Liquid–Liquid Equilibria of Mixtures Containing Methyl Acetate + Methanol + Hexane or Heptane

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This paper reports the results of a new experimental study of liquid–liquid equilibria for the mixtures methyl acetate + methanol + hexane or heptane at atmospheric pressure and at (268.15, 278.15, 288.15, and 298.15) K. The equilibrium compositions were measured by gas chromatography from samples split isothermally into a glass-stirred device, and phase diagrams are reported at each temperature. The experimentally determined liquid−liquid equilibria were satisfactorily correlated by the NRTL and UNIQUAC equations. A comparative analysis was performed by application of UNIFAC group contribution method and its modifications to predict experimental liquid–liquid equilibria (LLE) behavior of these ternary mixtures. A poor prediction was observed from these contribution methods.

Introduction

Nowadays, liquid–liquid extraction has become one of the main separation technologies for separation of complex liquid mixtures. Hence, there has been a significant growth in the number of publications devoted to the study on liquid–liquid equilibria (LLE) of ternary and quaternary mixtures, including experimental data and correlation parameters. Phase equilibria studies supply essential information to select appropriate solvents and to design extractors. Although simulation programs provide a variety of possibilities for process synthesis, design, and optimization, the quality of the results depends on the quality of the data and models used. In some cases, the results obtained predicted with group contribution methods might be sufficient; in other cases, experimental data and a good description of them with the thermodynamic models is necessary. Hence, experimental data and a study to determine the predictive capability of group contribution methods are required.

In this work, we extend our measurements of experimental liquid–liquid data[1,2] to the mixtures methyl acetate + methanol + n-alkanes (C_6 to C_7) at atmospheric pressure and (268.15, 278.15, 288.15, and 298.15) K. Experimental data for these mixtures are not available in the open literature.

A study of the predictive capability of the UNIFAC group contribution method[3] and its modifications is presented for these ternary mixtures. Group contribution methods are extensively used in the chemical industry, especially during the development of chemical processes,[4] and UNIFAC stand out because it is highly used, due to its wide application range, and its parameter matrix is the most comprehensive. VLE parameters obtained from extensive series of revisions and extensions of the parameter matrix can be used.[5–11] Or, special LLE data-fitted parameters can be used as those proposed by Magnussen et al.,[12] originating the UNIFAC-LLE model. Owing to some inherent limitations of the UNIFAC model,[13] several modifications to

this model have been proposed. Some of these modifications are the UNIFAC−Dortmund,[14–17] the UNIFAC−Lyngby,[18] and, more recently, the A-UNIFAC.[19–21]

Experimental Section

Materials. The chemicals used, of chromatographic quality, were supplied by Sigma. The mass fraction purities were better than 99.6 % for methyl acetate, 99.8 % for methanol, 99.1 % for hexane, and 99.7 % for heptane. The maximum water mass fraction (determined with a Coulometric Moisture Model CA-06) were $6.8 \cdot 10^{-3}$, $1.5 \cdot 10^{-2}$, $7.8 \cdot 10^{-4}$, and $8.1 \cdot 10^{-4}$, for methyl acetate, methanol, hexane, and heptane, respectively. Prior to use, the liquids were degassed in an ultrasonic bath for 4 h, stored into inert argon (N55, volume fraction of water less than $3 \cdot 10^{-6}$), and dried over molecular sieves type 3Å for methanol and 4Å for methyl acetate and n-alkanes, 1/16 in. (Aldrich cat. no. 20,860-4 or 20,858-2, respectively). The chemicals were checked using gas chromatography, and the purities were better than those from vendor specifications. These purities were checked periodically during manipulation.

Apparatus and Procedure. The device for liquid–liquid equilibria determination consists of a jacketed glass cell with a magnetic stirrer. The cell was connected to a PolyScience bath model 9510, whose temperature stability was $\pm 10^{-2}$ K. The cell temperature was measured with a given uncertainty of $\pm 5 \cdot 10^{-2}$ K with a Yokogawa 7563 digital thermometer with a precision of $\pm 10^{-2}$ K, calibrated with an Anton Paar MKT-100 digital thermometer (precision $\pm 10^{-3}$ K, temperature scale ITS-90) over the entire temperature range. The samples were prepared by mass using a Mettler AX 205 DeltaRange balance with a precision of ± 0.00008 g, which gives an uncertainty of $\pm 4 \cdot 10^{-4}$ mol fraction. Each mixture was stirred for 60 min and then left to settle for at least 12 h. After equilibrium was attained, the phases were allowed to separate and small samples of approximately 2 mL were taken from the upper and lower phase with a syringe.

Sample Analysis. The compositions were determined by gas chromatography using a Hewlett-Packard HP-6890 Series GC

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