Fluid Phase Equilibria 312 (2011) 20–30

Contents lists available at SciVerse ScienceDirect

Fluid Phase Equilibria

journal homepage: www.elsevier.com/locate/fluid

# Liquid–liquid equilibria for quaternary systems of imidazolium based ionic liquid + thiophene + pyridine + iso-octane at 298.15 K: Experiments and quantum chemical predictions

Ramalingam Anantharaj, Tamal Banerjee*

*Department of Chemical Engineering, Indian Institute of Technology Guwahati, Guwahati 781039, Assam, India*

ARTICLE INFO

*Article history:*
Received 3 May 2011
Received in revised form 6 September 2011
Accepted 10 September 2011
Available online 17 September 2011

*Keywords:*
Ionic liquids
Simultaneous extraction
COSMO-RS model
Thermodynamics models

ABSTRACT

In this work, 1-ethyl 3-methylimidazolium acetate [EMIM][OAc], 1-ethyl 3-methylimidazolium ethylsulphate [EMIM][$EtSO_4$] and 1-ethyl 3-methylimidazolium methylsulphonate [EMIM][$MeSO_3$] were investigated as green solvents for the simultaneous separation of thiophene and pyridine from iso-octane at 298.15 K and atmospheric pressure. The liquid–liquid equilibrium (LLE) data for the quaternary mixture of 1-ethyl 3-methylimidazolium acetate (1) + thiophene (2) + pyridine (3) + isooctane (4), 1-ethyl 3-methylimidazolium ethylsulphate (1) + thiophene (2) + pyridine (3) + isooctane (4) and 1-ethyl 3-methylimidazolium methylsulphonate (1) + thiophene (2) + pyridine (3) + isooctane (4) systems were experimentally determined at ambient conditions. The effectiveness of the simultaneous extraction of thiophene and pyridine from iso octane was evaluated by selectivity and distribution coefficient values. The experimental tie-line data were accurately correlated with the non-random two liquid (NRTL) and UNIversal QUAasi-Chemical (UNIQUAC) models, which provides a good correlation of the experimental data with root mean square deviation (RMSD) values lesser than unity for all the studied systems. The reliability of experimental data was further ascertained by applying the Quantum chemical based COnductor like Screening MOdel for Real Solvents (COSMO-RS) model. The predictions were compared with the RMSD, i.e. 7.4% ([EMIM][OAc]), 4.49% ([EMIM][$EtSO_4$]) and 8.26% ([EMIM][$MeSO_3$]). These results show that [EMIM][OAc], [EMIM][$EtSO_4$] and [EMIM][$MeSO_3$] ionic liquid can be used as an alternative solvent for the simultaneous separation of thiophene and pyridine from hydrocarbon stream via LLE processes at ambient conditions.

## 1. Introduction

Global emissions of oxidized sulphur (S) and nitrogen (N), collectively known as $SO_X$ and $NO_X$ results from the combustion of fuel in engine, petroleum refineries, chemical and coal burning power plants [1]. $SO_X$ and $NO_X$ can cause harmful effect to the environment by causing acid rain. It also acts as a poison in the catalytic converter of exhaust emission [2–5]. Thus it is imperative to remove sulphur and nitrogen compound from diesel oil. The regulation proposed for sulphur concentration in diesel oil is between 10 and 350 ppm, while for nitrogen concentration it is between 0.1 and 75 ppm [6].

The sulphur and nitrogen compounds are conventionally removed via hydrodesulphurization (HDS) and hydrodenitification (HDN), respectively. However, the aromatic sulphur (thiophene, benzothiophene and dibenzothiophene) and nitrogen compounds (pyrrole, indole, indoline, carbazole, pyridine, quinoline and its derivatives) react with traditional catalyst, even at severe operating conditions. Apart from that, it requires a large reactor volume, high hydrogen consumption and a low space velocity which ultimately leads to an increase in the investment and operating cost. It should be noted that the HDS and HDN process is efficient with aliphatic compounds of sulphur and nitrogen compounds such as thiols (R–SH), thioethers (R–S–R), disulphides (R–$S_2$–R), aliphatic amines and aniline [7].

The conventional unit operations used in the refineries are liquid–liquid extraction (LLE), precipitation, oxidative desulphurization, selective adsorption and biodesulphurization using bacteria as catalyst [1,2,8]. However, the process having catalyst produces volatile organic compounds (VOC) at severe operating conditions. Nevertheless, LLE is a well established process that can be carried out at ambient conditions with the help of a suitable solvent instead of catalyst. On the other hand the recovery of the solvent from extract phase requires an additional distillation step to separate the solvent from either phase. Thus in summary, the major advantages for LLE are: (1) no additional catalyst, (2) no special

---

* Corresponding author. Tel.: +91 361 2582266; fax: +91 361 2690762.
*E-mail address:* tamalb@iitg.ernet.in (T. Banerjee).

0378-3812/$ – see front matter © 2011 Elsevier B.V. All rights reserved.
doi:10.1016/j.fluid.2011.09.006

**Nomenclature**

| | |
|---|---|
| [EMIM] | cation: 1-ethyl 3-methylimidazolium |
| [$CH_3COO$] | anion: acetate |
| [$EtSO_4$] | anion: ethyl sulphate |
| [$MeSO_3$] | anion: methylsulphonate |
| $S$ | selectivity |
| $F$ | objective function |
| RMSD | root mean square deviation |
| $a_{\text{eff}}$ | effective segment surface area, Å$^2$ |
| $c_{\text{hb}}$ | misfit energy constant, kcal Å$^4$ mol$^{-1}$ e$^{-2}$ |
| $p_i(\sigma)$ | sigma profile of component $i$, i.e. probability of segment $i$ having a charge density $\sigma$ |
| $R$ | universal gas constant, J K$^{-1}$ mol$^{-1}$ |
| $T$ | temperature, K |
| $r_i$ | normalized volume parameter for the Staverman–Guggenheim combinatorial term, Å$^3$ |
| $q_i$ | normalized surface area parameter for the Staverman–Guggenheim combinatorial term, Å$^2$ |
| $r_{\text{std}}$ | standard volume parameter, 79.53 Å$^3$ |
| $q_{\text{std}}$ | standard surface area parameter, 66.69 Å$^2$ |
| $m$ | number of tie lines |
| $c$ | number of components in the LLE system |
| $x_i$ | mole fraction of component $i$ of either phase in the LLE system |
| $n_i$ | total number of segments on the surface of the molecular cavity |
| $H_i$ | peak area under NMR spectra of species $i$ |
| $z$ | coordination number = 10 |
| $l$ | Staverman–Guggenheim combinatorial term parameter |
| $g_{ji}$ | average interaction energy for the interaction of molecules of component $j$ with molecules of component $i$ |

*Greek symbols*

| | |
|---|---|
| $\alpha'$ | misfit energy constant, kcal Å$^4$ mol$^{-1}$ e$^{-2}$ |
| $\sigma_{\text{hb}}$ | hydrogen bonding cut-off value, 0.0084 e Å$^{-2}$ |
| $\gamma_{i/S}$ | activity coefficient of solute $i$ in solution $S$ |
| $\Gamma_S$ | segment activity coefficient of segment $\sigma_i$ in pure species |
| $H_i$ | peak area under NMR spectra of species $i$ |
| $\beta$ | distribution coefficient |
| $\theta$ | area fraction in UNIQUAC equation |
| $\tau$ | NRTL/UNIQUAC interaction parameter |
| $\Phi$ | segment fraction in UNIQUAC equation |
| $\alpha$ | NRTL non-randomness parameter |
| $\gamma_{i/S}^{SG}$ | Staverman–Guggenheim activity coefficient |

equipment requirement and (3) reduction in operating steps [9]. In contrast to organic solvent which produces VOC, ionic liquids (IL) have enormous advantages such as negligible vapor pressure, non-flammability, high thermal stability and recyclability which means that they are green in nature [9]. These properties make them a better selection with regards to health, safety and environmental concerns. In particularly IL is denser than other organic solvent and miscible with aromatic sulphur and nitrogen compounds. IL having high polarity [5] can simultaneously dissolve organic and inorganic molecules.

The possibility of IL as entrainer for the separation of aromatic sulphur and nitrogen compounds has already been explored earlier by experimental and computational studies [10,11]. However, ILs consisting of cation and anion is limitless in combination. Thus a judicious selection is required for its use as solvent. The quantum chemical based COnductor Like Screening MOdel for Real Solvent (COSMO-RS) is exactly used for evaluating ILs as solvents in extraction process. This is a novel and efficient method for a priori prediction of infinite dilution activity coefficient (IDAC). In our earlier work from the IDAC values, the selectivity ($S$), capacity ($C$) and performance index (PI) of IL were calculated for HDS, HDN [4,6] and simultaneous HDS and HDN process at $T$ = 298.15 K. According to our COSMO-RS predictions [4,6], considerably high selectivity and capacity were achieved for acetate ([OAc]), ethyl sulphate ([$EtSO_4$]) and methylsulphonate ([$MeSO_3$]) anion with [EMIM] cation. It was found that a smaller size of cation led to a higher selectivity. Thus we have chosen the ILs: 1-ethyl-3-methylimidazolium acetate ([EMIM][OAc]), 1-ethyl-3methylimidazolium ethylsulphate ([EMIM][$EtSO_4$]) and 1-ethyl-3-methylimidazolium methylsulphonate ([EMIM][$MesO_3$]) for the simultaneous removal of thiophene and pyridine from diesel oil.

The aim of this work is to investigate the quaternary LLE phase behavior of [EMIM][OAc], [EMIM][$EtSO_4$] and [EMIM][$MesO_3$] for the simultaneous extraction of thiophene and pyridine from hydrocarbon stream (i.e. Isooctane). This LLE data will be essential for the design of the extraction equipment and also helps us to know the thermodynamic limit of separation. Therefore the LLE diagram for quaternary mixture of [EMIM][OAc] + thiohphene + pyridine + isooctane, [EMIM][$EtSO_4$] + thiohphene + pyridine + isooctane and [EMIM][$MesO_3$] + thiohphene + pyridine + isooctane have been determined at ambient condition, i.e. at 298.15 K. From the experimental data the extraction efficiency of thiophene and pyridine, the selectivity and the distribution coefficient were also determined.

## 2. Computational

### 2.1. NRTL and UNIQUAC model

The non-ideal liquid phase activity coefficient ($\gamma$) of component $i$ are given conventionally using NRTL and UNIQUAC models. The details of the model can be found elsewhere [12,13] and hence are not stated here. The binary interaction parameters ($A_{ij}$) is calculated from the experimental LLE data by minimizing the objective function, which is defined as the sum of the square of errors between the experimental and calculated compositions of all the components over the entire set of tie lines as given by Eq. (1):

$$\text{Maximize}: F_{(\text{with respect to } A_{ij} \text{ where } i,j=1,2,3 \text{ and } j \neq i)}$$

$$= -\sum_{k=1}^{m}\sum_{l=I}^{II}\sum_{i=1}^{c} w_{ik}^{l}(x_{ik}^{l}-\hat{x}_{ik}^{l})^2, \ w_{ik}^{l}=1 \tag{1}$$

The methodology, application and the details are presented in our earlier work [14]. We have taken the population size, *npop* = 100, and the number of generations, *ngen* = 200 for the genetic algorithm (GA) program. As the GA toolbox [15] in MATLAB is for maximization, a negative objective function ($F$) is used for minimizing the total error between the experimental and the calculated mole fractions. The modified Rachford–Rice algorithm [16] was used to compute the tie lines. For the UNIQUAC model, the structure parameters $r$ and $q$ of the components are predicted using the polarizable continuum model (PCM) as outlined in our previous work [17].

### 2.2. COSMO-RS model

In 1995 Klamt proposed a novel combination of the Conductor-like Screening MOdel (COSMO) with statistical thermodynamic