



Quaternary (liquid + liquid) equilibria for systems of imidazolium based ionic liquid + thiophene + pyridine + cyclohexane at 298.15 K: Experiments and quantum chemical predictions

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ABSTRACT

1-Ethyl 3-methylimidazolium acetate [EMIM][OAc], 1-ethyl 3-methylimidazolium ethylsulfate [EMIM][EtSO₄] and 1-ethyl 3-methylimidazolium methylsulfonate [EMIM][MeSO₃] are found to be effective for the selective removal of a five member ring sulfur compound, viz. thiophene, and a six member ring nitrogen compound, viz. pyridine from a hydrocarbon, viz. cyclohexane at room temperature and atmospheric pressure. The liquid liquid equilibrium (LLE) data for the quaternary mixtures of ionic liquid (1) + thiophene (2) + pyridine (3) + cyclohexane (4) are experimentally determined. The experimental tie line data are successfully correlated with the Non Random Two Liquid (NRTL) and UNiversal QUAasi-Chemical (UNIQUAC) models, which provide a good correlation of the experimental data with root mean square deviation (RMSD) values less than unity for all the studied systems. The results suggest that the structure and size of the anion greatly affects the extractive performance of ionic liquids. The reliability of experimental data is ascertained by applying the quantum chemical based CONductor like Screening Model-Segment Activity Coefficient (COSMO-SAC) model. The goodness of the fit is determined by calculating the RMSD values. The RMSD values obtained for [EMIM][OAc], [EMIM][EtSO₄] and [EMIM][MeSO₃] are 10.4%, 8.1% and 12.2%, respectively.

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1. Introduction

In the past decade, much attention has been paid to the production and use of more environmentally friendly transportation fuels with lower concentration of aromatic nitrogen and sulfur [1]. Hydrodenitration (HDN) and hydrodesulfurization (HDS) are the conventional methods to remove these compounds in industrial processes. The main disadvantages of HDN and HDS are high operating temperatures (>300 °C), high pressures (>4 MPa), high energy costs, and large reactor size. These limitations can lead to an increase in the associated costs such as capital and operating costs. Moreover it is very difficult to remove both kinds of compounds in a single step at ambient conditions because the aromatic nitrogen compounds poison the active catalyst leading to coke formation. Nitrogen and sulfur in diesel oil also remain a major source of NO_x and SO_x which contribute to air pollution, global warming, greenhouse effect and

acid rain [2,3]. Thus the threshold limits for nitrogen and sulfur in diesel oil are expected to be regulated on a global level to less than 1 ppm of nitrogen and 10 ppm of sulfur [4–7].

Recently ionic liquids have been used as extracting solvents for the removal of nitrogen and sulfur from liquid fuel at ambient temperature and pressure. Usually, ionic liquids are salts which are in liquid state at a temperature below 100 °C. Ionic liquids have a negligible vapor pressure. Hence, there is no emission of volatile organic compounds to the environment. They are nonvolatile and exhibit a high ionic conductivity. Ionic liquids are also highly solvating and non-coordinating mediums [8–30]. Moreover, ionic liquids consist of cation and anion combinations. A large number of cations and anions that can form ionic liquids are available. Hence, the number of ionic liquids that can be synthesized from their combinations is large. As a result, their physiochemical properties (i.e. melting point, viscosity, density, solubility etc.) can be tuned by varying the cations and anions.

Generally aromatic nitrogen and sulfur based compounds have low activity coefficient at infinite dilution in ionic liquids, whereas diesel compounds shows high activity coefficients [3,31–33] in ionic liquids. Smaller the values of the activity coefficient, stronger are the interactions between the solute and ionic liquid. Since, there is a large difference in the activity coefficients of the nitrogen

Abbreviations: [EMIM], 1-ethyl 3-methylimidazolium cation; [OAc], acetate anion; [EtSO₄], ethylsulfate anion; [MeSO₃], methylsulfonate anion.

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Nomenclature

Latin symbols

F	objective function
H_i	peak area under NMR spectra of species i
$RMSD$	root mean square deviation
S	selectivity
c	number of components in the LLE system

m	number of tie lines
x_i	mole fraction of component i of either phase in the LLE system

Greek symbols

β	distribution coefficient
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and sulfur compound present in diesel in the ionic liquid, and the activity coefficient of the hydrocarbons in the ionic liquid, a high selectivity is obtained. In addition to the high selectivity (S), high capacity (C) is also essential. This can be achieved by selecting an ionic liquid with a large solubility of the nitrogen and sulfur compounds. The selectivity and capacity for different combinations of cation and anion can be measured. Alternatively, it can be calculated using predictive models such as the CONductor like Screening MOdel for Real solvent (COSMO-RS) [34] and the CONductor like Screening Model-Segment Activity Coefficient (COSMO-SAC) [35]. Previous work [36,37] shows the feasibility and ability of ionic liquids to remove various aromatic sulfur compounds viz. thiophene, benzothiophene, and dibenzothiophene, and nitrogen compounds (five member ring: pyrrole, indole, indoline, carbazole, benzocarbazole, and dibenzocarbazole, six member ring: pyridine, quinoline and benzoquinoline) from diesel oil. Simultaneous extraction of aromatic nitrogen and sulfur from diesel oil compounds with ionic liquids is expected to require less number of stages and less energy consumption than extraction with conventional solvents because ionic liquids have a negligible vapor pressure and hence can be recycled. Shah and Yadav [38] had provided a criterion for screening of ionic liquids for aromatic/aliphatic separations using the Cosmo-SAC model and the “Cosmo” files for eight cations and sixteen anions corresponding to 128 potential ionic liquids have been provided for the use of the general scientific community to predict any thermodynamic equilibria involving ionic liquids without the use of any molecular modeling software. They also used the model for prediction of liquid–liquid equilibria for biofuel applications [39] and prediction of sorption in polymeric membranes [40].

The aim of this work is to investigate the feasibility of the liquid–liquid extraction process for the separation of thiophene and pyridine from diesel compounds at ambient temperature using 1-ethyl-3-methylimidazolium acetate [EMIM][OAc], 1-ethyl-3-methylimidazolium ethylsulfate [EMIM][EtSO₄] and 1-ethyl-3-methylimidazolium methylsulfonate [EMIM][MeSO₃] ionic liquids. The cation and anions have been selected on the basis of the selectivities predicted by the COSMO-RS model [3,32,33]. The ability of the selected ionic liquids to separate the nitrogen and sulfur compounds from diesel has been evaluated by measurement of quaternary (liquid + liquid) equilibrium (LLE) data and the results have been shown in terms of a ternary diagram with the ionic liquid, (thiophene + pyridine) and cyclohexane as the three components in the ternary diagram. These data can be helpful in understanding the thermodynamic limit in separation, and the design of the liquid–liquid extraction column. The (liquid + liquid) equilibria for the quaternary mixtures of [EMIM][OAc] + thiophene + pyridine + cyclohexane, [EMIM][EtSO₄] + thiophene + pyridine + cyclohexane and [EMIM][MeSO₃] + thiophene + pyridine + cyclohexane have been determined at 298.15 K. The selectivity and the distribution coefficient have also been determined from the experimental data. Further, the obtained experimental data are benchmarked with the predictions of the COSMO-SAC model and correlated with the NRTL and UNIQUAC models.

2. Experimental section

The ionic liquids: 1-ethyl-3-methylimidazolium acetate [EMIM][OAc](C₈H₁₄N₂O₂) of purity >99% and 1-ethyl-3-methylimidazolium ethyl sulfate [EMIM][EtSO₄] (C₈H₁₆N₂O₄S) of purity >99% were supplied by Sigma Aldrich, Germany. 1-ethyl-3-methylimidazolium methanesulfonate [EMIM][MeSO₃] (C₈H₁₆N₂O₃S) ionic liquid was purchased from Fluka with a purity of >99%. Pyridine (C₅H₅N) and thiophene (C₄H₄S) were received from Sigma Aldrich with mass fractions greater than 98%. Cyclohexane (C₆H₁₂) was obtained from Merck with a purity of >99.5%. CDCl₃ of purity >99.8%, used for the NMR analysis of the extract and raffinate phase compositions, was supplied by Sigma Aldrich, Germany. The water content (in mole%) for 1-ethyl-3-methylimidazolium ethylsulfate, 1-ethyl-3-methylimidazolium acetate and 1-ethyl-3-methylimidazolium thiocyanate are found to be 0.08, 0.044 and 0.044, respectively. It has been measured by using Karl Fischer Titrator (KF 787, METROHM). The chemical structures of the studied compounds are given in table 1.

The purity of the chemicals is checked by measuring the density, refractive index and surface tension. Densities of the pure components are measured at $p = 1$ atm with Anton Paar DSA-4500MA digital vibrating U-tube densimeter where it has a thermoelectric temperature control system. The uncertainty in the density measurement is ± 0.0011 g · cm⁻³. The calibration is performed by measuring the density of Millipore quality water and ambient air. The surface tension is measured with a tensiometer by plate type method (Hanging drop tensiometer method, Kruss K9, Germany) with a precision of 0.01 mN/m. Here too the calibration is performed by measuring the surface tension of Millipore quality water at ambient temperature. Finally the refractive index is determined at ambient temperature using an automatic refractometer AD-13 model (ABBEMAT-WR Dr. Kernchen) having an uncertainty of ± 0.00004 . A third decimal place (table 2) variation for all the properties confirms purity for experimental studies.

A 3:1 M ratio of thiophene and pyridine is prepared and then added to an equimolar solution of ionic liquid and cyclohexane. Varying the concentration of thiophene and pyridine from 5% to 80% resulted in mixtures of different compositions. The exact amount of individual components is transferred into the stoppered bottles using 5 ml syringe. We have kept the total volume of the mixture to 8 ml for all the tie lines. Finally 15 ml stoppered bottles, properly sealed with parafilm tape, are used to hold the feed mixture. The bottles are then placed in thermostatic shaker bath (Dailhan Lab, China) which is set at a speed of 100 rpm and at $T = 298.15$ K. The temperature is maintained with an uncertainty of ± 0.01 K. The total duration of mixing is kept at 6 h. The mixture is then allowed to settle overnight for a minimum of 12 h so that equilibrium is attained.

The equilibrium phases (i.e. the ionic liquid and the cyclohexane rich phase) are analyzed using the NMR spectrometer of 11.74 Tesla (20 MHz response of ¹H). Initially a small amount of each phase is dissolved in 0.5 ml of CDCl₃ in separate NMR (thrift

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