Extractive separation of benzene and cyclohexane using 1-butyl-3-methylimidazolium acetate

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Abstract. Separation of benzene and cyclohexane is a challenging process in petrochemical industry due to the difficulty to separate them by a simple distillation. Recognizing ionic liquid as a potential alternative, this work investigated the performance of 1-butyl-3-methylimidazolium acetate ([C₄Mim][Ac]) as an extracting solvent in the separation of benzene and cyclohexane via liquid–liquid extraction. The ternary liquid–liquid equilibria for this IL with benzene and cyclohexane was investigated at 25 oC and 1 atm, with feed concentration of benzene ranging from 10 to 60 wt %. Good agreement was achieved for the tie-lines obtained from the COSMO-RS model and experimental data. The NRTL model was successfully employed to correlate the experimental tie lines. The performance of [C₄Mim][Ac] was compared with organic solvent and other ILs reported in literature. The selectivity and distribution ratio of benzene were in the range of 4.17–5.47 and 0.51–0.72, respectively. At equilibrium, no IL was present in the cyclohexane layer and the concentration of cyclohexane in the IL layer was very low. This observation indicated that there was minimum cross-contamination between the phases and less energy was required for solvent recovery.

1. Introduction
The separation of benzene and cyclohexane by conventional distillation is difficult and challenging because they have nearly equal boiling points, with the difference of only 0.64°C. This condition requires an advanced distillation process such as the azeotropic or extractive distillations [1]. Despite their application in industry, both processes suffer from some disadvantages such as process complexity, high capital and operating costs, and high energy consumption [2, 3]. Moreover, these processes are carried out by adding a third compound as the entrainer, in which the removal of the third compound from the distillate causes even higher process complexity and cost. In addition, azeotropic distillation and extractive distillation are only suitable for high (> 90%) and medium (65–90 %) concentration of benzene in the feed, respectively.

Liquid–liquid extraction (LLE) is widely used in the chemical industry because it is a simple process that can be operated at mild conditions. In the case of benzene-cyclohexane mixture, LLE is a suitable method to separate low concentrations of benzene (20–65 %). However, there is still no industrial process available for the concentrations less than 20 wt %. While the pervaporation process was reviewed as a potential technique, it was still limited by the challenges encountered during economic evaluation [2]. Several reports have investigated the performance of industrial organic solvents in LLE process such as ethylene glycol, tetra-ethylene glycol, sulfolane, and N-
methy1pyrrolidone as extractants [4-6]. The results revealed that their application is associated with several challenges because these solvents are usually volatile, toxic and flammable.

Interestingly, ionic liquids (ILs) have been extensively studied for wide applications of chemical processes. In the last decades, the potential of ILs in many industrial applications has become more diverse due to their appreciable advantages such as being non-flammable, non-volatile, environmentally benign, and thermally stable over a wide range of temperature. ILs have also been recognized for their ability to break the azeotropic properties in many mixtures such as ethanol-water, alcohol-alkane, aromatic-aliphatic, ketone-alkane, and others [7]. For the IL–benzene–cyclohexane system, the reports of new data for ternary phase equilibria proved the feasibility of using ILs as the extracting solvents. This is reflected from earlier studies involving some ILs such as [C₃Mim][BF₄][8], [C₄Mim][SCN][8], [C₂Mim][MeSO₄][9], [C₃im][DBP][10] [C₂Mpyr][EtSO₄][11] and many more. Despite the huge number of ILs available, [C₄Mim][Ac] is particularly an interesting IL because it is an affordable IL that consists of a common cation-anion pair. [C₄Mim][Ac] has been extensively studied in the process of CO₂ capture [12, 13]. Reports showed that the carboxylation reaction can occur between [C₄Mim][Ac] and CO₂, leading to the high solubility of CO₂ in the IL [14, 15]. It is known that CO₂ and benzene are both non-polar compounds. In addition, as observed in COSMO-RS programme, both compounds also showed similar σ-profiles and σ-potential. Thus, it can be hypothesized that benzene is also highly soluble in [C₄Mim][Ac], which will produce high selectivity of IL in LLE. This is the first study that investigates the performance of [C₄Mim][Ac] as an extracting solvent to separate benzene-cyclohexane mixture.

2. Methodology

2.1 Chemicals and materials
The following chemicals were obtained as follow and used without further purification: benzene (99.7 %) from Merck, cyclohexane (99.5%) from Merck and [C₄Mim][Ac] (95.0 %) from Sigma Aldrich. For the determination of ternary composition in extract and raffinate phases at equilibrium, the NMR analysis was performed using deuterated chloroform with purity ≥99.8% (stabilized with silver).

2.2 Liquid–liquid extraction experiment
The feed mixture containing 10 wt % benzene in cyclohexane was firstly prepared inside a 20-mL screw-capped scintillation vial using an analytical balance with accuracy of ±0.0001 g. This procedure was repeated for other concentrations of benzene (i.e., 20, 30, 40, 50, and 60 wt %) in the feed. Based on the binary composition, the total weight of the feed mixture was fixed at 2 g. The [C₄Mim][Ac] IL was then mixed into every feed mixture in a weight ratio of 1:1. Parafilm tape was used to seal each vial and avoid the component loss due to evaporation. The vials were then placed in an incubation shaker at 25°C and 1 atm, where spring clamps were used to tighten them upon shaking. The shaking was subsequently conducted at 200 rpm for 6 h. After stopping the mixing procedure, the mixture was left for approximately 12 h to reach equilibrium. This period is sufficient as we have conducted the settling time study to ensure the equilibrium state was fully reached.

2.3 Determination of ternary molar compositions
A drop (±0.035 mL) of sample was taken out from the extract and raffinate layers using a micropipette. For the extract layer, a few bubbles were purged from the micropipette tip to avoid cyclohexane contamination from the raffinate. This drop of sample was then dissolved in ±0.7 mL of deuterated chloroform placed inside an NMR tube. The sample and solvent in the tube were shaken carefully to form homogenous mixture. Each tube was tightly sealed with parafilm to avoid chemical loss. The ¹H NMR spectrometer of Bruker 400 MHz was used to measure the peak of hydrogen molecules in each component and calculate the molar fraction of each component in both layers.
2.4 Experimental selectivity and distribution ratio
The distribution ratio of benzene ($D_B$) and the solvent selectivity ($S$) of [C$_4$Mim][Ac] were used to evaluate the extraction performance by using Equations 1 and 2.

$$D_B = \frac{x_B^1}{x_B^2}$$  \hspace{1cm} (1)

$$S = \frac{x_B^1}{x_B^2} \frac{x_C^1}{x_C^2}$$  \hspace{1cm} (2)

where $x_B$ and $x_C$ are the concentrations of benzene and cyclohexane, respectively. The superscripts 1 and 2 represent the extract and raffinate phase, respectively.

3. Results and discussion

3.1 Ternary LLE
The LLE data for the ternary system of [C$_4$Mim][Ac] + benzene + cyclohexane is tabulated in Table 1, and the corresponding ternary plot is depicted in Figure 1. As seen in these results, the tie lines obtained from experimental and COSMO-RS approaches showed a good agreement, with the RMSD value of 1.59%. The tie lines also showed negative slope and they become more negative at higher concentrations of benzene in the feed. Interestingly, there was no trace of IL found in cyclohexane-rich layer. This indicates a favourable extraction process because the solvent cross contamination can be avoided. The concentration of cyclohexane in bottom layer was also very low in which indicates an easier regeneration of IL. Based on the measured tie lines, it was observed that the immiscibility region in [C$_4$Mim][Ac] is slightly higher than that in [C$_2$Mim][Ac] from our previous work [16]. This shows that the higher alkyl length of IL resulted into higher mutual solubility between IL and benzene/cyclohexane. This is mostly contributed by the stronger dispersive interaction between the three components at higher alkyl chain of imidazolium cation. This trend is consistent with another study using N-methylimidazole [C$_1$im] and N-ethylimidazole [C$_2$im] as the solvents [10].

| Raffinate phase | Extract phase | $D$ | $S$
|-----------------|--------------|-----|-----|
| $x_1$ | $x_2$ | $x_3$ | $x_1$ | $x_2$ | $x_3$ | 0.72 | 5.47 |
| 0.078 | 0.922 | 0.000 | 0.056 | 0.122 | 0.822 | 0.72 | 5.47 |
| 0.163 | 0.837 | 0.000 | 0.102 | 0.087 | 0.810 | 0.63 | 6.01 |
| 0.250 | 0.750 | 0.000 | 0.158 | 0.068 | 0.773 | 0.63 | 6.94 |
| 0.345 | 0.655 | 0.000 | 0.190 | 0.083 | 0.727 | 0.55 | 4.35 |
| 0.447 | 0.553 | 0.000 | 0.241 | 0.085 | 0.674 | 0.54 | 3.50 |
| 0.545 | 0.455 | 0.000 | 0.280 | 0.056 | 0.664 | 0.51 | 4.17 |
3.2 Selectivity and distribution ratio

Figure 2 shows the extractive performance of [C₄mim][Ac] in view of distribution ratio and selectivity. The values of selectivity were higher than unity which confirms the possibility of extraction. In general, the distribution ratio and selectivity slightly decreased at higher mole fraction of benzene in raffinate layer. Referring to our previous work [16], the benzene distribution ratio for the system using [C₄Mim][Ac] was higher than the one with [C₂Mim][Ac]. This is because at higher cation alkyl length, the ability of IL to dissolve benzene and cyclohexane increased. The selectivity, in contrast, decreased at higher cation alkyl length. Selectivity defines the ability of an IL to selectively extract benzene from cyclohexane, rather than extracting cyclohexane altogether. The longer alkyl chain of cation creates additional interaction between the IL and cyclohexane in the non-polar region, and therefore reduces the selectivity.

![Figure 2](image)

**Figure 2.** The distribution ratio (a) and selectivity (b) with respect to concentrations of benzene in the raffinate layer. The full symbol with solid line represent the experimental data, while the empty symbol with dashed line indicates the COSMO-RS predictions.
3.3 Consistency test
For the experimental results, the consistency tests were conducted using the Hand’s correlation. This correlation was used to obtain the following Hand’s equation [17].

\[
\ln \left( \frac{x_B}{x_{Cyc}} \right) = a + b \ln \left( \frac{x_B}{x_{IL}} \right)
\]

(3)

where \(x_{Cyc}, x_B, \) and \(x_{IL}\) represent the concentrations of cyclohexane, benzene, and IL, respectively. The superscripts ‘ and ” refer to the extract and raffinate phases, respectively. The value of parameters \(a, b,\) and \(R^2\) for each ternary system are 1.442, 2.558 and 0.983, respectively. The linearity of each plot (i.e. the value of \(R^2\) close to unity) indicates the excellent degree of consistency for the ternary LLE tie lines reported in this work.

3.4 NRTL correlation
In LLE calculations, an isothermal liquid-liquid flash is solved at a given temperature and pressure to obtain phase compositions. The flash calculation consists of the Equations 4, 5 and 6.

Material Balance

\[
x_i - (1 - \omega)x_i^{L1} - \omega x_i^{L2} = 0, \quad i = 1, N_c
\]

(4)

Equilibrium Equation

\[
x_i^{L1}y_i^{L1} - x_i^{L2}y_i^{L2} = 0, \quad i = 1, N_c
\]

(5)

Equation of Summation

\[
\sum_i x_i^{L1} - \sum_i x_i^{L2} = 0
\]

(6)

In these equations, \(\omega\) is the liquid-liquid splitting ratio; \(x_i\), the amount of component \(i\) in the mixture; \(x_i^{L1}\), the amount of component \(i\) in liquid phase \(L1\); \(x_i^{L2}\), the amount of component \(i\) in liquid phase \(L2\); and \(N_c\), the number of constituents of the liquid phases. The parameters \(y_i^{L1}\) and \(y_i^{L2}\) are the activity coefficients of component \(i\) in \(L1\) and \(L2\), respectively.

In this work, the activity coefficients were evaluated using the non-random two-liquid (NRTL) model [18]. This model was found to be useful for correlating the experimental LLE data of systems containing ILs without requiring any special modification. For a multicomponent system, the activity coefficient of component \(i\) is given by the general expression, shown in Equation 7:

\[
\ln y_i = \frac{\sum_j r_{ij} G_{ij} x_j}{\sum_j G_{ij} x_j} + \sum_j \frac{G_{ji} x_j}{\sum_k G_{kj} x_k} \left( \tau_{ij} + \frac{\sum_k \tau_{kj} G_{kj} x_k}{\sum_k G_{kj} x_k} \right)
\]

(7)

where \(r_{ij}\) and \(\tau_{ij}\) are binary interaction parameters and \(\alpha_i\) is the non-randomness parameter.

The binary interaction parameters \(r_{ij}\) and \(\tau_{ij}\) were estimated by minimizing the root mean square deviation (RMSD) between calculated and experimental solubilities of each constituent in each phase using the Simulis® software package [19]. The parameter \(\alpha_i\) in the NRTL model measures the non-randomness in the mixture; i.e. the mixture is said to be completely random when \(\alpha_i\) is zero. In this work, \(\alpha_i\) was fixed equal to 0.20 for all binary combinations. The choice of \(\alpha_{ij} = 0.2\) is made following successful fitting of NRTL model for ternary LLE data for systems containing ILs and deep eutectic solvents as reported in our previous works [16, 20, 21]. The RMSD value between experimental and NRTL calculation was 2.1 %, which indicates that NRTL correlation represents the experimental data very well. This excellent fitting is also observable in Figure 1. The values of NRTL binary interaction parameters regressed for this ternary system are shown in Table 2. In order to conserve coherence between this work and the previous one applied to deep eutectic solvents for the same binary mixture,
the binary interaction parameters between benzene and cyclohexane, despite the IL used, were taken from our previous work [21] without any adjustment.

**Table 2.** NRTL parameters for the ternary system [C₄Mim][Ac] + benzene + cyclohexane.

| i         | j         | τᵢⱼ   | τᵢᵢ |
|-----------|-----------|-------|------|
| Benzene   | Cyclohexane | -189.57 | 453.65 |
| Benzene   | [C₄Mim][Ac] | 4401.56 | 62.90 |
| Cyclohexane | [C₄Mim][Ac] | 1913.19 | 144.24 |

3.5 *Comparison with other solvents*

The efficiency of extraction process can be evaluated from its distribution ratio of solute (benzene for this case) and the selectivity of solvent. Figure 3 shows the comparison of these values from our work with some other reported works that used different types of ILs. Sulfolane [22] was included as a benchmark to represent the performance of common organic solvents used in industry.

![Figure 3](image-url)

Figure 3. Distribution ratio (a) and selectivity (b) of the reported ILs with respect to mole fraction of benzene in raffinate phase. The symbols are: ■-[C₄Mim][Ac](this work); ◆-[C₄Mim][AlCl₄] [23]; ▲-[C₄Mim][PF₆] [24]; ●-[C₄Mim][TF₂N] [25]; ▼-[C₄Pyr][BF₄] [8]; △-[C₄Mim][BF₄] [8]; □-[Mim][BF₄] [26]; ▲-[C₄Pyr][EtSO₄] [27]; ◆-[C₄Mim][EtSO₄] [28]; ○-[C₄Mpyr][BF₄] [29]; and x-sulfolane [22].

It was observed that at low concentration of benzene in raffinate phase (xᵢ < 0.3), the distribution ratio for [C₄Mim][Ac] was slightly higher than that with sulfolane. Even so, the selectivity of sulfolane is very low. Therefore, any IL that has better or comparable value of distribution ratio with respect to that in sulfolane will have more effective extraction. As seen in Figure 3, the distribution ratio of [C₄Mim][Ac] were generally in the intermediary region, as similar as most of the other reported ILs. The distribution ratio for [C₄Mim][Ac] is higher than [Mim][BF₄] [26], [C₄Mpyr][BF₄] [29], [C₄pyr][EtSO₄] [27], [C₄Mim][EtSO₄] [28], and [C₄pyr][BF₄] [8]. In addition, [C₄Mim][Ac] also have comparable distribution ratio with [C₄Mim][BF₄] [8] and [C₄pyr][BF₄] [8].

It was noteworthy that three ILs i.e. [C₄Mim][TF₂N] [25], [C₄Mim][PF₆] [24] and [C₄Mim][AlCl₄] [23] showed exceptionally higher distribution ratio than this work. However, their halide constitution must be considered carefully to ensure less effect towards the environment and process safety.
Besides, each of them could also bring significant drawbacks upon the application as the extracting solvent. Firstly, although the extraction using [C₄Mim][Tf₂N] showed the highest distribution ratio, its selectivity was relatively much lower than the other ILs. Next, for the extraction using [C₄Mim][PF₆] (n = 4, 5, 6) [24], the high distribution ratio would be interrogated by the cost of operation because it is a highly expensive type of IL. Finally for [C₄Mim][AlCl₄], it was reported that this IL is instable in humid air, thus creates difficulty in process handling. The selectivity of [C₄Mim][Ac] in this work is generally less than the other ILs. This could be possibly tolerated because the solvent capacity, which is directly related to distribution ratio, was reported to have much greater influence on the cost of production than does the selectivity [30].

4. Conclusion
In this work, the extractive performance of [C₄Mim][Ac] was investigated for the separation of benzene from its mixture with cyclohexane. Increasing cation alkyl chain resulted in increased distribution ratio and reduced selectivity. There was no IL presence in cyclohexane layer and the concentration of cyclohexane in IL layer was very low. Good agreement was also observed for the tie lines between COSMO-RS, experimental and NRTL. This study indicates that apart from being available commercially at affordable price, [C₄Mim][Ac] also showed good efficiency in the extraction of benzene from benzene–cyclohexane mixture.

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