

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

I. Hamzi ^{1,2,*}, S. Bouchakour ¹, B. Mostefa-Kara ¹ and Didier Villemin ³

¹ Laboratoire de Catalyse et Synthèse en Chimie Organique, Faculté des Sciences, Université de Tlemcen, B.P. 119, Tlemcen 13000, Algeria; email1@email.com (S.B.); email2@email.com (B.M.-K.)

² Faculté de Médecine, Université de Tlemcen, 12 B P 123 Hamri Ahmed, Tlemcen 13000, Algeria

³ Laboratoire de Chimie Moléculaire et Thioorganique, UMR CNRS 6507, INC3M, FR 3038, ENSICAEN et Université de Caen Normandie, 14050 Caen, France; email3@email.com

* Correspondence: imane.hamzi@univ-tlemcen.dz

[†] Presented at the 27th International Electronic Conference on Synthetic Organic Chemistry (ECSOC-27), 15–30 November 2023; Available online: <https://ecsoc-27.sciforum.net/>.

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. Results revealed [EtO₂C₂mim]Br as the most effective, extracting 99% of phenol, offering a promising alternative for efficient extraction of phenols from real coal liquefaction oil.

Keywords: ionic liquids; phenol; liquid extraction

Citation: Hamzi, I.; Bouchakour, S.; Mostefa-Kara, B.; Villemin, D. Efficient Solvent Extraction of Phenol Using Imidazolium-Based Ionic Liquids. *Chem. Proc.* **2023**, *14*, x. <https://doi.org/10.3390/xxxxx>

Academic Editor(s): Name

Published: 10 November 2023



Copyright: © 2023 by the authors. Submitted for possible open access publication under the terms and conditions of the Creative Commons Attribution (CC BY) license (<https://creativecommons.org/licenses/by/4.0/>).

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 Aldrich and Fluka 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 AscendTM-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, $[\text{EtO}_2\text{C}_2\text{mim}]\text{Br}$ (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), were prepared based on procedures reported in the literature [10,11].

$[\text{EtO}_2\text{C}_2\text{mim}]\text{Br}$: 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, NCH_2COOEt), 3.92 (q, 2H, $J = 7.5$ Hz, $-\text{COOCH}_2\text{CH}_3$), 3.77 (s, 3H, NCH_3), 0.93 (t, 3H, $J = 7.5$ Hz, $-\text{COOCH}_2\text{CH}_3$).

$[\text{EtO}_2\text{C}_2\text{mim}]\text{BF}_4$: 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, NCH_2COOEt), 4.22 (q, 2H, $J = 7.2$ Hz, $-\text{COOCH}_2\text{CH}_3$), 3.93 (s, 3H, NCH_3), 1.25 (t, 3H, $J = 7.2$ Hz, $-\text{COOCH}_2\text{CH}_3$).

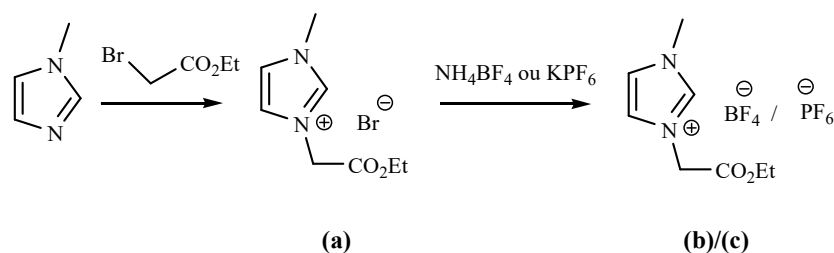
$[\text{EtO}_2\text{C}_2\text{mim}]\text{PF}_6$: Yield: 82%. IR (ν , cm^{-1}): 1754 (C=O); 1712 (C=N). ^1H NMR (400MHz, DMSO, TMS) δ ppm: 9.06 (s, 1H, NCHN), 7.70 (s, 2H, NCHCHN), 5.15 (s, 2H, NCH_2COOEt), 4.22 (q, 2H, $J = 6.6$ Hz, $-\text{COOCH}_2\text{CH}_3$), 3.90 (s, 3H, NCH_3), 1.25 (t, 3H, $J = 6.6$ Hz, $-\text{COOCH}_2\text{CH}_3$).

2.3. UV-Vis Titrations

In Erlenmeyer flask, a solution (phenol/hexane) is prepared by dissolving 1.26 g of phenol in 500 mL of hexane ($C = 0.026 \cdot 10^{-2}$ M). The mixture is agitated until the phenol is 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) are added. After stirring for 02 min, the phenol content in the various IL-hexane solutions is analyzed using UV-vis spectroscopy. Extraction efficiency was calculated by the difference of phenol contents before and after extraction.

3. Results and Discussion

The synthesis of imidazolium-based ionic liquids: $[\text{EtO}_2\text{C}_2\text{mim}]\text{Br}$ (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) is depicted in Scheme 1. The reaction of N-methylimidazole with one equivalent of ethyl bromoacetate at 0 °C led to the formation of $[\text{EtO}_2\text{C}_2\text{mim}]\text{Br}$ (a) in a 95% yield. Subsequently, treating $[\text{EtO}_2\text{C}_2\text{mim}]\text{Br}$ (a) with one equivalent of NH_4BF_4 or KPF_6 in acetone at room temperature for 22 h resulted in the formation of $[\text{EtO}_2\text{C}_2\text{mim}]\text{BF}_4$ (b), and $[\text{EtO}_2\text{C}_2\text{mim}]\text{PF}_6$ (c) 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. Spectra of the initial (free) phenol and the solutions obtained after each addition of the ionic liquid were recorded in the UV range between 220nm and 320nm.

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.

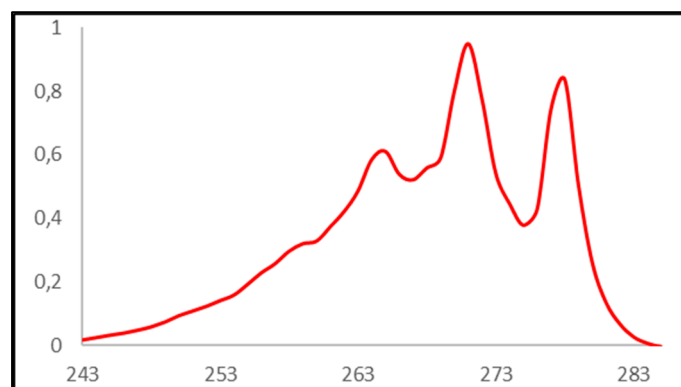


Figure 1. UV Absorption Spectrum of Phenol in Hexane at a concentration $C \approx 0.026\text{M}$.

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 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 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).

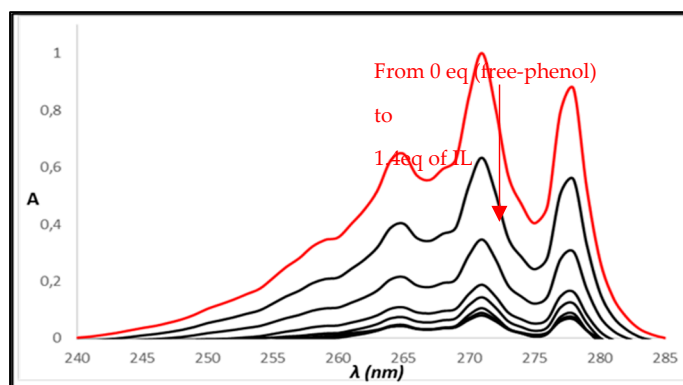


Figure 2. UV Absorption Spectra related to the extraction of phenol by the IL [EtO₂C₂mim]Br for IL/phenol ratios: 0 (the red spectrum) ≤ R ≤ 1.4 (black spectra) at 25 °C.

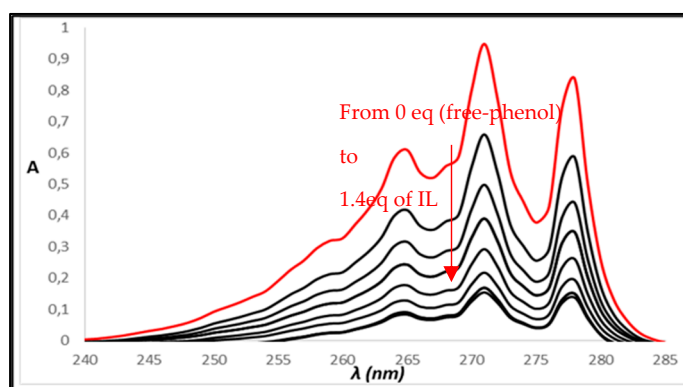


Figure 3. UV Absorption Spectra related to the extraction of phenol by the IL [EtO₂C₂mim]BF₄ for IL/phenol ratios: (the red spectrum) ≤ R ≤ 1.4 (black spectra) at 25 °C.

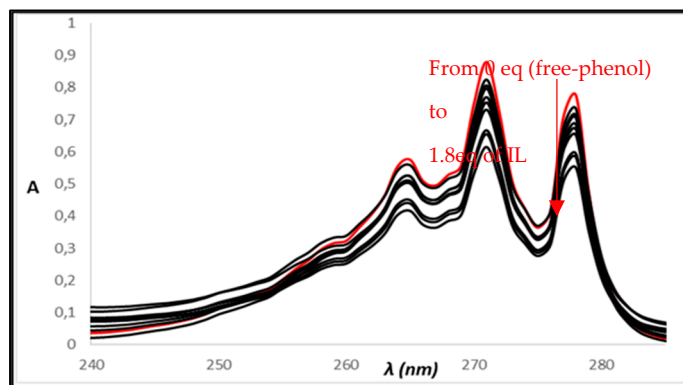


Figure 4. UV Absorption Spectra related to the extraction of phenol by the IL [EtO₂C₂mim]PF₆ for IL/phenol ratios: (the red spectrum) ≤ R ≤ 1.6 (black spectra) at 25 °C.

It is 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 1 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. How-

ever, both $[\text{EtO}_2\text{C}_2\text{mim}]\text{BF}_4$ and $[\text{EtO}_2\text{C}_2\text{mim}]\text{PF}_6$ lack free halogen atoms, instead featuring polyatomic anions. Furthermore, we observed poor solubility of $[\text{EtO}_2\text{C}_2\text{mim}]\text{PF}_6$ 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).

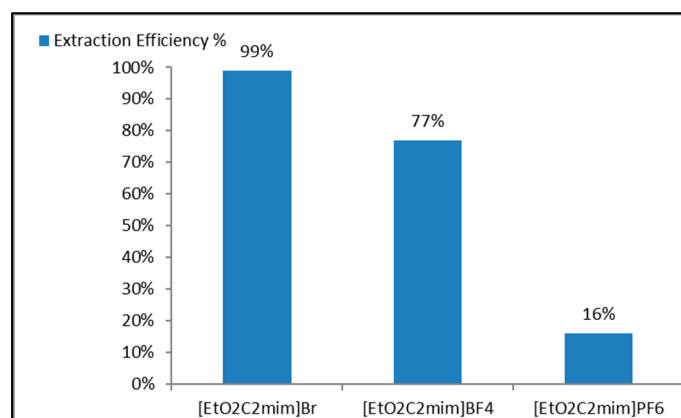


Figure 5. Effect of ILs structure on the phenol extraction efficiency.

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 $[\text{EtO}_2\text{CO}_2\text{mim}]^+$, the extraction efficiency follows this order: $[\text{EtO}_2\text{C}_2\text{mim}]\text{Br} > [\text{EtO}_2\text{C}_2\text{mim}]\text{BF}_4 > [\text{EtO}_2\text{C}_2\text{mim}]\text{PF}_6$. $[\text{EtO}_2\text{C}_2\text{mim}]\text{Br}$ exhibits the highest extraction efficiency, reaching approximately 99% at room temperature.

Author Contributions: All authors contributed to this proceeding paper article. All authors have read and agreed to the published version of the manuscript.

Funding: This research received no external funding.

Data Availability Statement: Data sharing not applicable.

Acknowledgments: The authors are grateful to the General Directorate for Scientific Research and Technological Development (DGRSDT) and the University of Tlemcen for their financial support.

Conflicts of Interest: The authors declare no conflict of interest.

References

- Kumar, A.; Mishra, A.K. Biological importance of phenol derivatives as potent bioactive compound: A review. *Lett. Org. Chem.* **2018**, *15*, 251–264.
- Davidson, P.M.; Branden, A.L. Antimicrobial activity of non-halogenated phenolic compounds. *J. Food Prot.* **1981**, *44*, 623–633.
- Bruce, R.M.; Santodonato, J.; Neal, M.W. Summary review of the health effects associated with phenol. *Toxicol. Ind. Health* **1987**, *3*, 535–568.
- Bukowska, B.; Kowalska, S. The presence and toxicity of phenol derivatives-their effect on human erythrocytes. *Curr. Top. Biophys.* **2003**, *27*, 43–51.
- Busca, G.; Berardinelli, S.; Resini, C.; Arrighi, L. Technologies for the removal of phenol from fluid streams: A short review of recent developments. *J. Hazard. Mater.* **2008**, *160*, 265–288.

6. Pang, K.; Hou, Y.; Wu, W.; Guo, W.; Peng, W.; Marsh, K.N. Efficient separation of phenols from oils via forming deep eutectic solvents. *Green Chem.* **2012**, *14*, 2398–2401.
7. Hou, Y.; Ren, Y.; Peng, W.; Ren, S.; Wu, W. Separation of phenols from oil using imidazolium-based ionic liquids. *Ind. Eng. Chem. Res.* **2013**, *52*, 18071–18075.
8. Xu, X.; Li, A.; Zhang, T.; Zhang, L.; Xu, D.; Gao, J.; Wang, Y. Efficient extraction of phenol from low-temperature coal tar model oil via imidazolium-based ionic liquid and mechanism analysis. *J. Mol. Liq.* **2020**, *306*, 112911.
9. Xu, D.; Wang, S.; Zhang, T.; Peng, L.; Bing, X.; Zhang, L.; Wang, Y. Extraction and interaction insights for enhanced separation of phenolic compounds from model coal tar using a hydroxyl-functionalized ionic liquid. *Chem. Eng. Res. Des.* **2022**, *178*, 567–574.
10. Dupont, J.; Consorti, C.S.; Suarez, P.A.Z.; de Souza, R.F. Preparation of 1-Butyl-3-Methyl Imidazolium-Based Room Temperature Ionic Liquids. *Org. Synth.* **2002**, *79*, 236–241.
11. Dupont, J.; Consorti, C.; Suarez, P.; de Souza, R. Preparation of 1-Butyl-3-methyl imidazolium-based Room Temperature Ionic Liquids. *Org. Synth.* **2004**, *10*, 184.

Disclaimer/Publisher's Note: The statements, opinions and data contained in all publications are solely those of the individual author(s) and contributor(s) and not of MDPI and/or the editor(s). MDPI and/or the editor(s) disclaim responsibility for any injury to people or property resulting from any ideas, methods, instructions or products referred to in the content.