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Quaternary liquid–liquid equilibria for systems of {(water + methanol or ethanol) + *m*-xylene + *n*-dodecane}

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Abstract

Liquid–liquid equilibrium (LLE) data were determined for the quaternary systems of {(water + methanol or ethanol) + *m*-xylene + *n*-dodecane} at three temperatures 298.15, 303.15 and 313.15 K and atmospheric pressure. The composition of liquid phases at equilibrium was determined by gas–liquid chromatography and the results were correlated with the UNIQUAC and NRTL activity coefficient models. The partition coefficients and the selectivity factor of the solvent are calculated and compared. The phase diagrams for the quaternary systems including both the experimental and correlated tie lines are presented.

Keywords: Quaternary mixtures; Extraction; Methanol; Ethanol; *m*-Xylene; *n*-Dodecane; Activity coefficient; NRTL; UNIQUAC

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1. Introduction

Liquid–liquid equilibria (LLE) of ternary and quaternary systems have been the subject of interest of many researchers from various aspects. In ternary systems, one of the components may be considered as the solvent, whereas in quaternary systems usually a mixture of two components is considered as the mixed solvent. However, water as a solvent or as a co-solvent affects the phase behavior and solubility of components in these systems. For example, in {isooctane + aromatic + methanol + water} system the presence of water greatly modifies the solubility of methanol in hydrocarbon mixture [1] and a very small quantity of water can produce a phase separation [2,3].

Interesting work on quaternary systems water + acetone + acetic acid + chloroform has been done by applying a systematic method of selection of points to be measured. This method permits two-phase region to be fully characterized as well as allowing a graphical representation of the equilibrium data in a form suitable for extraction computations [4]. Also, experimental data of quaternary system 1-octanol + 2-methoxy-2-methylbutane + water + methanol have been correlated using three equations as modified Wilson, NRTL and UNIQUAC [5]. Various thermodynamic models have been used for predicting the phase behavior of multicomponents systems containing water [6].

There has been a considerable interest in using suitable co-solvents for extracting aromatic hydrocarbons from alkane mixtures in different chemical and oil industries [7–10]. Unfortunately, in spite of economical and environmental importance of water, not much attention has been paid to the role of water as a co-solvent in solvent extraction of aromatic compounds from alkane mixtures.

In previous work [7], we reported the LLE results for the systems {tetramethylene sulfone or dimethyl solfoxide or ethylene carbonate + toluene or *m*-xylene + *n*-heptane or *n*-octane or cyclohexane} at different temperatures (298.15, 303.15 and 313.15 K) and the results were correlated with the UNIQUAC [11] and NRTL [12] activity coefficient models. On the basis of this work it was suggested that ethylene carbonate as a solvent was more suitable than tetramethylene sulfone or dimethyl solfoxide for extracting aromatic hydrocarbons from alkane mixtures.

Methanol and ethanol may be considered as the suitable solvents in the recovery of aromatics, such as toluene and *m*-xylene

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from refinery process streams. Unfortunately, the experimental LLE data of interest for the extraction of aromatic hydrocarbon by solvent alcohol, such as methanol and ethanol, are scarce. Therefore, it is worth while to study the LLE of quaternary mixtures of $\{$(water + methanol) or (water + ethanol) or (methanol + ethanol) + *m*-xylene + alkanes$\}$. The results of this study can lead to decide which solvent has a higher selectivity factor and is more suitable for solvent extraction of aromatic hydrocarbons from alkanes.

In continuation of the previous work [7] and to investigate the effect of water as co-solvent in extracting aromatic hydrocarbons from alkane mixtures we report, in this work, the LLE results for the mixtures $\{$mixed-solvent (1) + aromatic hydrocarbon (2) + alkane (3)$\}$ at three temperatures (298.15, 303.15 and 313.15 K) where the mixed-solvents (1) are: $\{$water $(1')$ + methanol $(1'')\}$ or $\{$water $(1')$ + ethanol $(1'')\}$ or $\{$methanol $(1')$ + ethanol $(1'')\}$ and the aromatic hydrocarbon is *m*-xylene (2) and the alkane is *n*-dodecane (3).

2. Experimental

Pure grade compounds, methanol, ethanol, *n*-dodecane, *m*-xylene were supplied by Merck Co. Inc., Germany. Double distilled water was used throughout all experiments. The purity of each compound was checked by gas chromatography, and the results confirmed the mass fraction purity was higher than 0.99.

The experimental procedure in sample mixture preparation was described in previous work [7]. The gas–liquid chromatography (GLC) measurement was used to determine the composition of mixtures. The operating condition of GLC measurements is given in Table 1. In the GLC measurements for the quaternary systems $\{$alcohol + water + *m*-xylene + dodecane$\}$ the standard mixtures were prepared gravimetrically and the relative response factor of the component i (alcohol or *m*-xylene) to the component j (dodecane) in the standard mixtures was determined by averaging the results obtained from the following equation [13]:

$$(\mathrm{RRF}_i)_\mathrm{s} = \frac{(\mathrm{RF}_i)_\mathrm{s}}{(\mathrm{RF}_j)_\mathrm{s}} = \left(\frac{A_j}{A_i}\right)_\mathrm{s} \left(\frac{W_i}{W_j}\right)_\mathrm{s} \qquad (1)$$

where RRF, RF, A, and W represent, respectively, the relative response factor, the response factor, the peak area and the weight the components (i and j) in the standard mixture. The weight of component i in the mixture x was calculated by the following equation:

$$(W_i)_x = \frac{(A_i)_x (W_i)_\mathrm{s}}{(A_i)_\mathrm{s} (\mathrm{RRF}_i)_\mathrm{s}} \qquad (2)$$

Table 1
Operating condition for gas–liquid chromatographic analysis

Column size	2 m × 2.2 mm
Column packing	6% Silar 10 Csorb WHP 100–200 mesh
Detector temperature	523.15 K
Injector temperature	523.15 K
Oven temperature	$333.15\,\mathrm{K}(\text{isotime} = 1\,\mathrm{min}) \xrightarrow{298.15\,\mathrm{K\,min^{-1}}} 463.15\,\mathrm{K}$
Carrier gas	Nitrogen
Flow rate	$25\,\mathrm{cm^3\,min^{-1}}$

The weight fraction of water in the mixture x was calculated via the following equation:

$$(W_{\mathrm{H_2O}})_x = \frac{[(W)_x - \sum_i (W_i)_x]}{(W)_x} \qquad (3)$$

where $(W)_x$ is the weight of the quaternary mixture x and i represents each component in the mixture except water. For the same mixtures the weight fractions of water was also measured directly by Karl Fisher method using a Metrohm device (KF Coulometer, 684, Switzerland) and the results were in agreement with the calculated values by Eq. (3) within accuracy of ±0.001. The weight fractions were converted to mole fractions and were used for phase equilibrium calculations.

3. Results and discussion

The schematic representation [4] of quaternary system of $\{$methanol + ethanol + *m*-xylene + dodecane$\}$ is shown in Fig. 1. The sectional planes represent the ternary systems of $\{$mixed-solvent (methanol + ethanol) + *m*-xylene + dodecane$\}$. A similar figure can be drawn for the systems $\{$mixed-solvent (methanol + water) + *m*-xylene + dodecane$\}$ and $\{$mixed-solvent (ethanol + water) + *m*-xylene + dodecane$\}$. The shaded sectional plane in Fig. 1 represents the equimolar mixed-solvent used in this work. As examples, the phase diagrams of the ternary systems $\{$equimolar mixed-solvent (1) + *m*-xylene (2) + dodecane (3)$\}$ are represented in Figs. 2–4, respectively, for equimolar mixed-solvents (methanol + water), (ethanol + water) and (methanol + ethanol) at 303.15 K. For the studied quaternary systems the equilibrium mole fractions of constituent i in the solvent rich-phase x_i^s and in the alkane rich-phase x_i^a are reported in Table 2.

The experimental data were correlated by using UNIQUAC and NRTL models by minimizing the following objective

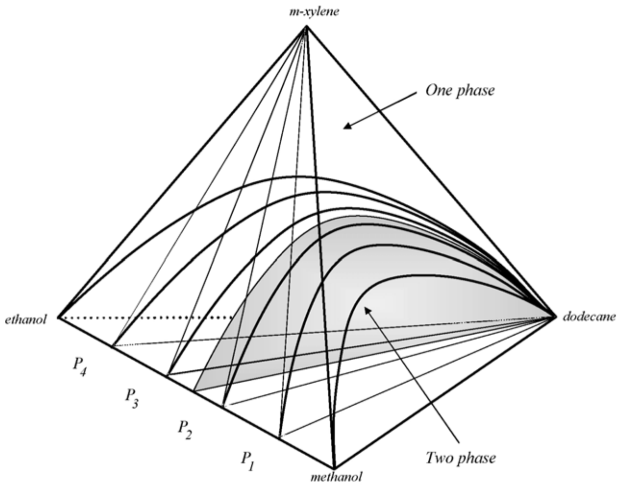

Fig. 1. Schematic representation of quaternary system (mixed solvent $(1'$ and $1'')$ + *m*–*m*-xylene (2) + dodecane (3). P_1–P_4 are sectional planes for the determining of the bimodal surface.