Fluid Phase Equilibria 395 (2015) 9–14

Contents lists available at ScienceDirect

Fluid Phase Equilibria

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

Separation of pyridine from heptane with tricyanomethanide-based ionic liquids

Urszula Domańska [a,b,*], Elena Vadimovna Lukoshko [a]

[a] *Department of Physical Chemistry, Faculty of Chemistry, Warsaw University of Technology, Noakowskiego 3, 00-664 Warsaw, Poland*
[b] *Thermodynamic Research Unit, School of Engineering, University of KwaZulu-Natal, Howard College Campus, King George V Avenue, Durban 4041, South Africa*

ARTICLE INFO

Article history:
Received 17 February 2015
Received in revised form 10 March 2015
Accepted 12 March 2015
Available online 14 March 2015

Keywords:
Denitrogenation
Ionic liquids
1-Butyl-3-methylimidazolium tricyanomethanide
1-Butyl-1-methylmorpholinium tricyanomethanide
1-Butyl-1-methylpyridinium tricyanomethanide
Ternary (liquid–liquid) phase equilibrium
Selectivity
Solute distribution ratio
NRTL correlation

ABSTRACT

Recent approaches employ three tricyanomethanide-based ionic liquids (ILs) as selective solvents of the extraction of pyridine as a model compound of nitrogen compounds in fuels from heptane at $T = 298.15$ K and ambient pressure. Experimental data for liquid–liquid phase equilibrium (LLE) were obtained for three ternary systems. The 1-butyl-3-methylimidazolium tricyanomethanide, [BMIM][TCM], 1-butyl-1-methylmorpholinium tricyanomethanide, [BMMOR][TCM] and 1-butyl-1-methylpyridinium tricyanomethanide, [BMPY][TCM] were used due to their immiscibility with gasoline and diesel, negligible vapor pressure, and high selectivity to sulfur- and nitrogen-containing compounds. All of proposed ILs showed similar excellent selectivity with the best $S_{max} = 609.3$ for and similar high distribution ratio with $\beta_{max} = 9.2$ for [BMMOR][TCM] in the extraction of pyridine from heptane and much higher to what is currently published for different ILs. Chromatography analysis showed that IL was not present in the heptane layer. This eliminate the process of the separation of the solvent from the raffinate layer. The data obtained have been correlated with the non-random two liquid NRTL model. The experimental tie-lines and the phase composition in mole fraction in the ternary systems were calculated with an average root mean square deviation (RMSD) of 0.004.

1. Introduction

The emission of sulfur from petrol and diesel oils, which is linked to acid rain phenomena, plays a crucial role in pollution problems of large conglomerates. Commercially, the hydrodesulfurization (HDS) processes are the established method used in some industrial technologies to remove organic sulfur compounds from fuels. However, the aromatic sulfur compounds including thiophene, benzothiophene, methyldibenzothiophenes, 4,6-dibenzothiophenethiols, thioethers, and disulfides are more difficult to convert over HDS catalysts. Therefore, the liquid–liquid extraction (LLE) is proposed for deep desulfurization and denitrogenation by using the extractive solvents with high selectivity of absorption of sulfur and nitrogen compounds at high capacity without affecting the olefin contents. Extraction desulfurization and denitrogenation with ionic liquids (ILs) have the potential for alternative and future complementary technology for deep desulfurization [1–4]. These new organic solvents are already very well known as a high selective entrainers in many processes. From the beginning the popular 1-ethyl-3-methyl imidazolium tetrafluoroborate, [EMIM][BF_4] or 1-butyl-3-methylimidazolium hexafluorophosphate, [BMIM][PF_6] were proposed for desulfurization with average removal of sulfur compounds on the level of 13 (wt%) and nitrogen compounds 25 (wt%) [1]. For the denitrogenation of diesel fuel the 1-butyl-3-methylimidazolium sulfate, [BMIM][HSO_4], or 1-butyl-3-methylimidazolium methylsulfate, [BMIM][CH_3SO_4], or 1-ethyl-3-methyl imidazolium ethylsulfate [EMIM][$EtSO_4$] were proposed with high selectivity [2]. The interaction with a diesel model feed with 41 ILs and the extraction possibility of thiophene, or benzothiophene and nitrogen containing heteroaromatic compounds was recently presented in an open literature [4]. The extraction level about 70–86 (wt% for sulfur compounds) and 99 (wt% for nitrogen compounds) was found [4]. The best ILs used in this process were pyridinium and imidazolium-based ILs with dicyanoamide anion, $[N(CN)_2]^-$, or tricyanomethanide, $[C(CN)_3]^-$, $[TCM]^-$ anion, or thiocyanate, $[SCN]^-$ anion [4].

---

* Corresponding author at: Department of Physical Chemistry, Faculty of Chemistry, Warsaw University of Technology, Noakowskiego 3, 00-664 Warsaw, Poland. Tel.: +48 22 6213115; fax: +48 22 6282741.
E-mail address: ula@ch.pw.edu.pl (U. Domańska).

http://dx.doi.org/10.1016/j.fluid.2015.03.027
0378-3812/© 2015 Elsevier B.V. All rights reserved.

Nomenclature

List of symbols

g	Parameters of NRTL equation
n	Number of experimental points
T	Temperature
F	Objection function
x	Mole fraction

Greek letters

γ	Activity coefficient
τ	Energy parameter in the NRTL equation
RMSD	The root-mean-square deviation
α_{ij}	Non-randomness parameter of NRTL equation

Superscripts

calc	Calculated mole fraction
exp	Experimental mole fraction
LLE	LLE experimental value
I	Hydrocarbon-rich phase
II	The IL-rich phase

Subscripts

1	Ionic liquid
2	Pyridine
3	Heptane
i	The component
l	The component
m	The component

The application of many ILs as LLE solvents for petrol desulfurization and/or denitrogenation has already been reported during the last decade [5–17]. Two ILs, namely 1-hexyl-3,5-dimethylpyridinium bis(trifluoromethylsulfonyl) imide, [HMMPY][NTf_2] and 1-heptyl-2,3-dimethylimidazolium bis(trifluoromethylsulfonyl) imide, [HMMIM][NTf_2] were found to show high extraction selectivity of pyridine from model fuel on the level of 70 and 50 (wt%), respectively [5]. The LLE data for the quaternary mixture of {IL + thiophene + pyridine + pentane} were shown with 1-ethyl-3-methylimidazolium acetate, or ethylsulfate or methylsulfonate with average selectivity and distribution ratio [7]. Acidic ILs were used to desulfurization and denitrogenation of model fuel (hexane, or octane) and the removal of pyridine after 6-stage extraction at $T = 298.15$ K with 1-butyl-3-methylimidazolium chloride/zinc dichloride, [BMIM]Cl/$ZnCl_2$ was 97.8 (wt%) [17].

The effect of cation and anion of 21 ILs on the desulfurization of model fuel was observed in liquid–liquid phase equilibrium data at $T = 298.15$ K [18]. The ILs were chosen after many years of experimental work with different ILs from the literature and in our laboratory [5–18]. The best extraction of sulfur-compounds was obtained with 1-butyl-1-methylmorpholinium tricyanomethanide, [BMMOR][TCM], 1-buty-3-methylimidazolium tricyanomethanide, [BMIM][TCM] and 1-butyl-1-methylpyridinium tricyanomethanide, [BMPY][TCM] with the selectivity of extraction of thiophene $S = 159.7$, $S = 85.0$ and $S = 86.3$, respectively [18].

The 1-alkylpyrrolidinium-based ILs with different anions have been recently studied in our laboratory in ternary LLE {IL + thiophene + heptane} at $T = 298.15$ K [13]. The highest selectivity ($S_{max} = 133.4$) with high solute distribution ratio ($\beta = 3.47$) was found for 1-butyl-1-methylpyrrolidinium tricyanomethanide [BMPYR][TCM] [13].

With these results in the current work we continue our systematic study with focus on denitrogenation of fuels with the best tricyanomethanide-based ILs: [BMIM][TCM], [BMMOR][TCM], and [BMPY][TCM]. We report experimental ternary LLE data for three ILs, which we expected to show high selectivity for the extraction of pyridine from heptane. The extraction selectivity and the solute distribution ratio were determined and discussed from the experimental work.

2. Experimental

The ILs studied: [BMIM][TCM], [BMMOR][TCM] (CAS No. 1620828-20-7), and [BMPY][TCM] were purchased from IoLiTec (the structure, name, abbreviation and molecular mass are presented in Table 1 [19,20]) and all solvents used from Sigma–Aldrich (the origins of the chemicals, CAS numbers, purity, water content and densities are listed in Table 1S in the Supplementary material). The samples of ILs were dried for 24 h at 300 K under reduced pressure to remove volatile impurities and trace amounts of water. Pyridine was stored over freshly activated molecular sieves of type 4 Å (Union Carbide). The densities for all substances were measured at $T = 298.15$ K (or 293.15 K) and 101 kPa. The method and uncertainties have been described previously [13].

The water content was analyzed by the Karl-Fischer titration technique (method TitroLine KF). The sample of IL, or solvent was dissolved in methanol and titrated in steps of 0.0025 cm^3. The error in the water content was $\pm 10 \times 10^{-6}$ for the 3 cm^3 injected IL. The water content is listed in Table 1S in the Supplementary material.

For the determination of the experimental LLE tie-lines, mixtures with compositions inside the immiscible region of the systems were introduced into a jacketed glass cell with a volume of 10×10^{-3} cm^3. Solution was mixed with a coated magnetic stirring bar. The vessel was properly closed to avoid losses by evaporation or to pickup of moisture from the atmosphere. The jackets were connected to a thermostatic water bath (LAUDA Alpha) to maintain a constant temperature of $T = 298.15 \pm 0.05$ K. The mixtures were stirred for 6 h to reach the thermodynamic equilibrium and after minimum of 12 h were analyzed. After the phase separation, the samples of about $0.1–0.3 \times 10^{-3}$ cm^3 were taken from both phases using glass syringes with coupled stainless steel needles. Sample of the phase was placed in an ampoule with a capacity of 2×10^{-3} cm^3. The ampoule was closed with a septum cap. Next, acetone (1.0 cm^3) was added to the samples to avoid phase splitting and to maintain a homogeneous mixture. Propan-1-ol was used as internal standard for the GC-analysis. Because of the low vapor pressure, the ILs used in this work cannot be analyzed by GC. Samples from both top and bottom layers were analyzed using GC (PerkinElmer Clarus 580 GC equipped with auto sampler and FID and TCD detectors). Only pyridine and heptane were analyzed; the mass fraction of the third component (IL) was determined by subtracting the mol fractions of the two other components from one. The capillary column of the chromatograph was protected with an pre-column to avoid the non-volatile ionic liquid reaching the column in case of leak from the glass wool in the liner. The TotalChrom Workstation software was used to obtain the chromatographic areas for the pyridine, heptane and internal standard, propan-1-ol. Samples were injected three times, and the average value was calculated. The details of the used GC method are given in Table 2. The estimated uncertainty in the determination of mole fraction compositions is ±0.003 for compositions of the hydrocarbon-rich phase and ±0.005 for compositions of the IL-rich phase.

3. Results and discussion

The extractive denitrogenation performance results are listed in Table 3. The equilibrium compositions of the experimental tie-line