Fluid Phase Equilibria 427 (2016) 421–428

Contents lists available at ScienceDirect

Fluid Phase Equilibria

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

Separation of hex-1-ene/hexane and cyclohexene/cyclohexane compounds with [EMIM]-based ionic liquids

Urszula Domańska [a], [b], [*], Monika Karpińska [a], Michał Wlazło [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 30 April 2016
Received in revised form
22 July 2016
Accepted 6 August 2016
Available online 8 August 2016

Keywords:
[EMIM]-based ionic liquids
Ternary (liquid-liquid) phase diagrams
Selectivity
Solute distribution ratio
NRTL correlation
Extraction

ABSTRACT

In this work we studied the applicability of three imidazolium-based ionic liquids (ILs) with different anions in the separation of hex-1-ene/hexane and cyclohexene/cyclohexane compounds. Experimental data for liquid–liquid equilibrium (LLE) were obtained for various binary and ternary mixtures of {IL (1) + hex-1-ene (2) + hexane (3)} or {IL (1) + cyclohexene (2) + cyclohexane (3)} at $T = 298.15$ K and ambient pressure. Three ILs have been studied: 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)-imide, [EMIM][NTf_2], 1-ethyl-3-methylimidazolium dicyanamide, [EMIM][DCA] and 1-ethyl-3-methylimidazolium tricyanomethanide, [EMIM][TCM]. ILs were chosen after a literature analysis and measurements of activity coefficient at infinite dilution in many ILs. Chosen ILs showed excellent results in terms of selectivity and solute distribution ratio. The chromatography analysis revealed that the ILs used as an entrainers were not present in the hydrocarbon-rich layer. This is convenient for planned technology, because eliminates the step needed for the separation of the solvent. A comparative study of the separation effectiveness of the [EMIM][TCM] in comparison with two other reported ILs was chosen as the better solvent for the intended two separation processes. The non-random two liquid NRTL model was used successfully to correlate the experimental tie-lines and to calculate the phase composition error in mole fraction in the ternary systems.

1. Introduction

Separation of olefins and paraffins is a specific problem provided in a form of a distillation process, which involves large energetic and technological efforts because the boiling points of olefins and paraffins lie within narrow temperature ranges. From the industrial point of view and according to the previous argument, it is beneficiary to totally remove olefins from the feed stream. The removal of olefins with a commercial separation methods used for the separation of organic compounds suggests the liquid–liquid extraction (LLE), or extractive distillation, or azeotropic distillation. The LLE was widely used in industry for the aromatic hydrocarbon separation and purification because of usually low temperature, mild operation conditions and due to its simplicity. Among them, it is crucial to develop new solvents, such as ionic liquids (ILs) with a high solute distribution coefficient of entrainer, high selectivity of olefins to alkanes, and with little entrainer loss. The liquid-liquid extraction with ILs is probably the most studied technique and solvents for different separation processes last decade [1–3]. Development of new ILs that are stable when contacted with air and water increased the potential for their industrial application [4,5]. The use of the imidazolium-based ILs with bis{(trifluomethyl)sulfonyl}imide anion have given satisfying results in the process of separation of sulfur compounds from alkanes [6], or in the extraction of alcohols from water [7–9]. The crucial however is the influence of anion, which was discussed in many works connected with extraction. It was found that ILs with cyano group, CN- in the molecule, and especially in anion reveal huge and unusual solvation properties. Anions, such as thiocyanate, $[SCN]^-$, dicyanamide, $[DCA]^-$, tricyanomethanide, $[TCM]^-$, $\{C(CN)_3\}$, or tetracyanoborate, $[TCB]^-$ have been studied recently by our group [10–13]. The $[TCM]^-$, anion revealed high selectivity and acceptable solute distribution ratio for extraction of thiophene, or benzothiophene, or pyridine from heptane [3,6,10–13]. The literature review on the influence of the cation and anion of the IL, based on activity

---

[*] Corresponding author. Department of Physical Chemistry, Faculty of Chemistry, Warsaw University of Technology, Noakowskiego 3, 00-664 Warsaw, Poland.
E-mail address: ula@ch.pw.edu.pl (U. Domańska).

http://dx.doi.org/10.1016/j.fluid.2016.08.008

coefficients at infinite dilution, presented by our group in 2010 [14] and in 2015 [13, Table 4] for hex-1-ene/hexane separation problem we can conclude that high selectivity and acceptable solute distribution ratio for that separation problem are expected for short chain substituents at the anion and cyano group, CN- in the anion is appreciated. The interesting results for the hex-1-ene/hexane separation were shown for dicyanamide anion [DCA]$^-$ [13]. The selectivities higher than two were observed for [EMIM][DCA] [13,15], for 1-butyl-1-methylpyridinium dicyanamide, [BMPY][DCA] [13,16] and for the tricyanomethanide, [TCM]$^-$ anion [13,17]. Having this in mind, we have measured and analyzed the activity coefficients for around 60 solvents in many ionic liquids with thiocyanate, [SCN]$^-$, dicyanamide, [DCA]$^-$, tricyanomethanide, [TCM]$^-$, {C(CN)$_3^-$}, or tetracyanoborate, [TCB]$^-$ anions to have the possibility to make analysis of the selectivity of extraction for many processes, as for example for 1-butyl-3-methylimidazolium dicyanamide, [BMIM][DCA] [13], or for 1-ethyl-3-methylimidazolium tetracyanoborate, [EMIM][TCB] [18]. The recently published by us literature review on hex-1-ene/hexane separation process based on the activity coefficients at infinite dilution data shows high selectivity for many ILs with these attractive anions [13].

Thus the aim of this work was to investigate the ternary LLE using the ILs with [DCA]$^-$, [TCM]$^-$ and for comparison popular [NTf$_2$]$^-$ anion as: 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)-imide, [EMIM][NTf$_2$], 1-ethyl-3-methylimidazolium dicyanamide, [EMIM][DCA] and 1-ethyl-3-methylimidazolium tricyanomethanide, [EMIM][TCM]. The experimental tie lines for three ternary mixtures of {IL (1) + hex-1-ene (2) + hexane (3)} or {IL (1) + cyclohexene (2) + cyclohexane (3)} at $T = 298.15$ K and ambient pressure were investigated. From the experimental data the extraction selectivity and the solute distribution ratio were determined and discussed for two processes hex-1-ene/hexane and cyclohexene/cyclohexane.

2. Experimental

2.1. Materials

All ILs investigated in this work with structure, name, abbreviation of name, CAS number, molar mass (M) purification method and purity are presented in Table 1. Solvents are presented in Table 1S in the Supplementary Data (SD). The samples of ILs were dried for 24 h at 320 K with stirring under reduced pressure to remove volatile impurities and trace water. Hydrocarbons were stored over freshly activated molecular sieves of type 4 Å (Union Carbide).

2.2. Water content

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 with steps of 0.0025 cm^3. The error on the water content was $\pm 10 \cdot 10^{-6}$ for the 3 cm^3 injected IL. The water content in ILs and in solvents used was less than $350 \cdot 10^{-6}$ in mass.

2.3. Procedure in ternary system

The mixtures of two, or three compounds with compositions inside the immiscible region of the ternary system were introduced into a jacketed glass cell with a volume of 10 cm^3. 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 getting the phase separation for a minimum of 12 h were analyzed. The samples of about $0.1–0.3 \cdot 10^{-3}$ 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 $2 \cdot 10^{-3}$ 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. Ethyl acetate, or methyl acetate was used as internal standard for the GC-analysis. The analysis were made only for hex-1-ene, hexane, cyclohexene and cyclohexane. The mass fraction of the third component, the IL (low vapor pressure), was determined by subtracting the mol fractions of the two other components from one.

The composition was analyzed by gas chromatography (PerkinElmer Clarus 580 GC equipped with auto sampler and FID and TCD detectors). The capillary column of the chromatograph was protected with a pre-column to avoid the non-volatile IL 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 hex-1-ene, hexane, cyclohexene, cyclohexane and external standard, ethyl acetate, or methyl acetate. Samples were injected three times, and the average value was calculated. Details of the operational conditions of the apparatus are reported in Tables 2S and 3S in the SD for hex-1-en/hexane and cyclohexene/cyclohexane, respectively. 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 IL-rich phase.

3. Results and discussion

The LLE data for the experimental tie-line ends of the three ternary systems {IL (1) + hex-1-ene (2) + hexane (3)} and three of {IL (1) + cyclohexene (2) + cyclohexane (3)} at $T = 298.15$ K and ambient pressure are reported in Tables 2 and 3 The determined ternary phase equilibrium of each system (including results in binary systems) is plotted in a form of the Gibbs triangle with the experimental tie-lines in Figs. 1–3 and in Figs. 4–6 for hex-1-en/hexane and cyclohexene/cyclohexane, respectively. These figures show that the two-phase region is almost the same for three ILs. Only [EMIM][NTf$_2$] reveals small miscibility (one phase) in the IL-rich region for hex-1-ene/hexane system and [EMIM][NTf$_2$] as well as [EMIM][TCM] for cyclohexene/cyclohexane system. The reason was the highest solubility of hexane in [EMIM][NTf$_2$] and of cyclohexane in [EMIM][NTf$_2$], or in [EMIM][TCM] between three ILs used. In binary {IL (1) + hexane (3)} system the complete miscibility in the liquid phase is from mole fraction $x_1 = 0.966$, $x_1 = 0.994$, $x_1 = 0.988$ for [EMIM][NTf$_2$], [EMIM][DCA] and [EMIM][TCM], respectively. Similar solubility of cyclohexane in the IL is observed (see Figs. 1–3). The immiscibility region is from mole fraction $x_1 = 0.930$, $x_1 = 0.985$, $x_1 = 0.953$ for [EMIM][NTf$_2$], [EMIM][DCA] and [EMIM][TCM] (see Figs. 4–6).

In binary {IL (1) + hex-1-ene (2)} system, the complete miscibility in the liquid phase is from mole fraction $x_1 = 0.921$, $x_1 = 0.980$, $x_1 = 0.960$ for [EMIM][NTf$_2$], [EMIM][DCA] and [EMIM][TCM], respectively. The largest solubility of hex-1-ene in the IL is observed for [EMIM][NTf$_2$] (see Figs. 1–3).

In binary {IL (1) + cyclohexene (2)} system the complete miscibility in the liquid phase is from mole fraction $x_1 = 0.862$, $x_1 = 0.942$, $x_1 = 0.907$ for [EMIM][NTf$_2$], [EMIM][DCA] and [EMIM][TCM], respectively. As above, the largest solubility of cyclohexene