(Vapor + liquid) equilibria of the binary mixtures of m-cresol with C_1–C_4 aliphatic alcohols at 95.5 kPa

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Abstract

Bubble point temperatures at 95.5 kPa, over the entire composition range, are measured for the binary mixtures formed by m-cresol with: methanol, ethanol, 1-propanol, 2-propanol, and n-, iso-, sec-, and $tert$-butanols – using a Swietoslawski-type ebulliometer. The liquid phase composition – bubble point temperature measurements are well represented by the Wilson model. (Vapor + liquid) equilibria predicted from the model are presented.
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1. Introduction

m-Cresol is used essentially in the manufacture of phenolic based anti-oxidants (good at stabilizing polymers in contact with copper against thermal oxidative degradation). Information leading to the phase equilibria of the binary mixtures formed by m-cresol is expected to be of use in the design and operation of the separation processes for the compounds contained in the mixture. This investigation on the bubble point temperatures of the binary mixtures, mentioned in the abstract, is a continuation of our recent studies on the phase equilibria of the binary mixtures containing hydrocarbons or alcohols [1,2]. The experimental studies have been carried out at 95.5 kPa. We could not locate any (vapor + liquid) equilibrium data on the mixtures chosen for the present study in the open literature.

2. Experimental section

2.1. Method

A Swietoslawski-type ebulliometer, very similar to the one described by Hala *et al.* [3] is used for this experimental investigation. Connection of the ebulliometer, to a good vacuum system and dry nitrogen gas cylinder, helped in the creation and maintenance of the chosen pressure within ±0.05 kPa. An open end manometer, provided in line, is frequently read and the needed corrective action, of adjusting the opening of the needle valve attached to the gas cylinder or the by pass line of the vacuum pump, is performed according to the requirement. Equilibrium temperatures are measured to an accuracy of ±0.05 K by means of a platinum resistance thermometer, carefully calibrated by means of point-to-point comparison with a Standard Platinum Resistance Thermometer certified by the National Institute of Standards and Technology, Boulder, USA. Liquid mixtures for the studies are prepared by weighing the necessary quantities of the pure liquids, using an electronic balance precise to ±0.0001 g, and stirring well. After the liquid mixture is carefully introduced into the

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ebulliometer, the heating rate is adjusted to yield the desired condensate drop rate of 30 drops per minute, in accordance with the suggestion of Hala *et al.* [3]. The equilibrium temperatures reported are those measured after the steady condensate drop rate and constancy of temperature are maintained for at least 30 min.

2.2. Materials

Analytical reagent grade *m*-cresol (SISCO Research Laboratories, Mumbai, India) is fractionally distilled, after prior drying over silica gel for two days.

Spectroscopic grade methanol (SDS Fine Chemicals, Boisar, India) is fractionally distilled after drying over silica gel and molecular sieves. Anhydrous ethanol (Aldrich Chemical Co., Gillingham, England) is dried over silica gel and fractionally distilled. AR grade 1-propanol (SD's Fine-Chem. Ltd., Poicha, India) is dried over anhydrous sodium. GR grade 2-propanol (Loba Chemie Pvt. Ltd., Mumbai, India) is dried over calcium chloride followed by barium oxide and fractionally distilled.

Guarenteed reagent grade *n*-butanol (Loba Chemie Pvt. Ltd., Mumbai, India) is fractionaaly distilled after initial overnight drying over silica gel. Extrapure AR grade *iso*-butanol (SISCO Research Laboratories, Mumbai,India) is purified by drying over silica gel and fractional distillation. Extrapure AR grade *sec*-butanol (SISCO Research Laboratories, Mumbai, India) is fractionally distilled twice, after drying over silica gel. *tert*-Butanol (Ranbaxy Laboratories, SAS Nagar, Panjab, India) is dried over phosphorous pentoxide and fractionally distilled twice.

Fractional distillations are carried out using a packed column (length equivalent to 30 theoretical plates). The middle fractions of the second distillations are collected in amber colored bottles for use in the experiments. The final distillations are performed only a few hours before the commencement of the phase equilibrium experiments and enough care is taken to prevent absorption of moisture, oxidation, *etc.*, during the intervening period. The purity of the chemicals is ascertained by measuring their density and refractive-index, which compare favourably with the literature values of Riddick *et al.* [4] as shown in table 1.

TABLE 1
Comparison of the density (ρ) and refractive-index (n_D) of the pure liquids used in this study with the literature data of Riddick *et al.* [4] at 298.15 K

Substance	$\rho/(kg \cdot m^{-3})$		n_D	
	This work	Literature	This work	Literature
m-Cresol	1030.0	1030.19	1.5395	1.53960
Methanol	786.4	786.37	1.3265	1.32652
Ethanol	784.9	784.93	1.3594	1.35941
1-Propanol	799.6	799.60	1.3837	1.38370
2-Propanol	781.3	781.26	1.3752	1.37520
n-Butanol	805.8	805.75	1.3974	1.39741
iso-Butanol	797.8	797.80	1.3939	1.39389
sec-Butanol	802.4	802.41	1.3953	1.39530
tert-Butanol	781.2	781.20	1.3852	1.38520

3. Results and discussion

The experimental liquid phase composition (x_1) *versus* temperature (T) data, summarized in table 2, are fitted to the Wilson [5] model

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

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

where

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

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

where V_1^L and V_2^L are the liquid molar volumes of the pure components and λ's are the energies of interaction between the molecules designated by the subscripts. As can be seen from the functional forms, the temperature variation of the Wilson parameters is effective through the changes in the pure liquid molar volumes (not considered in the present work) and also in the exponential term. The optimum Wilson parameters are obtained by minimizing the objective function φ defined as

$$\varphi = \sum [(P_{cal(Wilson)} - P_{expt})/P_{expt} - 1]^2, \tag{5}$$

where P_{expt} stands for the experimental total pressure and $P_{cal(Wilson)}$ is the total pressure calculated from the following equation:

$$P_{cal(Wilson)} = \gamma_{1(Wilson)}x_1 P_1^\circ + \gamma_{2(Wilson)}x_2 P_2^\circ \tag{6}$$

with $\gamma_{1(Wilson)}$ and $\gamma_{2(Wilson)}$ calculated from the trial values of the Wilson parameters chosen for regression. Nelder-Mead optimization technique described by Kuester and Mize [6] is used. Pure component vapor pressures needed in the computations are calculated from the Antoine constants noted in table 3. The Antoine equation, with the constants noted in table 3, represents the literature vapor pressure data as well the present measurements on pure liquids with an average absolute deviation of 0.5%. The molar volumes of the pure liquids, calculated from the density measurements of this study (recorded in table 1) are used as the input in obtaining the optimum Wilson parameters. The results of the representation of the phase equilibrium data by the Wilson [5] model, summarized in table 4, indicate that the data and the representation are quite good.

The optimum Wilson parameters, determined as described above and noted in table 4, are used to re-evaluate the phase diagram at 95.5 kPa. The activity coefficients at the observed liquid phase compositions are first calculated and subsequently used to regress the bubble point temperatures and the vapor phase compositions at the observed total pressure (making use of the other necessary input data like vapor pressures and molar volumes). The standard deviations of the predicted bubble