



Effect of task specific thiocyanate based ionic liquids on relative volatility of cyclohexane and benzene azeotropic mixture



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ABSTRACT

The relative volatilities of cyclohexane (Cy) to benzene (Bz) in the presence of eight task-specific imidazolium thiocyanate ionic liquids (ILs) were measured using headspace gas chromatography. The ILs contain nitrile, ally, benzyl and hydroxyl functional group in their imidazolium cations and thiocyanate as anion. The effects of incorporation of nitrile, allyl, benzyl and hydroxyl functional groups in imidazolium alkyl chain on the relative volatility of Cy to Bz were investigated using experiment and quantum calculations. COSMO-RS model was used to study the polarity (charge distribution) of the ILs and the solutes. Density functional theory (DFT) was employed to investigate the cation-anion interaction energies and IL-Bz/Cy binding energies. The structural variations of the imidazolium cation influence the performance of the ILs. Moreover, the performances of the ILs were compared with two typical conventional entrainers, dimethyl sulfoxide (DMSO) and N,N-dimethylformamide (DMF). Except two hydroxyl containing ILs, the remaining six ILs show higher Cy to Bz relative volatility values compared to the bench marked conventional solvents.

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1. Introduction

Cyclohexane (Cy) is used as in varnishes, paints and as a solvent in the plastic industry and for the extraction of essential oils [1]. However, the major demand for Cy mainly results from its conversion to intermediate products which are the feed stocks for Nylon precursors [1,2]. Cy is mainly produced by catalytic hydrogenation of benzene (Bz) in the presence of catalyst. Separation of the unreacted Bz from product stream is very important and challenging. Bz and Cy form azeotropic mixture (at 45 vol% Cy) whose constant boiling point is 77.5 °C [1,2]. Moreover, the boiling points of Bz and Cy are very close (Bz, 80.10 °C; Cy, 80.74 °C) in other composition ranges. Consequently, it is not possible to separate Bz and Cy by using conventional distillation. Special separation processes such as extractive distillation is presently used for this system [1]. In extractive distillation, a high boiling point and relatively stable third component (commonly known as entrainer) is introduced into the distillation column in order to change the relative volatility of Cy to Bz. Bz strongly interacts with the entrainer and remains at the bottom the column whereas Cy is withdrawn from the top of the distillation column. The bottom mixture is then fed into second distillation column to separate and recycle the entrainer.

The most common entrainers reported for separation of Bz and Cy mixtures are liquid solvents such as sulfolane, dimethylformamide

(DMF), N-methylpyrrolidone (NMP), and dimethylsulfoxide (DMSO) [3–5]. In some cases, where solubility permits, combination of solid salts and liquid solvents are also used for this separation process [6]. Combinations of solid salt and liquid solvent give higher separation performance compared to pure liquid solvents which leads to low solvent to feed ratio, high production capacity and low energy consumption. However, extractive distillation with solid salts are not widely used because its difficulties in industrial operation, dissolution, reuse and transport [7]. In addition, since the solubility of the salts in the solvents is limited, extractive distillation with solid salt is not flexible in designing the process. Thus, extractive distillation with salt is not common for separation of Bz and Cy. Consequently, Bz and Cy are separated mainly using extractive distillation with liquid solvents. However, extractive distillation with these solvents suffer from process complexity and high-energy consumption due to their low extractive capacity, and need of additional distillation steps to separate the solvent from top and bottom products [7].

Recently, ionic liquids (ILs) attracted attention as alternative solvents/entrainers in separation of azeotropic and close boiling mixtures [8]. ILs can overcome most of the limitations associated with the use of solid salts (dissolution, reuse, and transport) and liquid solvent (low performance, thermal degradability and volatility). That means, extractive distillation with ILs integrates the advantages of liquid solvent (easy operation) and solid salt (high separation ability). Since ILs have negligible vapour pressure, they will not be distilled and entrapped in the top product. This helps to obtain pure Cy and avoid

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second separation column to purify the product. The negligible vapour pressure of the ILs also facilitates the separation and recycling of ILs without additional distillation column. Moreover, using ILs as solvents in extractive distillation avoid the chance of emission of solvent to atmosphere. The high thermal and chemical stabilities of ILs help to recycle and use the ILs without performance degradation. In addition, ILs have a wide liquid range with a melting point around room temperature and high decomposition temperatures [9]. This is useful to optimize and control temperature dependent processes such as extractive distillation. Furthermore, the chemical and thermophysical properties of the ILs can be tailored which allow a flexible design in extractive distillation.

ILs have been studied as solvents for aromatic/aliphatic using liquid-liquid extraction and extractive distillation processes [10–16]. From these studies, it was found that ILs that contain anions with delocalized electrons show strong affinity for aromatic hydrocarbons than non-aromatic hydrocarbons [13–15]. However, the effect of structural variations of cations, particularly the effect of functional group in the cation alkyl chain, on the separation of this system was not systematically studied. Moreover, only few works have been reported on the use of ILs as entrainer for separation of Bz and Cy using extractive distillation [11,12]. In this work, eight task-specific imidazolium thiocyanate ILs were investigated as potential entrainers for separation of Bz and Cy through experimental and quantum calculations. The ILs contain nitrile, allyl, hydroxyl and benzyl functional groups in their imidazolium alkyl spacer and thiocyanate as anion. Thiocyanate based ILs were selected because thiocyanate is one of the anions with delocalized electrons [16]. Moreover, thiocyanate based ILs have lower viscosity which is an important characteristics for entrainer used in extractive distillation [14]. The structure of the studied ILs are shown in Fig. 1.

2. Materials and methods

2.1. Chemicals

The ionic liquids were synthesized using analytical grade chemicals without further purifications. The starting materials with case no and purities are acrylonitrile (Aldrich, 107-13-1, 99%), methanol (anhydrous, Aldrich, 67-56-1, 99.8%), acetone (Aldrich, 67-64-1, 99.8%), ethyl acetate (anhydrous, Aldrich, 141-78-6, 99.8%), imidazole (Aldrich,

288-32-4, 99%), 1-methylimidazole (Merck, 616-47-7, 99%), allyl chloride (Aldrich, 107-05-1, 98%), benzyl chloride (Merck, 100-44-7, 99%), 2-chloroethanol (Merck, 107-07-3, 99.8%), 1-chlorobutane (Merck, 109-69-3, 99%), and sodium thiocyanate (Sigma-Aldrich, 540-72-7, 98%), 1-butyl-3-methylimidazolium chloride (79917-90-1, 98%) was obtained from Sigma Aldrich. Benzene (71-43-2, 99.5%) and cyclohexane (110-82-7, 99%) were supplied by Merck GmbH and dried over a molecular sieve (3 Å, 8–12 meshes) before use. Dimethyl sulfoxide (67-68-5, 99.9%) and *N,N*-dimethylformamide (68-12-2, 99.8%) were obtained from Sigma-Aldrich.

2.2. Preparation of ionic liquids

The ILs were prepared using the procedures described in our previous works [17,18]. 1-Butyl-3-methylimidazolium thiocyanate ([Bmim][SCN]) was synthesized through metathesis reaction of sodium thiocyanate and 1-butyl-3-methylimidazolium chloride ([Bmim]Cl). The synthesis procedure adopted for the remaining ILs consists of three steps: incorporation of nitrile group into the imidazolium cation through Michael addition reaction, preparation of chloride-based ILs, and then further exchange of chloride with thiocyanate anion. Bruker Avance 500 NMR spectrometer was used to record the ^1H and ^{13}C NMR spectra and elemental analyses were performed using CHNS-932 (LECO instruments). The ^1H NMR and ^{13}C NMR and elemental analyses of the ILs are shown as follows.

1-Butyl-3-methylimidazolium thiocyanate: ^1H NMR (CDCl_3): δ (ppm) = 0.89 (3H, t), 1.31 (2H, m), 1.86 (2H, m), 4.12 (3H, s), 4.28 (2H, t), 7.42 (1H, m), 7.56 (1H, m), 10.55 (1H, s). ^{13}C NMR (CDCl_3): δ (ppm) = 13.5, 19.9, 32.1, 35.8, 51.3, 122.3, 126.7, 134.5, 138.1. Elemental analysis: C (54.7%), H (7.8%), N (21.3%), S (16.2%).

1-Allyl-3-methylimidazolium thiocyanate: ^1H NMR (CDCl_3): δ (ppm) = 3.94 (3H, s), 4.65 (2H, d), 5.47 (1H, d), 5.48 (1H, d), 5.90–6.04 (1H, m), 7.33 (1H, s), 7.37 (1H, s), 9.11 (1H, s). ^{13}C NMR (CDCl_3): δ (ppm) = 36.5, 51.6, 121.9, 122.0, 123.7, 129.8, 130.1, 136.2. Elemental analysis: C (53.05%), H (6.09%), N (23.21%), S (17.65%).

1-Benzyl-3-methylimidazolium thiocyanate: ^1H NMR (CDCl_3): δ (ppm) = 4.01 (3H, s), 5.43 (2H, s), 7.35 (1H, d), 7.35 (1H, d), 7.40–7.53 (5H, m), 9.25 (1H, s). ^{13}C NMR (CDCl_3): δ (ppm) = 36.78, 53.17, 121.6, 122.03, 123.53, 128.78, 129.35, 129.31, 129.38, 129.39, 133.12,

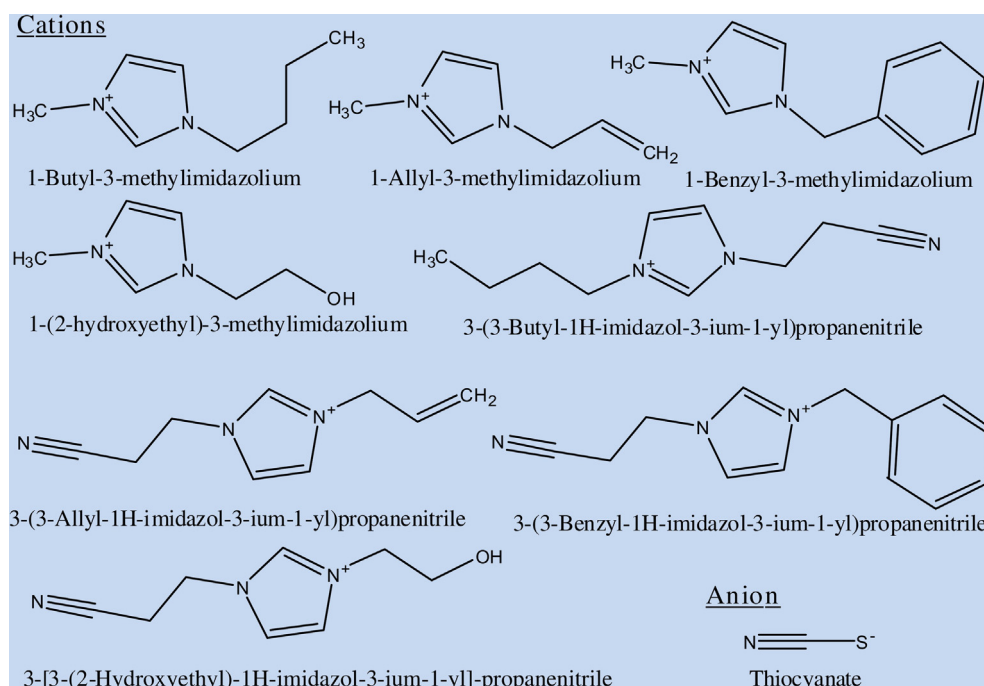


Fig. 1. Structure of cations and anion of the studied ILs.

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