Thiocyanate Based Task-specific Ionic Liquids for Separation of Benzene and Cyclohexane

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Separation of benzene and cyclohexane is one of the most important processes in the petrochemical industry. However, due to their close boiling points and azeotrope formation, it is difficult to separate cyclohexane and benzene by conventional distillation processes. In this work, five thiocynate-based ionic liquids were investigated as solvent for separation of benzene and cyclohexane using extractvie distillation. The separation performances of the ionic liquids were evaluated in terms of their selectivity for benzene and relative volatility of the components the presence of the ionic liquids. The relative volatility and selectivity values were obtained from the experimental vapour-liquid equilibrium measured using head space gas chromatography.The effect of the structural variations of the ionic liquids on the separation performance was explained by COSMO-RS model. The result shows the ionic liquids studied can break the azeotropic mixture and increase the relative volatility of the cyclohexane to benzene.

1. Introduction

Cyclohexane is an important bulk chemical for production of adipic acid and ε-caprolactam, which are feedstock for Nylon 6 and Nylon 6,6 production (Garcia Villaluenga and Tabe-Mohammadi, 2000). Cyclohexane is mainly produced by catalytic hydrogenation of benzene in the presence of hydrogen and catalyst. Therefore, the removal of the remaining benzene from the reactor's effluent stream is a very important process. However, separation of benzene and cyclohexane mixtures has been proved one of the most difficult tasks in petrochemical industry because of their close boiling points and formation of an azeotropic mixture (Garcia Villaluenga and Tabe-Mohammadi, 2000; García et al., 2011). Since conventional distillation cannot be used for this separation process, extractive distillation is the main technology presently available to separate benzene and cyclohexane mixtures (Garcia Villaluenga and Tabe-Mohammadi, 2000).

In extractive distillation, higher boiling point and relatively stable solvent; sometimes called entrainer, is used to change the phase equilibrium of the system in such a way that the relative volatility of the interest component is increased. The most common entrainers currently used in extractive distillation of benzene and cyclohexane are N,N-dimethylformamide (DMF), N-formylmorpholine (NFM), N-methylpyrrolidone (NMP), N,N-dimethylacetamide (DMAC) or their mixtures (Vega et al., 1997; Yin et al., 2010). However, extractive distillation with these solvents suffers from process complexity and high-energy consumption due to their low extractive capacity, considerable volatility and high mutual solubility with both benzene and cyclohexane (Garcia Villaluenga and Tabe-Mohammadi, 2000).

Recently, ionic liquids have attracted attention in replacement of the conventional entrainers in extractive distillation (Pereiro et al., 2012). Preliminary studies on the infinite activity coefficients show that the activity coefficients of benzene in ionic liquids are significantly lower compared to cyclohexane, which indicate the possibilities of ionic liquids for the separation of the two components (Pereiro et al., 2012; Marciniak, 2010). Most authors reported the possibilities of ionic liquids for separation of benzene and cyclohexane based on the selectivity and solvent capacity obtained from infinite activity coefficient values. Since activity coefficient depends on concentration, the values of the selectivity and solvent capacity obtained at infinite

dilution do not show the practical extractive distillation operation. Usually, the relative volatility values at finite dilution are determined to investigate the applicability of the ionic liquids in extractive distillation.

The aim of the present work is to investigate the applicability five thiocyanate based task-specific ionic liquids for separation of benzene and cyclohexane mixtures. The ionic liquids selected contain nitrile, allyl, hydroxyl and benzyl functional groups in cation alkyl chain and thiocyanate anion. It is already reported that introduction of the nitrile group (-C≡N) in ionic liquids, both in anion and cation, increases the selectivity of the ionic liquids in benzene and cyclohexane separation (Marciniak, 2010). In this work, other functional groups, namely, allyl, hydroxyl and benzyl functional groups, were introduced into the imidazolium alkyl chain besides the nitrile functional group. The performances of the ionic liquids were investigated by measuring the relative volatility and selectivity values. COSMO-RS theory was applied to understand the effect of the functional groups on the polarity of imidazolium cations, which affects the separation efficiency of ionic liquids. The structure of the ionic liquids is shown Figure 1.

1-propyronitrile-3-methylimidazolim thiocyanate

1-propyronitrile-3-allylimidazolim thiocyanate

1-butyl-3-methylimidazolium thiocyanate

1-propyronitrile-3-(2-hydroxyethyl) imidazolium thiocyanate

1-propyronitrile-3-benzylimidazolium thiocyanate
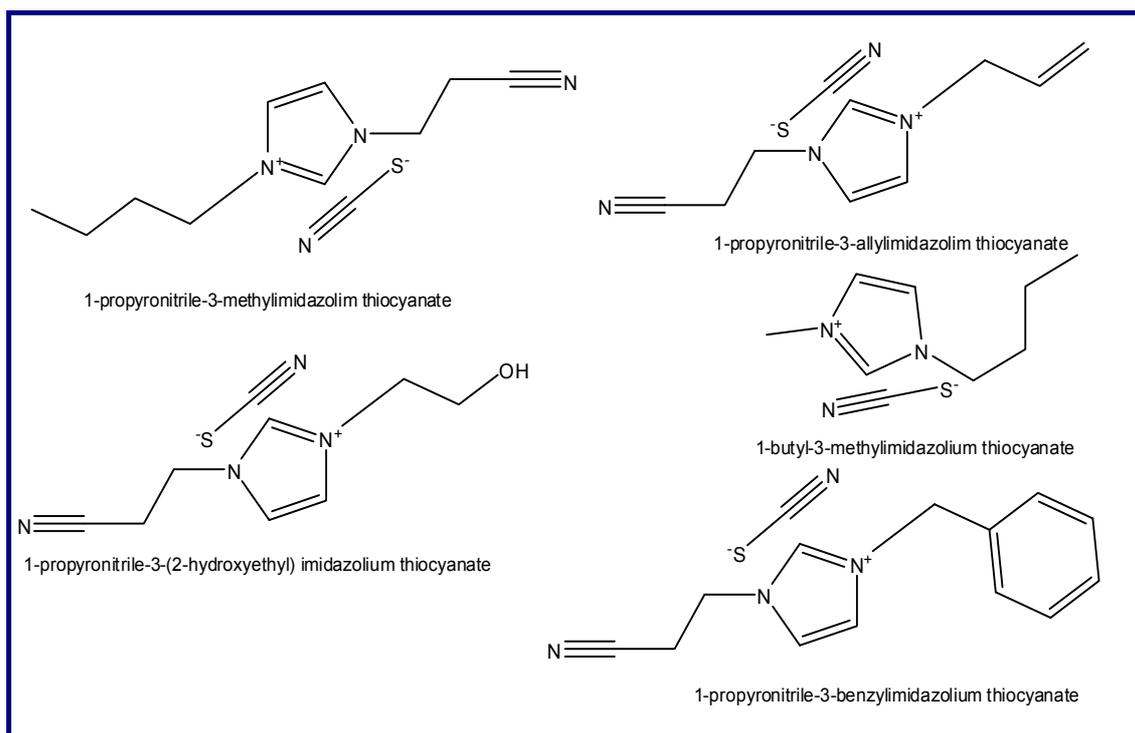
Figure 1: Structures of the ionic liquids used in the present studies

2. Experimental Section

2.1 Chemicals

All chemicals were used as received without further purifications. The starting materials are: imidazole (Sigma-Aldrich, 99 %), methanol (anhydrous, Sigma-Aldrich, 99.8 %)**,** acrylonitrile (Sigma-Aldrich, 99 %), 2-chloroethanol (Merck, 99.8 %), benzyl chloride (Merck, 99 %), allyl chloride (Sigma-Aldrich, 98 %), sodium thiocyanate (Sigma-Aldrich, 98%), acetone (Sigma-Aldrich, 99.8 %), 1-chlorobutane (Sigma-Aldrich, 99.5 %), and ethyl acetate (anhydrous, Sigma-Aldrich, 99.8 %). Benzene (99.5 %), cyclohexane (99 %) and 1-butyl-3-methylimidazolium chloride were supplied by Merck. Cyclohexane and benzene and was dried over a molecular sieve (3 Å, 8 -12 meshes) before use.

2.2 Synthesis of ionic liquids

The syntheses of the ionic liquids were based on the metathesis reaction of sodium thiocyanate with 1-propyronitrile-3-butylimidazolium chloride ([C$_2$CNBIM]Cl), 1-butyl-3-methylimidazolium chloride ([BMIM]Cl), 1-propyronitrile-3-(2-hydroxyethyl)imidazolium chloride ([C$_2$CNHEIM]Cl), 1-propyronitrile-3-allylimidazolium chloride ([C$_2$CNAIM]Cl]), and 1-propyronitrile-3-benzylimidazolium chloride ([C$_2$CNBzIM]Cl). [C$_2$CNBIM]Cl, [C$_2$CNAIM]Cl], [C$_2$CNBzIM]Cl, and [C$_2$CNHEIM]Cl were prepared as previously reported by our research group (Ziyada et al., 2010; Muhammad et al., 2012). 1-butyl-3-methylimidazolium chloride ([BMIM]Cl) was supplied by Merck. Briefly, 1-propyronitrile-3-butylimidazolium thiocyanate ([C$_2$CNBIM][SCN]) was synthesized by mixing [C$_2$CNBIM]Cl (0 .1 mol) with equimolar sodium thiocyanate (NaSCN) in acetone at

room temperature. After mixing the system for 48 h, the solid precipitate was separated, and the solvent was removed under vacuum at 70 °C. The resulting compound was washed with ethyl acetate, the remaining ethyl acetate was removed under vacuum, and the sample was dried in vacuum oven at 80 °C for 72 h. The same procedure was followed to synthesis the other four ionic liquids. Here, [BMIM]Cl, [C$_2$CNAIM]Cl, [C$_2$CNHEIM]Cl and [C$_2$CNBzIM]Cl were used to synthesize 1-butyl-3-methylidazolium thiocyanate ([BMIM][SCN]), 1-propyronitrile-3-allylimidazolium thiocyanate ([C$_2$CNAIM][SCN]), 1-propyronitrile-3-(2-hydroxyethyl)imidazolium thiocyanate ([C$_2$CNHEIM][SCN]), and 1-propyronitrile-3-benzylimidazolium thiocyanate, ([C$_2$CNBzIM]Cl), respectively, instead of [C$_2$CNBIM]Cl. The structure of the synthesized ionic liquids was confirmed by ^{1}H NMR, FTIR and elemental analysis. The ^{1}H NMR spectra were taken in deuterated solvents and recorded on a Bruker Avance 500 spectrometer.

2.3 Determination of relative volatility and selectivity

The relative volatility and selectivity values were obtained from the vapour-liquid equilibrium (VLE) of benzene and cyclohexane in the presence of the ionic liquids. The vapour-liquid equilibrium data were measured by using the head space gas chromatography. The isothermal VLE data for binary system (benzene + cyclohexane) and ternary systems (benzene + cyclohexane + ionic liquid) were determined at a temperature of (323.15, 338.15, and 353.15) K by head space GC (HS-GC), Trace GC-2000. The apparatus consists of a head space sampler with 20-sample vial tray, oven with 6 sample tray, and gas chromatography.

A feed containing azeotropic mixture of benzene and cyclohexane (cyclohexane, 45 % vol) was prepared. For ternary systems (benzene + cyclohexane+ ionic liquid) 6 mL of azeotropic feed and 6 mL of ionic liquid was added to 20 mL vials, and closed tightly with cap and septum to avoid the losses. For binary system (benzene + cyclohexane) 12 mL samples were added the vials. The vials were thermostatted at experimental temperatures until the vapour liquid equilibrium is reached. The equilibration time for the present experimental condition of was established experimentally by thermostatting a number of vials with the same samples at different thermostatting times. The HS-GC was calibrated by injecting sample containing known compositions of benzene and cyclohexane binary mixtures. The peak area ratios measured by gas chromatography were related with injected samples composition. The values of peak area ratio (peak area of benzene to total peak area) were plotted versus benzene mole fraction to obtain the calibration curve.

3. Result and Discussion

The structures of the synthesized ionic liquids are confirmed using H[1] NMR, elemental analysis, and FTIR. The ^{1}H NMR obtained is as follows. [C$_2$CNBIM][SCN]. ^{1}H NMR (Methanol-d$_3$): δ (ppm) = 0.96 (3H, t), 1.31 (2H, m), 1.81 (2H, m), 3.07 (2H, t), 4.18 (2H, t), 4.47 (2H, t), 7.66 (1H, s). [C$_2$CNAIM][SCN]. ^{1}H NMR (DMSO-d$_6$): δ = 3.20 (2H, t), 4.55 (2H, t), 4.91 (2H, d), 5.35 (2H, d), 6.15 (1H, m), 7.75 (1H, s), 7.89 (1H, s), 9.15 (1H, s). [C$_2$CNBzIM][SCN]. ^{1}H NMR (Methanol-d$_3$): δ = 1.66 (2H, t), 3.06 (2H, t), 3.96 (2H, s), 5.93 (5H, m), 6.19 (1H, s), 6.27 (1H, s), 7.75 (1H, s). [C$_2$CNHEim][SCN]. ^{1}H NMR (DMSO-d6): δ = 3.25 (2H, t), 3.75 (2H, t), 4.22 (2H, t), 5.37 (2H, d), 5.45 (1H, t), 7.91 (1H, s), 7.85 (1H, s), 9.45 (1H, s). [BMIM][SCN]. ^{1}H 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).

The experimental VLE data for binary system (cyclohexane + benzene) and ternary mixture (cyclohexane + benzene + ionic liquid) were determined at temperature of (323.15, 338.15, and 353.15) K. In order to evaluate the effect of the ionic liquids on the phase equilibrium of benzene and cyclohexane, the values of separation factor (relative volatility) were calculated. The relative volatility ($α_{12}$) is defined as follows (Pereiro et al., 2012):

$$\alpha_{12} = \frac{y_1/x_1}{y_2/x_2} = \frac{\gamma_1 p_1^0}{\gamma_2 p_2^0} \tag{1}$$

where, x and y are mole fractions of the components in the liquid and the vapour phase and the subscript *1* and *2* stands for cyclohexane and benzene, respectively. The values of x and y in Eq(1) is based on ionic liquid free compositions. Both in binary and ternary system, the feed samples contain benzene and cyclohexane at azeotropic composition, that is, 45 % vol cyclohexane on ionic liquid free basis.

The selectivity of ionic liquid for benzene compared to cyclohexane (S_{21}) can be approximated using the following equation (Jongmans et al., 2011):

$$s_{21} = \alpha_{12} \frac{p_2^0}{p_1^0} \tag{2}$$

where, P^0 is the pure components vapour pressure at experimental temperature, which was determined by using Antoine equation (Thomson, 1946). The selectivity and relative volatility values obtained from the experimental VLE data are depicted in Table 1. The relative volatility values are close to 1 in the absence ionic liquids (for binary mixtures of benzene and cyclohexane) at experimental temperatures. On addition of ionic liquids, the values of the relative volatility of cyclohexane to benzene are improved.

Table 1: Experimental relative volatility and selectivity of benzene and cyclohexane in the presence of ionic liquids

	323.15 K		338.15 K		353.15 K	
	α_{12}	S_{21}	α_{12}	S_{21}	α_{12}	S_{21}
Without Ionic Liquid	1.025	1.023	1.024	1.022	1.024	1.022
[BMIM][SCN]	1.584	1.584	1.554	1.540	1.456	1.429
[C$_2$CNBIM][SCN]	1.661	1.658	1.658	1.674	1.534	1.562
[C$_2$CNAIM][SCN]	1.649	1.664	1.525	1.523	1.429	1.456
[C$_2$CNHEIM][SCN]	1.475	1.472	1.402	1.415	1.397	1.423
[C$_2$CNBzIM][SCN]	1.582	1.579	1.541	1.555	1.481	1.508

The effect of temperature on the relative volatility of cyclohexane to benzene is illustrated in Figure 2. The relative volatility shows decreasing behavior with increasing temperature. This may be due to the fact that the effect of temperature on cyclohexane-ionic liquid interaction is stronger compared to benzene-ionic liquid interaction. This can be explained by the influence of temperature on the activity coefficients of benzene and cyclohexane in ionic liquids. Previous studies show that the activity coefficient of cyclohexane in ionic liquids considerably decreases with increasing temperature; however, the dependency is reversed or insignificant for benzene (Domańska et al., 2009). This shows that the value of the ratio of activity coefficients of cyclohexane to benzene decreases with increasing temperature. According to Eq(1), the relative volatility of cyclohexane to benzene decreases with increasing temperature since the change in ratio of pure components vapour pressure is insignificant. The result is consistent with the effect of temperature on selectivity of ionic liquid for benzene compared to cyclohexane (Marciniak, 2010). The results also show that the selectivity of ionic liquids decreases with increasing temperature (Table 1).
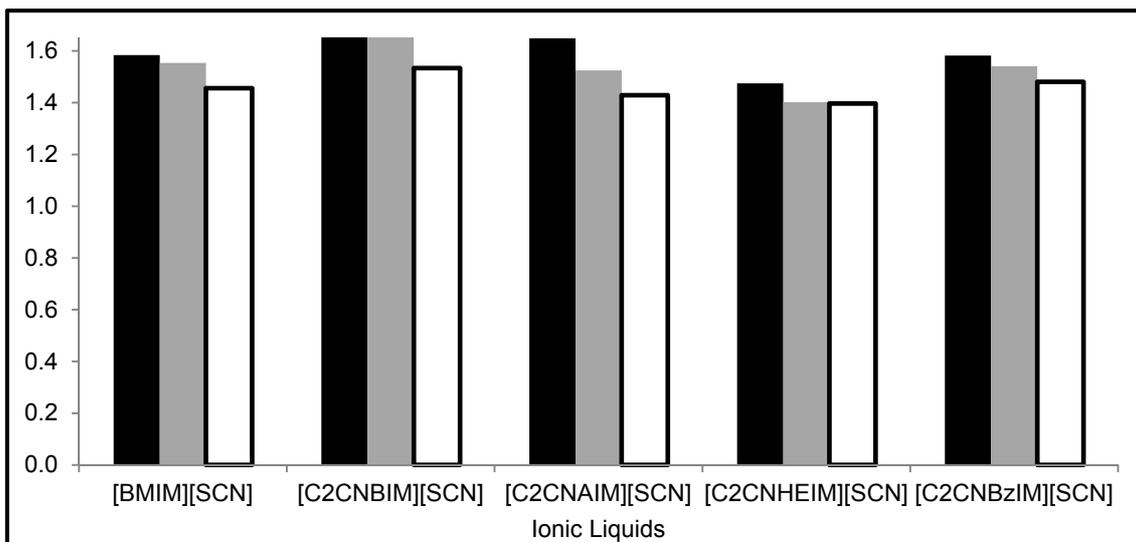
Figure 2: Influence of temperature on the relative volatility of cyclohexane to benzene for a model feed, consisting of 45 vol % cyclohexane. Black bars, gray bars and white bars denote relative volatility at 323.15, 338.15 and 353.15 K, respectively.

COSMO-RS theory was applied in order to understand the effect of nitrile, benzyl, allyl and hydroxyl functional groups on the separation efficiency the ionic liquids. The COSMO-RS model was used to obtain the charge distribution (sigma-profile) of benzene, cyclohexane and the ionic liquids. The full description of the COSMO-RS theory has been given elsewhere (Klamt, 2005). According to COSMO-RS theory, the charge distribution on a molecule is expressed by sigma profile (σ-profile). The σ-profile shows the relative amount of surface segment of the molecule with given amount of charge density (σ) and represented in histogram. In COSMO-Rs theory, non polar and less-polar molecules have relatively narrow σ-profile located at the center of the histogram compared with polar compounds.

Figure 3 shows the σ-profile and COSMO surface of benzene, cyclohexane, ionic liquids investigated in this study. The σ-profile of cyclohexane ranges from -0.005 to 0.005 [e/Å^2] with a maximum at -0.001 [e/Å^2] arising from hydrogen, and another shoulder at about 0.002 [e/Å^2] from the exposed surfaces of carbon atoms. Due to its delocalized π-electrons, benzene has more pronounced polarity than cyclohexane. The negatively charged π-surface appears yellow, corresponding to positive σ, and the hydrogen surfaces are light blue, with moderately negative σ. The σ-profile of benzene is separated in two symmetrical peaks centered at ± 0.06 [e/Å^2]. On the other hand, ionic liquids have two main peaks, the negative and positive peaks, resulting cation and anion, respectively. The position of the peaks may shift to the right or left depending on the nature of the cation and anion (see Figure 3). Since, part of the benzene molecule that is available for interaction are they π-electron clouds, corresponding cation's peaks should have values that match with the π-cloud peaks of the benzene molecule.

According to COSMO-RS model, for the strong benzene-ionic liquid interaction and better separation efficiency, the tallest peak of the cation should overlap with benzene and the overlap with cyclohexane should be minimum. From the σ-profile and sigma surface shown in Figure 3a, replacing methyl alkyl chain of imidazolium cation with 1-propyronitrile creates two additional minor peaks resulted from the nitrile functional group. Moreover, since the non-polar methyl alkyl chain is replaced by polar propyronitrile functional group, the height of the maximum peak is also reduced. These results in lower cyclohexane-[C$_2$CNBIM][SCN] interaction and stronger benzene-[C$_2$CNBIM][SCN] interaction compared to that of [BMIM][SCN], which agree with the experimental relative volatility of cyclohexane to benzene showed in Table 1.

As it can be seen from Figure 3b, [C$_2$CNAMIM]$^+$, [C$_2$CNBzMIM]$^+$ and [C$_2$CNHEIM]$^+$ have additional two minor peaks results from the introduced allyl, benzyl and hydroxyl functional group, respectively. However the σ-profile these cations are wider (extended to the right and left of the histogram) compared to [C$_2$CNBMIM]$^+$. Moreover, the σ-profile of [C$_2$CNHEIM]$^+$ is more extended to the right and left compared to other cations due to the strong hydrogen bond donor and acceptor capacity of the hydroxyl functional group. The strong hydrogen bond acceptor and donor of the cation lead to a stronger cation-anion interaction, which finally results in a weaker affinity of the cation toward the benzene molecule.
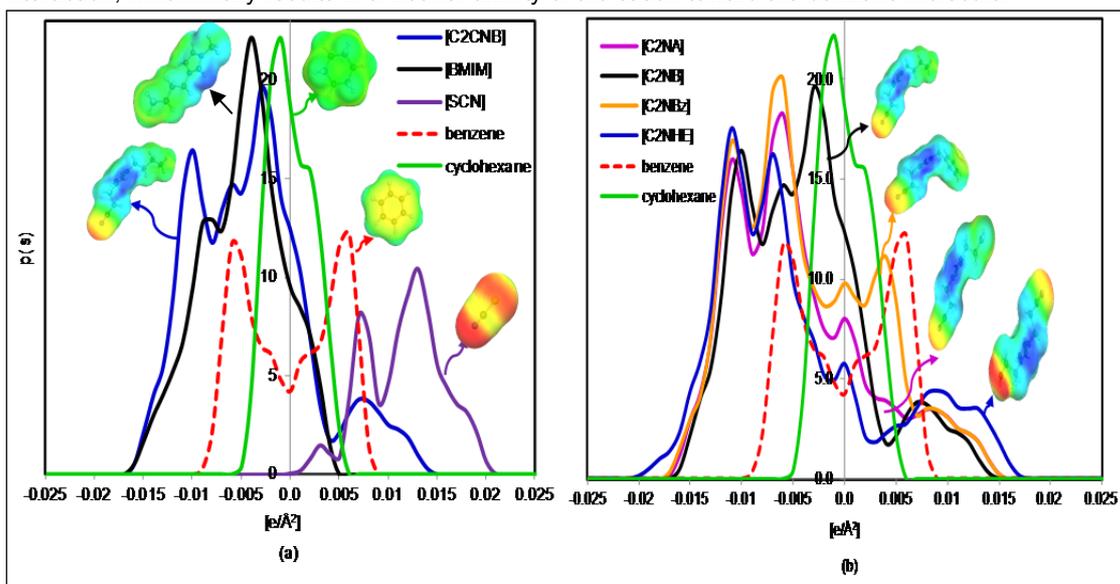
Figure 3: σ-profile and σ-surface of benzene, cyclohexane and cations and anions used in this study.

Therefore, the relative volatility cyclohexane to benzene in the presence of [C$_2$CNHEIM][SCN] is lower compared to other ionic liquid studied as shown in Table 2. [C$_2$CNAIM][SCN] has less extended σ- profile distribution compared to [C$_2$CNHEIM][SCN] which indicates less cation-anion interaction in [C$_2$CNAIM][SCN]. The lower cation-anion interaction in [C$_2$CNAIM][SCN] favour higher relative volatility values compared to [C$_2$CNHEIM][SCN]. Introduction of the benzyl functional group in the imidazolium cation causes more σ-profile overlap with cyclohexane. This leads to higher cyclohexane solubility in the ionic liquids which reduces its selectivity for benzene compared to [C$_2$CNBIM] [SCN]. Therefore, the overall separation efficiency of the ionic liquids follows the sequence [C$_2$CNBEIM] [SCN] > [BMIM] [SCN] > [C$_2$CNBzIM] [SCN] > [C$_2$CNAIM] [SCN] > [C$_2$CNHEIM] [SCN] for thiocyanate anion. Note that the sequence may change for other anions since the cation-anion interaction strongly depends on the strength of the anions used.

4. Conclusions

A comparative evaluation of five ionic liquids as entrainer in separation of benzene and cyclohexane has been done. The evaluation was performed in terms of experimentally determined relative volatility and with the aid of COSMO-RS model. The result shows the all the thiocyanate based task-specific ionic liquid studied in this work increases the relative volatility of cyclohexane to benzene. The value of the relative volatility slightly decreases with increasing temperature. The overall separation performances of the present ionic liquids can be ranked as [C$_2$CNBEIM][SCN] > [BMIM][SCN] > [C$_2$CNBzIM][SCN] > [C$_2$CNAIM][SCN] > [C$_2$CNHEIM][SCN].

Acknowledgements

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