



Separation of binary mixtures hexane/hex-1-ene, cyclohexane/cyclohexene and ethylbenzene/styrene based on gamma infinity data measurements



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ABSTRACT

The activity coefficients γ_{13}^{∞} at infinite dilution for 64 solutes were determined in the 1-(3-hydroxypropyl)-3-methylimidazolium dicyanamide, [*N*-C₃OHMIM][DCA] and 58 solutes in (3-hydroxypropyl)-1-methylmorpholinium dicyanamide, [*N*-C₃OHMMor][DCA] using the gas-liquid chromatography technique. Measurements were undertaken at six temperatures, in 10 K intervals, in the range of (298.15–368.15) K. The solutes studied included both non-polar and polar compounds, as alkanes, alkenes, and alkynes, as well as aromatic hydrocarbons, alcohols, water, ethers, ketones, acetonitrile, pyridine, 1-nitropropane, thiophene, and esters. Density, ρ , measurements for a range of temperatures (298.15–368.15) K for the synthesized, new ionic liquids (ILs) were also undertaken at pressure, $p = 101$ kPa. The gas-liquid partition coefficients, K_L at infinite dilution, and the fundamental thermodynamic functions, partial molar excess Gibbs energy, enthalpy and entropy at infinite dilution were calculated from the experimental data measurements. The values of selectivity and capacity for three separation cases, viz. hexane/hex-1-ene, cyclohexane/cyclohexene, and ethylbenzene/styrene were calculated from γ_{13}^{∞} values and compared to literature for imidazolium-based, morfolinium-based, or dicyanamide-based, ILs. The results from the study indicate that [*N*-C₃OHMIM][DCA] has large selectivity values for all three of the separation cases studied and that [*N*-C₃OHMMor][DCA] has the largest selectivity ever noted for cyclohexane/cyclohexene, and ethylbenzene/styrene separation processes.

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1. Introduction

Ionic liquids (ILs) are non-volatile salts with unusual properties, such as high thermal stability, non-flammability, and high solvation properties. They have been widely studied, and have been proposed as potential replacement solvents for conventional organic solvents in separation processes [1–5]. One of the most relevant separation process in petrochemistry is the employment of ILs as extractants for separation of alkenes from alkanes. Alkenes are particularly useful as substrates for the production of polymers and many petrochemical products. The conventional separation technique for the alkane/alkene system is the energy-intensive and technologically complex distillation process. Other separation methods, such as membranes technology or adsorption processes generally achieve a poor separation selectivity [6,7].

Fundamental information about suitable solvents for many different separation processes can be obtained from activity coefficients at infinite dilution measurements, (γ_{13}^{∞}) by the gas-liquid chromatography (GLC) technique. In this study we propose to estimate the solvent separation ability for two ILs by an analysis of their selectivities and capacities, calculated from γ_{13}^{∞} values.

In recent years, we demonstrated that ILs may be very successful solvents for alkane/alkene separations [8–11]. The first study of alkane/alkene separations using ILs reported in the literature were mostly presented for short chain hydrocarbons [12,13]. The imidazolium-based ILs were proposed for the propane/prop-1-ene [12] and the hexane/hex-1-ene separations [13]. Recently, very successful selectivity and capacity for the hexane/hex-1-ene, cyclohexane/cyclohexene, and ethylbenzene/styrene separation processes were observed by us from the γ_{13}^{∞} data for 1-butyl-3-methylimidazolium dicyanamide, [BMIM][DCA] [8], and 1-allyl-3-methylimidazolium dicyanamide, [AMIM][DCA] [9].

The review by Domańska et al. [8] have shown that high selectivity for the hexane/hex-1-ene separation were obtained for the

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ILs containing CN-groups in the molecule. High selectivities were observed also for 1-ethyl-3-methylimidazolium dicyanamide, [EMIM][DCA] [14], 1-(3-cyano-propyl)-3-methyl-imidazolium bis(trifluoromethyl)sulfonylimide, [CN-C₃MIM][NTf₂] [15], and 1-(3-cyano-propyl)2,4-dimethyl-imidazolium dicyanamide, [CN-C₃MIM][DCA] [15]. The selectivity in the hexane/hex-1-ene separation process using [AMIM][DCA] was ($S_{12}^{\infty} = \gamma_{13}^{\infty}/\gamma_{23}^{\infty} = 2.51$) at $T = 328.15$ K [9].

In this work we continue our investigations on the measurements of γ_{13}^{∞} and an analysis of the obtained selectivities and capacities for hexane/hex-1-ene, cyclohexane/cyclohexene and ethylbenzene/styrene separation processes. The present work is focused on new attractive ILs, synthesized in our laboratory, namely 1-(3-hydroxypropyl)-3-methylimidazolium dicyanamide, [N-C₃OHMIM][DCA] and (3-hydroxypropyl)-1-methylmorpholinium dicyanamide, [N-C₃OHMMor][DCA]. Additionally, we report the gas-liquid partition coefficients K_L and thermodynamic functions at infinite dilution for all measured solutes. The thermodynamic properties obtained are analysed with regard to intermolecular interactions. The densities as a function of temperature were measured for these two ILs.

2. Materials and methods

2.1. Materials

The ILs were synthesized in our laboratory. The synthesis of dicyanamide ILs was carried out by metathesis reaction with sodium dicyanamide of corresponding chlorides. Chlorides were synthesized according to modified literature procedure [16]. The synthesis was carried out using drying socket instead of nitrogen. In our procedure we used acetone instead of dichloromethane due to the low solubility of synthesized compounds in dichloromethane. The names, abbreviation of names, structures and molar masses of used ILs are presented in Table 1. Spectra NMR of used ILs are shown in Figs. 1S–8S in the Supplementary Material (SM).

2.1.1. 1-(3-Hydroxypropyl)-3-methylimidazolium dicyanamide, [N-C₃OHMIM][DCA]

To a round flask 250 cm³ equipped with a condenser and a drying socket 70.65 g 1-methyl-3-*H*-imidazole (0.8605 mol, Io-Li-Tec 98%, used as received), 90.02 g 3-chloropropanol (0.9522 mol, Sigma-Aldrich 98%, 11% excess, used as received), and 100 cm³ of acetonitrile (P.O.Ch cz.d.a) were added. The mixture was stirred for 48 h in oil bath at $T = 363.2$ K. Solvents were removed by evaporation. Product was crystallized from ethanol, added drop wise into an ethyl acetate–acetone mixture (1:3 ratio). Obtained solid was washed with diethyl ether. Product, 1-(3-hydroxypropyl)-3-

methylimidazolium chloride was obtained as a 81.84 g of crystalline solid. Yield 53.8% (0.4633 mol).

¹H NMR δ_H (500 MHz; D₂O) ppm: 2.022 (2H, m), 3.521 (2H, t, ³J_{H,H} = 5.87 Hz), 3.806 (3H, s), 4.206 (2H, t, ³J_{H,H} = 7.1 Hz), 7.352–7.416 (2H, m), 8.657 (1H, s).

¹³C NMR δ_C (100 MHz; D₂O) ppm: 31.667, 35.783, 46.505, 57.942, 122.339, 123.662, 136.087.

Next to a solution of 36.11 g of 1-(3-hydroxypropyl)-3-methylimidazolium chloride (0.2044 mol, synthesized) in 500 cm³ of water 42.63 g of silver dicyanamide (0.2451 mol, 1.2 equivalent, synthesized by addition of equimolar amounts of sodium dicyanamide (Io-Li-Tec 97%) and sodium nitrate (Alfa Aesar 99%) followed by filtration, washing with water and drying) was added. Mixture was stirred at the temperature of $T = 323$ K for 1 h. Afterwards, the solution was filtered on a column with 5 g of silica gel 60 (Machery Nagel for column chromatography). Water was removed by evaporation and the oil was further dried in vacuum for 3 days in $T = 373$ K. The product, 38.59 g of oil was obtained (0.1862 mol, yield 91.09%).

¹H NMR: δ_H (500 MHz; D₂O): 2.14 (2H, quin, ³J_{H,H} = 7.09 Hz), 3.65 (2H, t, ³J_{H,H} = 6.11 Hz), 3.94 (3H, s), 4.34 (2H, t, ³J_{H,H} = 7.09 Hz), 7.52 (2H, dd, ³J_{H,H} = 1.96 Hz, ³J_{H,H} = 26.17 Hz), 8.78 (1H, s).

¹³C NMR: δ_C (100 MHz; CDCl₃): 31.97, 35.95, 46.72, 58.08, 119.77, 122.50, 123.83, 136.04.

Elemental Analysis: found C, 52.05; N, 33.67; H, 6.43. Calculated for C₉H₁₃N₅O C, 52.16; N, 33.79; H, 6.32%.

2.1.2. 1-(3-Hydroxypropyl)-1-methylmorpholinium dicyanamide, [N-C₃OHMMor][DCA]

To 17.17 g of *N*-methylmorpholine (0.1698 mol, Sigma-Aldrich 99%, Reagent Plus, used as received), a total of 18.51 g of 3-chloropropanol (0.1979 mol, 17% excess, Sigma-Aldrich 98%, used as received) in 25 cm³ of acetonitrile (POCH) was added. The mixture was stirred in the temperature of $T = 358$ K for 48 h. Afterwards all solvents were evaporated and residue was crystallized from isopropanol to give 26.22 g of yellow crystalline powder. Reaction yield of 1-(3-hydroxypropyl)-1-methylmorpholinium chloride 78.9%.

¹H NMR δ_H (500 MHz; D₂O) ppm: 1.950 (2H, m), 3.111 (3H, s), 3.370–3.485 (6H, m), 3.614 (2H, t, ³J_{H,H} = 5.87 Hz), 3.958 (4H, m).

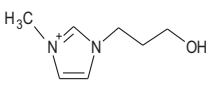
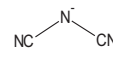
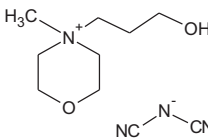
¹³C NMR δ_C (100 MHz; D₂O) ppm: 23.988, 46.839, 58.136, 59.731, 60.400, 62.734.

Elemental analysis: Found: C, 49.0; N, 7.2; H, 9.2. Calc. for C₈H₁₈N: C, 49.1; N, 7.2; H, 9.3%.

Next to a solution of 43.23 g of 1-(3-hydroxypropyl)-1-methylmorpholinium chloride (0.2209 mol, synthesized) in water 20.10 g of sodium dicyanamide (0.2258 mol, 1.02 equivalent, Io-Li-Tec 97%, used as received) was added. Mixture was stirred in the room

Table 1

Investigated ionic liquid: structure, name, abbreviation of name, molar mass, purification method, analysis method, mass fraction purity and water content.

Structure	Name, abbreviation	Molar mass M/(g·mol ⁻¹)	Purif. method	Analys. method	Mass fraction purity/water content (mass fraction)
	1-(3-Hydroxypropyl)-3-methylimidazolium dicyanamide, [N-C ₃ OHMIM][DCA]	207.23	Low pressure, 24 h, 370 K	¹ H NMR Water content	>0.94/429 × 10 ⁻⁶
	(3-Hydroxypropyl)-1-methylmorpholinium dicyanamide, [N-C ₃ OHMMor][DCA]	226.27	Low pressure, 24 h, 370 K	¹ H NMR Water content	>0.97/358 × 10 ⁻⁶
					

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