



Separation of water/butan-1-ol based on activity coefficients at infinite dilution in 1,3-didecyl-2-methylimidazolium dicyanamide ionic liquid



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ABSTRACT

The activity coefficients (γ_{13}^{∞}) at infinite dilution for 65 solutes and the effect of interaction between organic solvents or water on the interfacial and bulk properties of 1,3-didecyl-2-methylimidazolium dicyanamide, [D₂MIM][DCA] were detected by the gas-liquid chromatography at six temperatures in range of (358.15–408.15) K. The data are provided for polar and non-polar solutes as alkanes, alkenes and alkynes, aromatic hydrocarbons, alcohols, ethers, ketones, acetonitrile, pyridine, 1-nitropropane, thiophene, esters as well as for water. The synthesis and the thermal properties of [D₂MIM][DCA] are presented. The fundamental thermodynamic functions, the partial molar excess Gibbs energy, enthalpy and entropy at infinite dilution were calculated and discussed. The values of selectivity and capacity for the separation problem water/butan-1-ol were calculated from γ_{13}^{∞} and compared to literature values for imidazolium-based, or dicyanamide-based ionic liquids (ILs) for the same separation problem. The data presented here shows that [D₂MIM][DCA] reveals attractive selectivity and capacity in the comparison to measured earlier ILs in the chosen separation problem. These findings seem useful for future applications of this IL in projects of new technologies for water/butan-1-ol separation process.

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1. Introduction

Ionic liquids (ILs) are interesting new solvents for extraction processes [1–3], the reaction media [4,5], biphasic catalysis [6,7], lithium battery systems, electrochemical deposition and electrochemistry [8], or as active pharmaceutical ingredients [9]. The huge number of cation-anion combinations helps to design of appropriate ILs for particular application. The properties of ILs such as a high thermal stability, non-volatility, non-flammability and high solvation to organic solvents makes them attractive alternatives to the popular, conventional organic solvents [10–12].

Many laboratories of the world have been focusing their interest in biomass based fuels, which currently is the only alternative for sustainable development in a context of both economical and environmental postulates. Bio-fuels like alcohols are produced from biomass by fermentation, and distillation. This method is commonly used to separate an alcohol from the fermentation broth [13,14]. Nowadays, bioethanol is the most common biofuel, accounting for >90% of total biofuel usage. Conventional production is a well known process based on enzymatic conversion of

starchy biomass into sugars, and/or fermentation of 6-carbon sugars with final distillation of ethanol to fuel grade. Ethanol can be produced from many feedstocks, including cereal crops, corn (maize), sugar cane, sugar beets, potatoes, sorghum, cassava. The world's largest producers of bio-ethanol are Brazil (sugar-cane ethanol) and the United States (corn ethanol). In Brazil, gasoline must contain a minimum of 22% bioethanol. New ideas focuses on advanced processes that utilise the all available ligno-cellulosic materials. These processes hold the potential to increase variety and quantity of suitable feedstock including cellulosic wastes, maize stove, cereal straw, food-processing wastes, as well as dedicated fast-growing plants such as popular trees and switch-grass. Advanced biofuels are expected to play an important role in replacing fossil fuels because they have improved properties compared with ethanol and some of these may have the energy density required for use in heavy duty vehicles, ships, and aviation. The yeast cell factory *Saccharomyces cerevisiae* can be turned into a producer of higher alcohols butan-1-ol and isobutanol, sesquiterpenes (farnesene and bisabolene), and fatty acid ethyl esters [15–17]. Also alternative technologies (e.g. fuel cells, hydrogen, and electricity) will probably not play a substantial role in heavy duty vehicles, shipping, and aviation because of their limited capacity or energy density [18]. Biofuels can be used in current internal combustion engines and hence as drop-in fuels. This compatibility with

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the current infrastructure makes them attractive for replacing fossil transport fuels in the future. Possibly, the 2nd generation biofuels will be derived from biomass [19–21].

While ethanol has received the most attention as a fuel additive and biofuel; butan-1-ol is proposed as a better direct fuel alternative [22]. Butan-1-ol may be produced biologically through fermentation of biomass containing sugars, starch, cellulose, beetroot and others using yeast or bacteria. A great number of industrial separation processes are concerned with liquid mixtures containing isomers of butan-1-ol (butan-1-ol, butan-2-ol, tert-butanol) and water. The separation *via* distillation is a high energy consumption process and is not economical (higher boiling temperature of butan-1-ol than that of ethanol). The alternative recovery methods have been proposed in scientific literature including liquid-liquid equilibrium using ionic liquids (ILs) [23–27], stripping, pervaporation, or liquid membranes with ILs [28] or without using ILs [29–33].

Butan-1-ol is also a popular organic solvent, and is an important substance with a wide range of industrial uses as surface coating, superb-sorbents, fibers, plastics, resins, hard-surface cleaners, electronics, paints, as fragrance material and in pharmaceuticals [28]. The physicochemical parameters of butan-1-ol, as low vapour pressure, higher than that of water boiling temperature, low solubility in water makes it a medium, which could be potentially used as an additive to gasoline without concerning about evaporation and subsequent related complications, which are observed for ethanol.

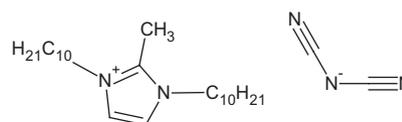
Novel applications of ILs continue to be regularly projected as an extractive solvents based on their excellent properties. However, the choice of an appropriate environmental friendly solvent is a key to a successful separation. In recent years ILs have been widely investigated as non-volatile new solvents with high chemical stability, with potential recoverability and design possibility. The requirements of a suitable IL for the extraction of butan-1-ol from aqueous phase are the high, or complete miscibility of butan-1-ol with the IL and non-miscibility, or low miscibility of water with the IL. The first information of the interactions of volatile organic compounds as solutes with ILs as a solvents may be obtained from the experimental determination of activity coefficients at infinite dilution (γ_{13}^{∞}) by gas-liquid chromatography (GLC). This information can be used as a starting point for the considered new entrainer for different separation processes. The extraction of alcohols from water was proposed by now with many ILs. Large selectivities were obtained in ternary liquid-liquid equilibrium (LLE) measurements with 1-decyl-3-methylimidazolium tetracyanoborate, [DMIM][TCB], 4-decyl-4-methylmorpholinium tetracyanoborate, [DMMOR][TCB], 1-decyl-3-methylimidazolium bis((trifluoromethyl)sulfonyl)imide, [DMIM][NTf₂] and decyl-4-methylmorpholinium bis((trifluoromethyl)sulfonyl)imide, [DMMOR][NTf₂] [27]. Optimistic results were obtained with tetracyanoborate-based ILs, such as 1-hexyl-3-methylimidazolium tetracyanoborate, [HMIM][TCB] [25], 1-decyl-3-methylimidazolium tetracyanoborate, [DMIM][TCB] [25] and trihexyltetradecylphosphonium tetracyanoborate, [P_{14,6,6,6}][TCB] [25]. The production of bio-butanol using [DMIM][TCB] was recovered by MERCK as both, low energy process and co-extraction with acetone from water and fast mixing-settling process. In this work we continue our systematic analysis of selectivity ($S_{12}^{\infty} = \gamma_1^{\infty}/\gamma_2^{\infty}$) calculated from activity coefficients at infinite dilution (γ_{13}^{∞}) for dicyanamide-based IL. For example the values of selectivity for water/butan-1-ol process for 1-butyl-3-methylimidazolium dicyanamide, [BMIM][DCA] was $S_{12}^{\infty} = 0.29$ [34], which is lower than those for [HMIM][TCB] $S_{12}^{\infty} = 1.42$ [35] or for [DMIM][TCB] $S_{12}^{\infty} = 2.04$ [36]. Thus the idea was to change cation of the IL. Much better values of selectivity were obtained

with the IL synthesized by us for this process, the tributyltetradecylphosphonium dodecylbenzenesulfonate, [P_{14,4,4,4}][DBS] [37]. The long alkane substituent was added to the cation and to the anion. This resulted in the largest selectivity ($S_{12}^{\infty} = 3.77$) and capacity ($k_2^{\infty} = 5.29$) ever noticed in the published data [37]. In this work we decided to improve selectivity by adding the long alkane chains in the cation, 1,3-didecyl-2-methylimidazolium. This work also provides an opportunity to make comparisons with previously published by us results and found in the literature for this separation problem. The obtained thermodynamic properties help to analyse the intermolecular interactions and to identify the potential of the synthesized IL to be used in solvent-aided extraction.

2. Experimental

2.1. Chemicals and materials

The 50.22 g 1,3-didecyl-2-methylimidazolium chloride (0.1258 mol, Io-Li-Tec, >98%, used as received) and 12.40 g sodium dicyanamide (0.1393 mol, Io-Li-Tec 97%, 10% excess, used as received) were added to a round flask 500 cm³. The mixture was dissolved in 150 cm³ of deionized water and 150 cm³ of dichloromethane. Mixture was stirred at room temperature for 4 h and phases were separated by draining. Then organic phase was extracted with 10 × 15 cm³ of water (removal of residual sodium chloride and excess of sodium dicyanamide). Solvents were removed in rotary evaporator and product was further dried under vacuum at $T = 413$ K for 12 h. After cooling the product crystallized. Product was obtained as a 49.03 g of light yellow solid. Yield 90.7% (49.03 g).



The spectra have been done using CD₃CN as the solvent. Please find the spectra (0–10 ppm) as well as broadened range (0.5–4.5) 10⁻⁶ in the SM. The only impurity signal visible is acetone. Since acetone was not used during synthesis, it is probably residue from cleaning of NMR tubes. Only other signal is 1.968 from residual acetonitrile within the deuterated solvent. Since no other signals are observed, the purity should be better than 0.97 wt fraction.

Main impurities [10110Im][DCA] 0.018 wt fraction, and water 0.01 wt fraction.

The NMR spectra using CD₃CN:

¹H NMR: δH(500 MHz; CD₃CN): 0.898 (6 H, t, 3JH,H = 7.34 Hz), 1.293 (28 H, m), 1.800 (4H, pent, 3JH,H = 7.34 Hz), 2.554 (3 H, s), 4.059 (4 H, t, 3JH,H = 7.34 Hz), 7.356 (2 H, s).

¹³C NMR: δC(100 MHz; CDCl₃): 9.843, 13.990, 22.525, 26.260, 28.897, 29.115, 29.255, 29.325, 29.605, 31.714, 48.854, 119.717, 121.328, 142.911.

Elemental analysis, found: C, 72.76; N, 16.17; H, 11.00%. Calc. for C₂₅H₄₇N₅: C, 72.68; N, 16.30; H, 11.02%.

The purity was calculated from the NMR spectra as a mole and wt% purity. <79.4 mol%, <96.9 wt%. Main impurity acetonitrile 12.6 mol%, 1.47 wt%, and ethyl acetate 7.94 mol%, 1.62 wt% (probably induced with [Im 10,10,1]Cl salt, residue from synthesis at Io-Li-Tec).

The name, abbreviation, structure and molar mass of investigated IL is presented in Table 1. The ¹H NMR and ¹³C NMR spectra are shown in the Fig. 1S in the Supplementary Material (SM). All solutes, purchased from Aldrich and Fluka, were used without

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