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Efficient Solvent Extraction of Phenol Using Imidazolium-Based Ionic Liquids [†]

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Abstract: Ionic Liquids (ILs) have gained significant attention in both industry and academia due to their unique properties and diverse applications. With countless possible combinations of cations (e.g., Ammonium, Sulfonium, Phosphonium) and anions (Organic or Inorganic), the variety of ILs is immense. Among them, Imidazolium salts form the largest IL family, making them a focal point in this study. Phenolic compounds, essential in the chemical industry, become hazardous to both human and aquatic life when released into the environment. Traditional separation methods for phenolics unfortunately involve environmentally problematic processes. This research focuses on synthesizing and characterizing Imidazolium-functionalized ILs ([EtO₂C₂mim]Br, [EtO₂C₂mim]BF₄, [EtO₂C₂mim]PF₆) and studying their phenol extraction abilities. The results revealed [EtO₂C₂mim]Br as the most effective, extracting 99% of phenol and offering a promising alternative for the efficient extraction of phenols from real coal liquefaction oil.

Keywords: ionic liquids; phenol; liquid extraction



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1. Introduction

The phenol, an organic compound, plays a pivotal role in various industrial processes, serving as a vital component in the production of phenolic resins and related chemicals. It also boasts versatility as a solvent, antiseptic, and an additive in disinfectants [1,2]. However, phenol's classification as a toxic and carcinogenic substance [3,4] raises significant concerns for both human health and the environment when it is released into natural ecosystems.

The conventional approach for phenol extraction relies on the use of potent alkaline and acidic chemicals. Unfortunately, this method generates substantial volumes of wastewater laden with phenol [5,6]. Consequently, there exists an urgent need for an environmentally friendly and highly efficient alternative method to extract phenols, thus mitigating the environmental impact associated with the traditional approach.

Over the past decades, there has been a burgeoning interest in harnessing the potential of room temperature ionic liquids (ILs) for the removal of phenolic compounds from both oil mixtures and aqueous solutions [7–9].

This study aims to present the advancements in utilizing ILs for phenolic compound extraction. To achieve this, a series of Imidazolium-functionalized Ionic Liquids (ILs: [EtO₂C₂mim]Br (a), [EtO₂C₂mim]BF₄ (b), and [EtO₂C₂mim]PF₆ (c)) were synthesized, characterized, and their phenol extraction capabilities were investigated using a UV-visible spectrophotometry titration method. Additionally, the effects of IL structural characteristics on phenol extraction will be discussed.

2. Materials and Methods

2.1. Instruments and Reagents

N-methylimidazole, ethyl bromoacetate, sodium tetrafluoroborate, potassium hexafluorophosphate, phenol, and solvents were purchased from Sigma-Aldrich (St. Louis, MO, USA) and used as received.

UV-visible absorption spectra were measured with an Agilent Cary 60 spectrophotometer.

For IR spectroscopy, solid samples were taken neat on a Thermo Scientific IR200 FT-IR spectrophotometer; only significant absorptions are listed.

¹H NMR spectra were performed on a Bruker Ascend™-400 spectrometer at 298 K in DMSO solutions. Chemical shifts were reported relative to TMS as an internal standard.

2.2. Synthesis of ILs (a, b and c)

Imidazolium-based ionic liquids, [EtO₂C₂mim]Br (a), [EtO₂C₂mim]BF₄ (b), and [EtO₂C₂mim]PF₆ (c), were prepared based on procedures reported in the literature [10].

[EtO₂C₂mim]Br: Yield: 95%. IR (ν , cm⁻¹): 1744 (C=O); 1709 (C=N). ¹H NMR (400MHz, DMSO, TMS) δ ppm: 9.34 (s, 1H, NCHN), 7.49 (s, 2H, NCHCHN), 5.12 (s, 2H, NCH₂COOEt), 3.92 (q, 2H, J = 7.5 Hz, -COOCH₂CH₃), 3.77 (s, 3H, NCH₃), 0.93 (t, 3H, J = 7.5 Hz, -COOCH₂CH₃).

[EtO₂C₂mim]BF₄: Yield: 86%. IR (ν , cm⁻¹): 1749 (C=O); 1708 (C=N).

¹H NMR (400MHz, DMSO, TMS) δ ppm: 9.10 (s, 1H, NCHN), 7.73 (s, 2H, NCHCHN), 5.2 (s, 2H, NCH₂COOEt), 4.22 (q, 2H, J = 7.2 Hz, -COOCH₂CH₃), 3.93 (s, 3H, NCH₃), 1.25 (t, 3H, J = 7.2 Hz, -COOCH₂CH₃).

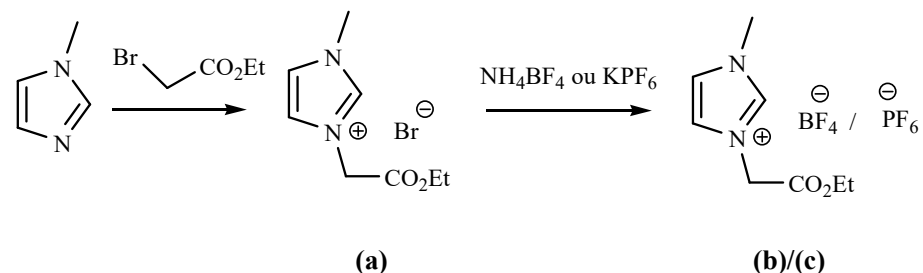
[EtO₂C₂mim]PF₆: Yield: 82%. IR (ν , cm⁻¹): 1754 (C=O); 1712 (C=N). ¹H NMR (400MHz, DMSO, TMS) δ ppm: 9.06 (s, 1H, NCHN), 7.70 (s, 2H, NCHCHN), 5.15 (s, 2H, NCH₂COOEt), 4.22 (q, 2H, J = 6.6 Hz, -COOCH₂CH₃), 3.90 (s, 3H, NCH₃), 1.25 (t, 3H, J = 6.6 Hz, -COOCH₂CH₃).

2.3. UV-Vis Titrations

In an Erlenmeyer flask, a solution (phenol/hexane) was prepared by dissolving 1.26 g of phenol in 500 mL of hexane ($C = 0.026 \times 10^{-2}$ M). The mixture was agitated until the phenol was fully dissolved. In test tubes, 10 mL of the prepared solution and a specific amount of the ionic liquid (according to precise IL/phenol ratios in hexane) were added. After stirring for 2 min, the phenol content in the various IL-hexane solutions was analyzed using UV-vis spectroscopy. The extraction efficiency was calculated via the difference of phenol contents before and after extraction.

3. Results and Discussion

The synthesis of imidazolium-based ionic liquids: [EtO₂C₂mim]Br (a), [EtO₂C₂mim]BF₄ (b), and [EtO₂C₂mim]PF₆ (c) is depicted in Scheme 1. The reaction of N-methylimidazole with one equivalent of ethyl bromoacetate at 0 °C led to the formation of [EtO₂C₂mim]Br (a) in a 95% yield. Subsequently, treating [EtO₂C₂mim]Br (a) with one equivalent of NH₄BF₄ or KPF₆ in acetone at room temperature for 22 h resulted in the formation of [EtO₂C₂mim]BF₄ (b) and [EtO₂C₂mim]PF₆ (c) in yields of 86% and 82%, respectively.



Scheme 1. Synthesis route of Ionic Liquids (a–c).

The ILs (a–c) were identified by $^1\text{H-NMR}$ and infrared spectroscopy (as detailed in the experimental section). All the spectra are consistent with the proposed molecular structures.

In this study, we aimed to utilize imidazolium-based functionalized ionic liquids for the extraction of phenol. A model solution containing hexane and phenol was employed for testing. Additionally, to investigate the impact of the anion type on the efficiency of our ionic liquid, we conducted a comparative study of phenol extraction using three ionic liquids prepared previously: $[\text{EtO}_2\text{C}_2\text{mim}]\text{Br}$ (a), $[\text{EtO}_2\text{C}_2\text{mim}]\text{BF}_4$ (b), and $[\text{EtO}_2\text{C}_2\text{mim}]\text{PF}_6$ (c).

The interactions between the ionic liquid and phenol in hexane were examined through titration conducted via UV-visible spectrophotometry, a sensitive method for tracking the progress of the extraction. The spectra of the initial (free) phenol and the solutions obtained after each addition of the ionic liquid were recorded in the UV range between 220 nm and 320 nm.

In the following figure, the UV absorption spectrum of phenol in hexane is presented (Figure 1). The spectrum is characterized by the presence of three main absorption bands between 260 and 280 nm, with the most intense band occurring at 271 nm.

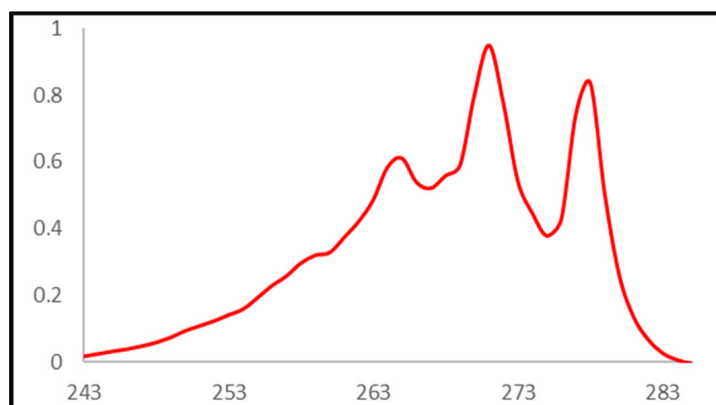


Figure 1. UV absorption spectrum of phenol in hexane at a concentration $C \approx 0.026$ M.

The experimental spectra obtained after the gradual addition of the ionic liquid to a phenol solution (IL/phenol ratios change from 0 to 1.4 in the case of ILs $[\text{EtO}_2\text{C}_2\text{mim}]\text{Br}$ and $[\text{EtO}_2\text{C}_2\text{mim}]\text{BF}_4$, and from 0 to 1.8 in the case of $[\text{EtO}_2\text{C}_2\text{mim}]\text{PF}_6$) exhibit a characteristic spectral change for each experiment, which varies from one ionic liquid to another. Typically, these variations are characterized by a reduction in the maximum absorbance, resulting from the decrease in phenol concentration (Figures 2–4).

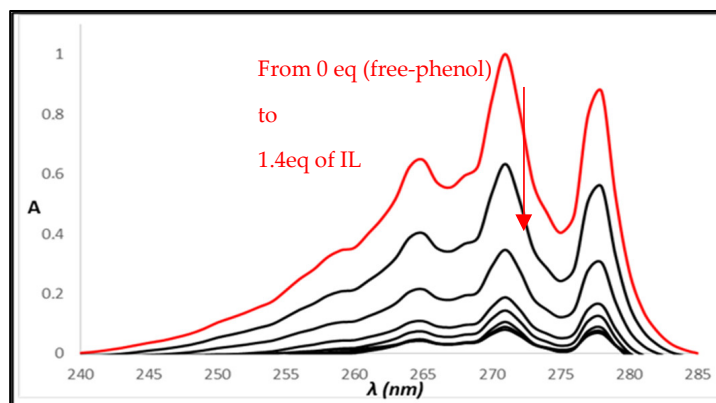


Figure 2. UV absorption spectra related to the extraction of phenol by the IL $[\text{EtO}_2\text{C}_2\text{mim}]\text{Br}$ for IL/phenol ratios: 0 (the red spectrum) $\leq R \leq 1.4$ (black spectra) at 25°C .

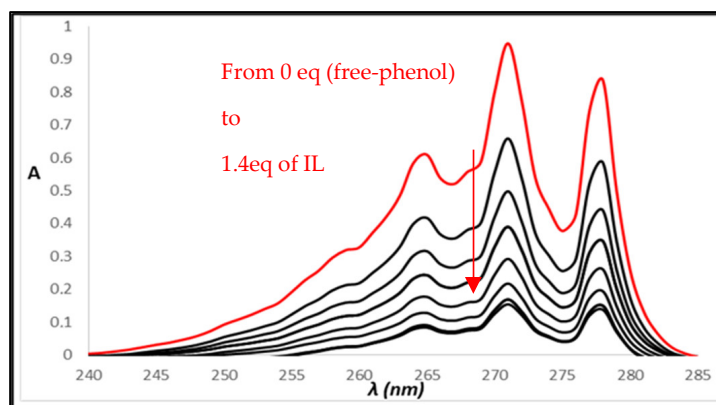


Figure 3. UV absorption spectra related to the extraction of phenol by the IL [EtO₂C₂mim]BF₄ for IL/phenol ratios: (the red spectrum) $\leq R \leq 1.4$ (black spectra) at 25 °C.

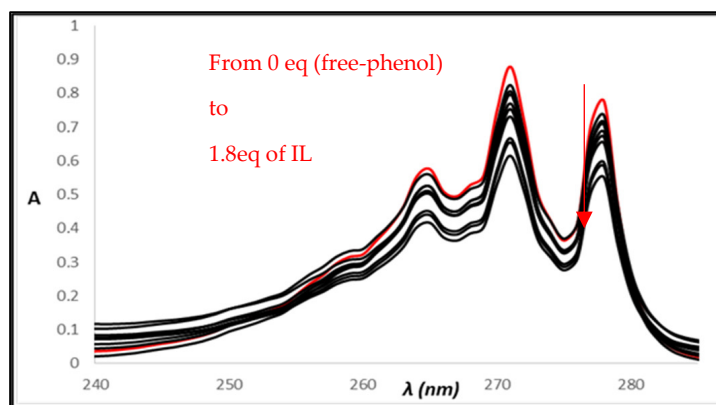


Figure 4. UV absorption spectra related to the extraction of phenol by the IL [EtO₂C₂mim]PF₆ for IL/phenol ratios: (the red spectrum) $\leq R \leq 1.6$ (black spectra) at 25 °C.

It can be noticed that Figure 2 illustrates a gradual decrease in absorbance with each addition of the ionic liquid, reaching an IL/Phenol ratio of 1 (maximum absorbance for the last spectrum = 0.1). This suggests that one equivalent of [EtO₂C₂mim]Br (a) was adequate for phenol elimination in hexane. Similarly, during phenol extraction by [EtO₂C₂mim]BF₄, the addition of the ionic liquid leads to a reduction in absorption intensity (maximum absorbance for the last spectrum = 0.16), and the spectra overlap after an IL/Phenol ratio of 1.2. In contrast, the ionic liquid [EtO₂C₂mim]PF₆ exhibits low extraction efficiency due to its limited solubility in the phenol–hexane solution. Hence, it can be inferred that the halogen anion in quaternary ammonium salts plays a pivotal role in phenol extraction by establishing hydrogen bonds with the phenol's OH group. However, both [EtO₂C₂mim]BF₄ and [EtO₂C₂mim]PF₆ lack free halogen atoms, instead featuring polyatomic anions. Furthermore, we observed poor solubility of [EtO₂C₂mim]PF₆ in hexane at room temperature, which likely affects phenol extraction.

To determine the new phenol concentration after each addition of the ionic liquid, we used the Beer–Lambert law, which provides the relationship between absorbance (A) and concentration (C): $A = \epsilon l C$.

To calculate the extraction efficiency, we determined the ratio between the final phenol concentration remaining in the solution and the initial phenol concentration before the addition of the ionic liquid ($R\% = C_{\text{final}}/C_{\text{initial}}$). The results obtained are summarized in the following diagram (Figure 5).

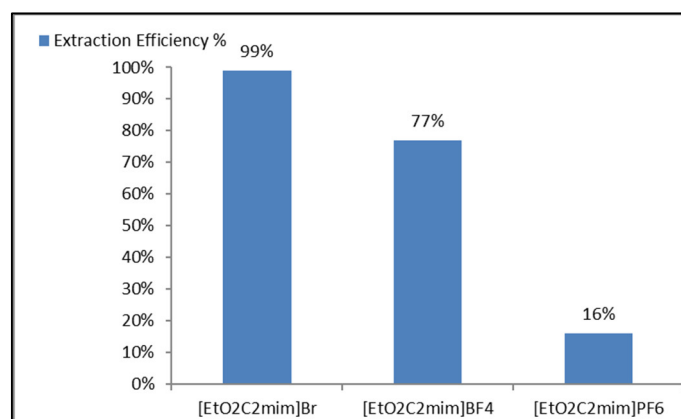


Figure 5. Effect of ILs structure on the phenol extraction efficiency.

4. Conclusions

Imidazolium-based ionic liquids were investigated for the extraction of phenol from a model solution composed of hexane and phenol. The molar amount of ionic liquid (IL) used was either equal to or close to that of phenol in the model solution. The results indicated that the choice of IL-anion significantly influences the efficiency of phenol extraction in the hexane solution.

For the same cation, [EtO₂CO₂mim]⁺, the extraction efficiency follows this order: [EtO₂C₂mim]Br > [EtO₂C₂mim]BF₄ > [EtO₂C₂mim]PF₆. [EtO₂C₂mim]Br exhibits the highest extraction efficiency, reaching approximately 99% at room temperature.

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