the phase equilibrium experiment and enough care was taken to prevent the absorption of moisture, oxidation, etc., during the intervening period. Based on the non-appearance of multiple significant peaks in the gas chromatograms and the comparison of the physical properties data with the literature values [4,5], presented in Table 1, the pure liquids used in the present work were expected to be at least 99.9% pure.

3. Results and discussion

The experimental liquid phase composition (x_1) versus temperature (T) data, summarized in Table 2, was fitted to the Wilson model. The optimum Wilson parameters were obtained by minimizimg the objective function φ defined as

$$\varphi = \left[\frac{P_{\text{cal}}}{P_{\text{expt}}} - 1\right]^2 \tag{1}$$

Nelder-Mead optimization technique, described by Kuster and Mize [6] was used. Vapor pressures, needed in the computations were calculated from the Antoine equation (with the constants noted in Table 3 for ready reference). Previously, the Antoine equation with the constants noted in Table 3 has been used to test the applicability to the available literature vapor pressure data and found to represent the available pure liquid vapor pressure data, including the pure liquid boiling temperatures of the present experiments, with an average absolute deviation of 0.5%. Molar volumes of the pure liquids, calculated from the liquid density data given in Table 1, were used in the calculation of the Wilson parameters. A summary of the results of the representation of the data by Wilson model is given Table 4.

The computational methodology followed in brief is:

$$P_{\text{expt}} = P_1^0 x_1 \gamma_1 + P_2^0 x_2 \gamma_2 \tag{2}$$

where P_{expt} is total pressure maintained, P_1^0 and P_2^0 the vapor pressures of the two pure components at the temperature of the

Table 1
Comparison of the density (ρ) and refractive index (n_D) with literature data

Substance	T (K)	ρ (kg m^{-3})		n_D	
		This work	Literature	This work	Literature
o-Cresol	293.15	1046.0	1046.00 [4]	1.5467	1.54670 [4]
1,2-Dichloroethane	293.15	1252.9	1252.92 [4]	1.4196	1.41959 [4]
1,1,2,2-Tetrachloroethane	293.15	1593.0	1593.02 [4]	1.4940	1.49389 [4]
Trichloroethylene	298.15	1464.0	1463.90 [5]	1.4782	1.47820 [5]
Tetrachloroethylene	293.15	1625.0	1625.00 [4]	1.5050	1.50499 [4]
o-Xylene	293.15	880.1	880.14 [4]	1.5055	1.50545 [4]
m-Xylene	293.15	864.4	864.36 [4]	1.4972	1.49722 [4]
p-Xylene	293.15	861.0	868.98 [4]	1.4858	1.49582 [4]
n-Heptane	293.15	683.8	683.75 [4]	1.3876	1.38764 [4]