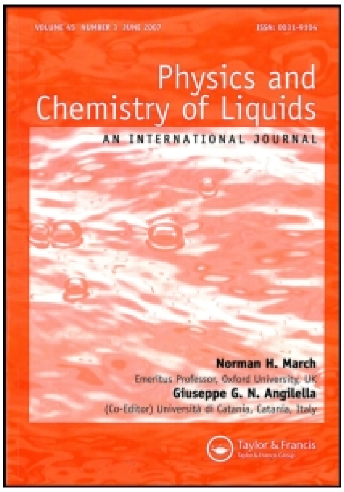

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# Vapor–liquid equilibria of binary mixtures formed by *m*-xylene with some chlorohydrocarbons at 95.75 kPa

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Vapor–liquid equilibria (at 95.75 kPa) over the entire composition range are obtained for the binary mixtures formed by *m*-xylene with 1,2-dichloroethane, 1,1,2,2-tetrachloroethane, trichloroethylene and tetrachloroethylene. A Swietoslawski type ebulliometer is used to measure the bubble point temperatures necessary to determine the vapor–liquid equilibria. The Wilson equation is used to represent the measured liquid phase composition versus temperature data and the computed values of the vapor phase compositions are tabulated.

*Keywords:* Vapor–liquid equilibria; Bubble temperatures; *m*-Xylene; Chloroethanes; Chloroethylenes

## 1. Introduction

This investigation on the vapor–liquid equilibria of the binary mixtures formed by *m*-xylene with some chlorohydrocarbons, is in continuation of our recent systematic studies leading to the phase equilibria of the binary mixtures formed by different types of compounds [1,2]. There are no published vapor–liquid equilibrium data on the systems chosen for the present study.

## 2. Experimental

### 2.1. *Method*

Bubble point temperatures of gravimetrically prepared liquid mixture samples (covering the whole composition range) are measured for all the four systems making use of a Swietoslawski type ebulliometer similar to the one described by Hala *et al.* [3]

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and mentioned in some detail in our earlier paper [1]. The ebulliometer 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 95.75 kPa, by adjusting the opening of the needle valve of the gas cylinder/the opening of the bypass line of the vacuum pump. The total pressure in this set of experiments is maintained within ±0.05 kPa of the chosen value, by frequently reading the mercury columns of the manometer and applying the needed 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) is used to measure the equilibrium temperature to an accuracy of ±0.05 K. The thermometer is placed in a thermowell (in the apparatus), the outer surface of which is constantly impinged by equilibrium vapor–liquid mixture. The thermowell has a small quantity of mercury to provide for good contact.

The mixtures to be studied are prepared gravimetrically, by weighing the required components, making use of a Mettler balance accurate to 0.0001 g, and are stirred well before being introduced to the apparatus. The heating rate is maintained at a level capable of producing a condensate drop rate of thirty drops per minute, following the suggestion of Hala *et al.* [3] by carefully adjusting the energy supply to the heater. The normally practiced method of subjecting the sample to the probable lowest pressure or highest temperature, likely to be encountered and reverting to ambient conditions several times, before starting the actual experiment is followed to achieve and retain the constancy of composition throughout the experiment. A gas chromatograph is used to verify the constancy of the composition of the sample at the beginning and the end of each experimental phase equilibrium measurement. Equilibrium temperature is recorded, after the steady state conditions (observation of constant temperature and uniform boiling rate indicated by the maintenance of the chosen condensate liquid drop rate of 30 drops per minute) are observed for at least 30 minutes.

### 2.2. *Materials*

*m*-Xylene, Laboratory Reagent grade (E. Merck, Mumbai, India) is stored over molecular sieves for two days and fractionally distilled twice.

AR grade 1,2-dichloroethane (BDH Chemicals, Mumbai, India) is washed with dilute potassium hydroxide solution and water, dried over phosphorous pentoxide and fractional distillation.

AR grade 1,1,2,2-tetrachloroethane (SD's Fine Chemicals, Boisar, India) is shaken with concentrated sulfuric acid for ten minutes at 355 K. The discolored acid is removed and the acid washing is repeated several times until the acid discoloration stops. The product is then washed with water, dried over potassium carbonate and fractionally distilled.

Spectroscopic grade trichloroethylene (SD's Fine Chemicals, Boisar, India) is steam distilled from 10% calcium hydroxide slurry. The organic phase is collected at −30 to −50°C and the ice removed by filtration. The filtrate is purified by fractional distillation.

AR grade tetrachloroethylene (SD's Fine Chemicals, Boisar, India) is fractionally distilled after drying over anhydrous sodium sulfate.

Table 1. Comparison of the density ($d$) and refractive-index ($n_D$) with literature data.

| | | $d\,(\mathrm{kg\,m^{-3}})$ | | $n_D$ | |
|---|---|---|---|---|---|
| Substance | Temperature (K) | This work | Literature[Ref] | This work | Literature[Ref] |
| *m*-Xylene | 293.15 | 861.0 | 860.98[4] | 1.4953 | 1.49582[4] |
| 1,2-Dichloroethane | 293.15 | 1252.1 | 1252.09[4] | 1.4448 | 1.44480[4] |
| 1,1,2,2-Tetrachloroethane | 293.15 | 1594.5 | 1594.49[4] | 1.4940 | 1.49389[4] |
| Trichloroethylene | 293.15 | 1464.0 | 1464.00[5] | 1.4782 | 1.47820[5] |
| Tetrachloroethylene | 293.15 | 1622.8 | 1622.83[4] | 1.5058 | 1.50576[4] |

Table 2. Vapor–liquid equilibria of the binary mixtures of *m*-xylene with some chlorocompounds at 95.75 kPa.

| 1,2-Dichloroethane (1) + *m*-Xylene (2) | | | *m*-Xylene (1) + 1,1,2,2-Tetrachloroethane (2) | | | Trichloroethylene (1) + *m*-Xylene (2) | | | Tetrachloroethylene (1) + *m*-Xylene (2) | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| $x_1$ | $T$ (K) | $y_1$ | $x_1$ | $T$ (K) | $y_1$ | $x_1$ | $T$ (K) | $y_1$ | $x_1$ | $T$ (K) | $y_1$ |
| 0.0000 | 410.35 | 0.0000 | 0.0000 | 417.35 | 0.0000 | 0.0000 | 410.35 | 0.0000 | 0.0000 | 410.35 | 0.0000 |
| 0.0645 | 399.65 | 0.3051 | 0.0959 | 416.35 | 0.1177 | 0.0712 | 405.75 | 0.1827 | 0.0752 | 409.15 | 0.1051 |
| 0.1141 | 393.65 | 0.4468 | 0.1753 | 415.35 | 0.2099 | 0.1275 | 402.15 | 0.3083 | 0.1427 | 408.05 | 0.1965 |
| 0.1883 | 386.45 | 0.5898 | 0.2979 | 414.65 | 0.3442 | 0.1797 | 398.85 | 0.4110 | 0.1998 | 407.15 | 0.2715 |
| 0.2788 | 379.95 | 0.6996 | 0.3894 | 413.95 | 0.4388 | 0.3047 | 391.15 | 0.6099 | 0.2938 | 405.45 | 0.3895 |
| 0.3918 | 373.75 | 0.7869 | 0.4884 | 413.25 | 0.5367 | 0.3928 | 386.05 | 0.7160 | 0.3996 | 403.55 | 0.5135 |
| 0.4742 | 370.25 | 0.8320 | 0.6165 | 412.35 | 0.6577 | 0.4870 | 380.75 | 0.8042 | 0.4996 | 401.65 | 0.6024 |
| 0.5863 | 366.25 | 0.8792 | 0.7196 | 411.75 | 0.7517 | 0.5634 | 376.65 | 0.8597 | 0.6040 | 399.65 | 0.7214 |
| 0.7026 | 362.65 | 0.9184 | 0.8019 | 411.25 | 0.8331 | 0.6593 | 371.75 | 0.9127 | 0.6959 | 397.95 | 0.8008 |
| 0.7799 | 360.65 | 0.9441 | 0.8652 | 419.25 | 0.8811 | 0.7633 | 366.85 | 0.9534 | 0.7923 | 396.05 | 0.8744 |
| 0.8855 | 358.85 | 0.9700 | 0.9328 | 410.65 | 0.9407 | 0.8856 | 361.85 | 0.9839 | 0.9015 | 394.05 | 0.9459 |
| 0.9328 | 356.85 | 0.9824 | 1.0000 | 410.35 | 1.0000 | 0.9521 | 359.45 | 0.9945 | 1.0000 | 392.25 | 1.0000 |
| 1.0000 | 355.25 | 1.0000 | | | | 1.0000 | 357.95 | 1.0000 | | | |

The final step of the purification of all the liquids (fractional distillation) is carried by means of a packed column of height equivalent to 30 theoretical plates – only a few hours before the commencement of the phase equilibrium experiment and enough care is 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 are expected to be at least 99.9% pure.

## 3. Results and discussion

The experimental composition ($x_1$) versus temperature ($T$) data, summarized in table 2, are fitted to the Wilson model, expressing the activity coefficients as

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

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

Table 3. Antoine constant used in $\ln P(\mathrm{kPa}) = A - B/(T/\mathrm{K}) + C]$.

| Substance | $A$ | $B$ | $C$ |
|---|---|---|---|
| *m*-Xylene | 14.1216 | 3366.99 | −58.04 |
| 1,2-Dichloroethane | 14.1590 | 2927.17 | −50.22 |
| 1,1,2,2-Tetrachloroethane | 14.0632 | 3374.13 | −62.15 |
| Trichloroethylene | 14.1654 | 3028.13 | −43.15 |
| Tetrachloroethylene | 14.1469 | 3259.27 | −52.15 |

Table 4. Representation of the bubble point temperature measurements by Wilson Model.

| Mixture | $(\lambda_{12} - \lambda_{11})/R$ (K) | $(\lambda_{12} - \lambda_{22}/R$ (K) | Std. Dev. (K) |
|---|---|---|---|
| 1,2-Dichloroethane (1) + *m*-Xylene (2) | 56.97 | 100.23 | 0.04 |
| *m*-Xylene (1) + 1,1,2,2-Tetrachloroethane (2) | −81.52 | 118.26 | 0.03 |
| Trichloroethylene (1) + *m*-Xylene (2) | −235.25 | 102.55 | 0.03 |
| Tetrachloroethylene (1) + *m*-Xylene (2) | −105.16 | 52.28 | 0.03 |

where

$$\Lambda_{12} = \left(\frac{V_1^{\mathrm{L}}}{V_2^{\mathrm{L}}}\right) \exp\left[-\left\{\frac{\lambda_{12} - \lambda_{11}}{RT}\right\}\right] \tag{3}$$

and

$$\Lambda_{21} = \left(\frac{V_2^{\mathrm{L}}}{V_1^{\mathrm{L}}}\right) \exp\left[-\left\{\frac{\lambda_{12} - \lambda_{22}}{RT}\right\}\right]. \tag{4}$$

The optimum Wilson parameters are obtained by minimizing the objective function

$$\varphi = \left[\left(\frac{P_{\mathrm{cal}}}{P_{\mathrm{expt}}}\right) - 1\right]^2. \tag{5}$$

The Nelder–Mead optimization technique, described by Kuester and Mize [6] is used. Vapor pressures, needed in the computations, are calculated from the Antoine equation with the constants noted in table 3 for ready reference. These constants are 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, are used as inputs to the calculation of the Wilson parameters. The results of the representation of the data by the Wilson model are summarized in table 4. Vapor phase compositions determined from the Wilson model are also noted in table 2. In view of the care taken in carrying out the measurements and good representation by the model, the results presented in the article are expected to be useful for design purposes.

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