

Measurement of phase equilibria data for the extraction of toluene from alkane using different solvents



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ABSTRACT

In the petrochemical industry, the separation of aromatics from alkanes is a complex process due to the overlapping boiling points and azeotrope formation in specific operational conditions. In this work, 2-hydroxy ethylammonium formate (2-HEAF) and glycerol were evaluated as an extractor solvent of toluene from decane + toluene mixtures, by comparing with widespread solvent used in industrial applications, sulfolane. New liquid–liquid equilibrium (LLE) data for three ternary systems: {decane (1)+toluene (2)+glycerol (3); decane (1)+toluene (2)+[2-HEAF] (4); and decane (1)+toluene (2)+sulfolane (5)} at $T=(303.15$ and $333.15)$ K and atmospheric pressure has been studied. Heterogeneous region in LLE diagram presents a wide area and are not influenced by temperature, in the studied domain. From experimental data, distribution coefficients and selectivity parameters have been used determined and used to evaluate the efficiency of the studied solvents (sulfolane, glycerol and 2-HEAF) to extract toluene from decane. Two thermodynamics models (NRTL and UNIQUAC) were used to obtain binary interaction parameters. These models have been also used to correlate LLE experimental data for the studied ternary systems. A comparison between experimental and calculated data indicate that better agreement has been performed by using NRTL model.

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1. Introduction

Aromatics hydrocarbons (benzene, toluene and xylenes, also known as BTX's) are of great importance for petrochemical industry due to their large industrial use in several processes [1]. These components are usually obtained from naphtha, which are presented in multicomponent mixtures along with aliphatic hydrocarbons.

The separation of BTX aromatic mixtures from aliphatic hydrocarbon mixtures is still a challenge since these hydrocarbons present closer boiling points. In addition, it could present several combinations of azeotropes [2]. Currently, liquid–liquid extraction is the most widely process used to promote this separation.

The key to an effective liquid–liquid extraction process is the discovery of a suitable solvent [3]. Many organic solvents are used aromatic extraction processes, among them it could be mentioned: sulfolane [4–8], glycols [9–13], *N*-formylmorpholine (NFM) [2,14,15], *N*-methylpyrrolidone (NMP) [16,17], furfural [18],

dimethyl sulfoxide (DMSO) [19], and ionic liquids [20–24]. It is important to emphasize that ionic liquids have been proposed in the last years by academic community.

Liquid–liquid equilibria (LLE) data of aromatic hydrocarbons + aliphatic hydrocarbons + solvent are necessary for estimating the model parameters used for the design and modeling of aromatics extraction.

Therefore, in this work, ionic liquid [2-hydroxy ethylammonium formate (2-HEAF)] and glycerol were investigated as solvent for the extraction of toluene from decane. These results have been compared and contrasted to the use of a regular solvent employed in petrochemical industry, e.g., sulfolane. The ionic liquid 2-HEAF was selected due to its easy preparation under ambient conditions. Additionally, glycerol has been selected because of its properties, which can be used as extractor solvent for aromatics. Likewise, the use of glycerol presents two important characteristics. Firstly, it could reduce the impact of its production, once it is an environmental passive product (it is a side-product of biodiesel production). Secondly, it could be an inexpensive solvent.

LLE data for three ternary mixtures {aliphatic hydrocarbon + aromatic hydrocarbon + solvent} were determined at $T=(303.15$ and $333.15)$ K and atmospheric pressure. The selectivity

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and solute distribution ratio were calculated, and both parameters were used to analyze the efficiency these solvents as extractors of the aromatics. NRTL [25] and UNIQUAC [26] thermodynamic models were used to correlate the experimental LLE data.

2. Experimental

2.1. Reagents

Analytical grade decane (mass fraction $\geq 99\%$), toluene (mass fraction $\geq 99.8\%$), sulfolane (mass fraction $\geq 99\%$) and glycerol (mass fraction $\geq 99.5\%$) were supplied by Sigma–Aldrich and Vetec. It is important to mention that all chemicals were used without any further purification processes. The ionic liquid [2-HEAF] has been obtained by acid–base reaction, in which acid were added dropwise to base under stirring at a controlled constant temperature resulting the organic salt. This ionic liquid has been purified by intermediate of vacuum drying process [27]. Fig. 1 depicts ionic liquid structure determined by nuclear magnetic resonance (NMR). It is important to notice that 2-HEAF has been prepared by our Research Group (Phase Equilibria Laboratory). The properties of pure components are listed in Table 1.

2.2. Apparatus and procedure

The experimental LLE data of the {decane (1)+toluene (2)+glycerol (3), decane (1)+toluene (2)+[2-HEAF] (4) and decane (1)+toluene (2)+sulfolane (5)} ternary systems have been determined at $T=(303.15$ and $333.15)$ K and atmospheric pressure. Liquid–liquid equilibrium data have been obtained by using a glass cell jacketed with a volume capacity of approximately of 60 cm^3 . Homogenization has been carried out by using a suitable magnet bar.

Binodal curves were determined by titration method. Binary mixtures of known composition were prepared gravimetrically and these mixtures were then titrated with a third component to occur until the onset of turbidity in the solution.

Binodal experimental curves for decane-rich phase were determined from binary mixtures containing of decane + toluene. These mixtures were titrated with a third component (glycerol, for decane + toluene + glycerol system; 2-HEAF, for decane + toluene + 2-HEAF system; and sulfolane, for decane + toluene + sulfolane system). Since, binodal curves for the solvent-rich phase were obtained from titration technique from binary mixtures containing solvent (glycerol, 2-HEAF and sulfolane) + toluene, in which the titrant was decane.

The amount of titrant (third component) was calculated by intermediated of gravimetric analysis; and density data was determined by using an oscilating U-tube digital densimeter (DSA 5000, Anton Paar). A sample of approximately 5 mL is required to perform the analysis. For a single injection, analysis is performed in duplicate. The uncertainty of the experimental density estimated to be $\pm 0.00008\text{ g cm}^{-3}$. It is important to mention that the composition of the ternary mixture at the first appearance of turbidity matches a point on the binodal curve. The procedure was repeated a number of times, and a series of measurements were made by changing the composition of the mixtures.

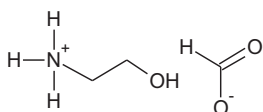


Fig. 1. Structure of 2-hydroxy ethylammonium formate.

Table 1

Supplier, CAS No., purity in mass fraction, density (ρ) of pure components at $T=303.15\text{ K}$.^a

Chemical name	Source	CAS No.	Purity Mass fraction	Density (g cm^{-3})
Decane	Sigma–Aldrich	124-18-5	$\geq 99\%$	0.722439
Toluene	Sigma–Aldrich	108-88-3	$\geq 99.8\%$	0.857606
Glycerol	Vetec	–	$\geq 99.5\%$	1.257128
2-HEAF ^b	LFQA	–	–	1.184462
Sulfolane	Sigma–Aldrich	126-33-0	$\geq 99\%$	1.265751

^a Standard uncertainty are $\sigma(T)=0.01\text{ K}$; $\sigma(\rho)=0.00008$.

^b 2-Hydroxy ethylammonium formate.

Points overall composition were determined graphically within the heterogeneous region bounded by the binodal curve. In the cell, the mass of the three components was measured gravimetrically with the aid of an analytical balance. After weighing, the cells were completely sealed and subjected to vigorous stirring for 3 h in order to ensure an efficient contact between both phases. Then, the system was allowed to stand for 16 h, time necessary for the formation to occur in two phases and a well-defined interface. Of each phase formed, a sample was collected approximately 5 mL for density analysis.

Samples of each phase in equilibrium have been collected and density data have been experimentally determined. From binodal curves, a set of parameters has been obtained by using a polynomial fit. From these data, calibration curves for each component were used to solve the second order polynomial equation. From this equation, all compositions from both phases could be quantified. This procedure has been described in detail previously [13].

2.3. Thermodynamics modeling

Liquid–liquid equilibria (LLE) experimental data were correlated with the NRTL model of Renon and Prausnitz [25] and the UNIQUAC model of Abrams and Prausnitz [26]. To correlate the LLE results of the ternary systems studied in this work the TML–LLE 2.0 program [28] was used.

The objective function (F.O.), proposed by Nelder and Mead [29], used in this case was determined by minimizing the square of the difference between the data fitted by the respective methods and these experimentally measured over all the tie-lines in the ternary system, by using experimental and modeling ternary compositions (Eq. (1)).

$$\text{F.O.} = \sum_k^D \sum_j^M \sum_i^{N-1} \left\{ \left(x_{ijk}^{D,\text{exp}} - x_{ijk}^{D,\text{calc}} \right)^2 + \left(x_{ijk}^{S,\text{exp}} - x_{ijk}^{S,\text{calc}} \right)^2 \right\} \quad (1)$$

where D is the number of data set, N and M are the number of components and tie-lines for each data set, respectively; superscripts D and S represent to the two liquid phases in equilibrium, while the superscript “exp” and “calc” denote to experimental values and calculated concentration.

The goodness of the fit was analyzed in terms of root mean square deviation (RMSD) values between experimental and model tie-lines, follow Eq. (2).

$$\Delta x = 100 \sqrt{\frac{\sum_i^M \sum_j^N \left(x_{ij}^{I,\text{exp}} - x_{ij}^{I,\text{calc}} \right)^2 + \left(x_{ij}^{II,\text{exp}} - x_{ij}^{II,\text{calc}} \right)^2}{2MN}} \quad (2)$$

where N and M are the number of components and tie-lines for each data set, respectively; superscripts D and S represent to the

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