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Phase behavior of tricyanomethanide-based ionic liquids with alcohols and hydrocarbons



FLUID PHASE

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ABSTRACT

lonic liquids (ILs) are known as attractive solvents showing high extraction capacity for aromatic hydrocarbons from aliphatic hydrocarbons and for sulfur compounds from alkanes. New experimental results on liquid–liquid phase equilibrium (LLE) in the binary systems of {1-butyl-1-methylpyrrolidinium tricyanomethanide, [BMPYR][TCM] + an alcohol (1-octanol, 1-decanol), or + hydrocarbons (benzene, toluene, ethylbenzene, and heptane)} and of {1-butyl-1-methylmorpholinium tricyanomethanide, [BMMOR][TCM] + an alcohol (1-hexanol, 1-decanol), or + hydrocarbons (benzene, toluene, ethylbenzene, thiophene, and heptane)} have been determined at atmospheric pressure using a dynamic method. Upper critical solution temperature type of phase behavior for alcohols and a visible tendency for heptane was observed. For aromatic hydrocarbons there is a visible tendency of the lower critical solution temperature of solubility of alcohol with an increase of its alkyl chain length and of aromatic hydrocarbons with an increase of the alkyl chain length of substituent for all studied systems was detected. The correlation of the experimental data has been carried out using the non-random two liquid (NRTL) equation. The influence of the cation structure on the phase behavior has been discussed. The phase diagrams reported here have been compared to the systems published earlier with the 1-butyl-1-methylpyrrolidinium, or TCM – based ionic liquids.

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1. Introduction

Correlation

lonic liquids (ILs) are novel media characterized by strong interaction with different organic substances which leads to a wide spectrum of applications. The ionic nature of these fluids provides many unique and attractive physical and chemical characteristics favorable to numerous extraction applications. For instance, for the latter application, it has been shown that hydrophobic ILs are capable of extracting 1-butanol from aqueous solutions with a high selectivity [1,2]. In this respect, mutual solubilities of ILs and alcohols are essential for the design and development of separation processes [3,4]. The identification of liquid–liquid demixing phenomena of ILs with alcohols can supply the technological data needed for the design and optimization of useful extraction units.

ILs may be also used as new entrainers in deep desulfurization of diesel fuel [5–7] and in the separation process of aromatic

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hydrocarbons from aliphatic hydrocarbons or for the close boiling mixtures by extractive distillation, or in binary and ternary liquidliquid extraction [7–11]. The unique properties of ILs are determined by the hydrogen bonded structure and interaction between the individual cations or anions with other solvents. To design any process involving the IL on an industrial scale it is necessary to know physicochemical properties and phase equilibrium. ILs can offer the set of favorable properties for extraction and separation due to their unique and tailor able properties. In particular, ILs because of their negligible vapor pressure can offer technologically favorable alternative to common organic solvents not only in the petroleum industry but also in biochemistry processes [12].

Tricyanomethanide-based ILs are thermally and chemically stable and offer the high selectivity of extraction. The ILs with polar tricyanomethanide anion have been recently studied in our laboratory in ternary LLE {IL+thiophene, or benzothiophene+ heptane} [10,11,13] and in model fuels [5,7] with very high selectivity of the extraction of sulfur compounds. The best results in ternary LLE were obtained with 1-ethyl-3-methylimidazolium tricyanomethanide, [EMIM][TCM] [11] as well as 1-butyl-1-methylpyrrolidinium tricyanomethanide, [BMPYR][TCM] [7], or



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Nomenclature

List of symbols

- *a* Coefficient of linear equation of the temperature dependent NRTL parameters *g*
- A Amplitude
- *b* Coefficient of linear equation of the temperature dependent NRTL parameters *g*
- *G* Gibss free energy
- g Parameters of NRTL equation
- *n* Number of experimental points
- T Temperature
- OF Objection function
- x Mole fraction

Greek letters

- β Universal critical exponent
- γ Activity coefficient
- τ Energy parameter in the NRTL equation
- σ The root-mean-square deviation
- α_{ii} Non-randomness parameter of NRTL equation

Superscripts

- calc Calculated mole fraction
- expt Experimental mole fraction
- LLE LLE experimental value

Subscripts

- c Critical point
- calc Calculated mole fraction
- expt Experimental mole fraction
- 1 Ionic liquid
- 2 1-Alcohol, or hydrocarbon

1-butyl-3-methylimidazolium tricyanomethanide, [BMIM][TCM] and 1-butyl-3-methylpyridinium dicyanoamide, [BMPy][DCA] [5] for extraction of thiophene from model fuels. The extraction of thiophene and dibenzothiophene from model fuels was as high as 70 wt% to 95 wt% [5,7].

The first information about high extractive properties of tricyanomethanide-based ILs were obtained after careful analysis of the values of activity coefficients at infinite dilution, especially for the selectivity of separation of thiophene from heptane using [BMPYR][TCM] [14], [BMMOR][TCM] [15], [BMIM][TCM] and [BMPy][TCM] [16]. The selectivity, S_{12}^{∞} and capacity, k_{2}^{∞} at infinite dilution for the separation problems heptane/thiophene at T = 328.15 K obtained for [BMPYR][TCM] are S_{12}^{∞} = 43.6 and k_{2}^{∞} = 1.37 and for [BMMOR][TCM] S_{12}^{∞} = 73.8 and k_{2}^{∞} = 0.96. These are quite high values in the comparison with other ILs.

Different pyrrolidinium-based ILs have been studied in our laboratory as 1-butyl-1-methylpyrrolidinium tris(pentafluoroethyl) trifluorophosphate, [BMPYR][FAP], 1-butyl-1-methylpyrrolidinium tetracyanoborate, [BMPYR][TCB] and [BMPYR][TCM] in ternary LLE. The [TCM]⁻ anion in comparison with [TCB]⁻ and [FAP]⁻ anions showed much higher selectivity and slightly lower distribution ratio for extraction of thiophene from aliphatic hydrocarbons [10].

Morpholinium-based ILs were found to have practical value in many electrochemical applications because of their easy synthesis procedures and cheap morpholinium cation [17–19]. The morpholinium-based ILs were tested on the survival of slugs and their damage to plants [20]. Synthesis, toxicity, biodegradability and

physicochemical properties of 4-benzyl-4-methylmorpholiniumbased ionic liquids were presented as well [21].

Two systems showed high solubility of thiophene in the IL, low solubility of heptane in the IL, and high solute distribution coefficient and selectivity of separation of thiophene from heptane in ternary LLE measurements of the system containing {(4-(2-methoxyethyl)-4-methylmorpholinium trifluorotris(perfluoroethyl) phosphate, [COC₂mMOR][FAP], or {(4-(2-methoxyethyl)-4-methylmorpholinium bis(trifluoromethylsulfonyl) imide, [COC₂mMOR][NTf₂] + thiophene + heptane} at *T* = 298.15 K [22,23]. Large selectivity of separation of thiophene from heptane was shown for these two ILs ([COC₂mMOR][FAP], [COC₂mMOR][NTf₂]) from the measurements of activity coefficients at infinite dilution, γ_{13}^{∞} [24,25].

The densities of [BMPYR][TCM] and [BMMOR][TCM] over the wide temperature range at ambient pressure have been also measured [14,15].

The measurements of phase equilibrium of binary systems containing tricyanomethanide-based ILs are rare. The (solid + liquid) and (liquid + liquid) phase equilibrium in a series of tricyanomethanide-based ILs with water have been measured recently in our laboratory over a wide temperature range and at atmospheric pressure [26]. Many ILs, including [BMPYR][TCM] and [BMMOR][TCM] revealed immiscibility gap with upper critical solution temperature, UCST. Only the binary mixture of ([EMIM] [TCM] + water) have shown complete miscibility.

In this work, we report experimental binary (liquid+liquid) phase equilibrium of two ILs, namely [BMPYR][TCM] and [BMMOR][TCM] in alcohols, aromatic hydrocarbons, thiophene, and heptane at pressure p = 0.1 MPa using a dynamic method. The investigation includes the effect of the alkyl chain length of the alcohol and the alkyl chain length of substituent on the benzene ring. The non-random two liquid (NRTL) thermodynamic model [27] was used to correlate the experimental data in binary systems.

2. Experimental

2.1. Materials

The ionic liquid 1-butyl-1-methylpyrrolidinium tricyanomethanide, [BMPYR][TCM] (CAS: 878027-72-6) and 1-butyl-1-methylmorpholinium tricyanomethanide, [BMMOR][TCM] (on request) were purchased from IoLiTec. The samples were dried for 48 h at 323 K under reduced pressure to remove volatile impurities and trace of water. The water content was 250 ppm and 313 ppm, as determined by Karl Fisher titration for [BMPYR][TCM] and [BMMOR][TCM], respectively. The structure of the ILs is shown in Table 1. Most of high purity solvents were fractionally distilled over different drving reagents to mass fraction purity better than 99.8 wt% and were stored over freshly activated molecular sieves of type 4A (Union Carbide). All compounds were checked by GLC analysis and no significant impurities were found. The purity of the substances was checked also by the density measurements at T = 298.15 K (see Table 2 [10,15,28]). The densities were measured using an Anton Paar GmbH 4500 vibrating-tube densimeter (Graz, Austria). The apparatus is precise to within 1×10^{-5} g cm⁻³, and the uncertainty of the measurements was estimated to be better than $\pm 5 \times 10^{-5} \, g \, cm^{-3}$.

2.2. Water content

The water content was systematically checked by coulometric titration (Karl Fischer method) using KF Trace Titroline. The analysis showed that the water mass fraction in the solvents and in the mixtures with the ionic liquid, were 250–313 ppm.

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