Journal of Advances and Scholarly Researches in Allied Education
Vol. 22, Issue No. 3, April-2025, ISSN 2230-7540

DOI: https://doi.org/10.29070/nv5yyk68

Efficiency comparision of synthesized versus commercially available carriers in polymer membranes for heavy metals ion (Cu^{2+}, Ni^{2+}, Zn^{2+}) removal

Aditi Kumawat [1] * , Dr. Sourabh Muktibodh [2]

1. Research Scholar, Mata Jijabai Govt. PG Girls College, Indore, Madhya Pradesh, India
aditikumawat132@gmail.com ,
2. Professor, Department of Chemistry, Mata Jijabai Govt. Girls. P. G. College (Affiliated to D. A. V. V. University) in Indore, Madhya Pradesh, India

Abstract: The contamination of ecosystems by heavy metals poses a substantial environmental and health hazard, primarily because Ions of metals such as copper (Cu^{2+}), nickel (Ni^{2+}), and zinc (Zn^{2+}) are very poisonous, do not break down naturally, and bioaccumulate in living things. In this study, Cu^{2+}, Ni^{2+}, and Zn^{2+} ions are removed from water using polymer inclusion membranes (PIMs). Three distinct carriers, Ia, Ib, and Ic, together with a commercially available carrier named Aliquat 336, are evaluated for their transport efficiency. The PIMs were made using polyvinyl chloride (PVC) as the main polymer., and 2-NPOE was used as the plasticizer at the same time. SEM, or scanning electron microscopy, was used to analyze the membranes, and the results showed that there were changes in the surface morphology. The results of the transport studies demonstrated that the metal ion flow increased as the concentration of the carrier grew. Aliquat 336 maintained a better efficiency than the synthetic carriers throughout the trials. Cu²⁺ ions had the greatest transit rate among the metal ions that were investigated, followed by zinc ions and nickel ions. It has been shown via the findings that Aliquat 336 has greater complexation and membrane compatibility, which makes it a more efficient carrier in order to isolate ions of heavy metals by use of membranes.

Keywords: Membrane, Scanning, Electron, Chloride, Vinyl

---------------------------X---------------------------

INTRODUCTION

In a base polymer, the liquid phase is housed inside the polymer network in a Polymer Inclusion Membrane, a specific form of liquid membrane. Base polymers (often PVC or cellulose triacetate), plasticizers or modifiers, cellulose triacetate, and an extractant or carrier make up most PIMs. Elasticity and flexibility are imparted by the plasticizer, while mechanical strength is provided by the basic polymer. The carrier's job is to bind to the target species and then transfer it across the membrane [1]. The advantages of Polymer Inclusion Membrane are its efficient separation process, low solvent consumption, rapid mass transfer, and good selectivity. Additionally, they have use in electrochemical sensing and other forms of sensing. Why? Because it's really selective. This means it has industrial applications, such as in the production of ion selective electrodes. Mancilla-Rico et al. performed an extensive study on polymer inclusion membranes (PIMs) that used cellulose triacetate (CTA) as a polymeric matrix, an extractant such as Ionquest® 801, and plasticizers such as 2-NPOE or TBEP. The research was carried out with the aim of characterizing the structural properties of PIMs. Several instrumental methods were used to evaluate the physical and chemical properties of the membranes. These included Differential Scanning Calorimetry (DSC), Electrochemical Impedance Spectroscopy (EIS), Reflection Infrared Mapping Microscopy (RIMM), and Fourier Transform Infrared Spectroscopy (FT-IR). Surface area, electrical resistance, dielectric constant, component distribution, structural composition, glass transition temperature (T_g), and overall stability were all illuminated by these methods. The goal was to have a better grasp of how the plasticizer affects the performance and features of the membrane [2]. Basic extraction reagents may be used to extract any metal from water that forms anions complexes. In the presence of water, metal ions may create a vast array of anionic complexes with ligands including sulphate, cyanate, thiocyanate, cyanide, chloride, and countless more. The principle of ion connection is the bedrock of the fundamental carrier extraction procedure. Organic compounds with long chains carry basic, secondary, and tertiary amino functions. This class also includes additional weakly basic compounds, as well as alkyl pyridine N-oxide derivatives such TDPNO stands for 4-(1'n-tridecyl) pyridine N-oxide. Despite nitrogen's lack of electron pairs, quaternary alkyl ammonium compounds such as Aliquat 336 serve as basic carriers. We arrange quaternary ammonium compounds and amines according to their degree of substitution. as belonging to the same category since they undergo the same extraction procedure [3].

EXPERIMENTAL

Carriers

Used for transport of metal ions (Aliquat 336, synthesized oxo-crown ethers (I_a, I_b, I_c).

Aliquat 336

- The molecular formula is $C_{25}H_{54}ClN$
- Molar mass: 404.16 g.mol^{-1}
- Visual Characteristics: Clear, thick liquid
- Density: 0.884 g/cm^3
- Melting Point: -20°C
- Boiling Point: 225^{o}C

Structure of principal ingredient matrix (PIM), carriers, and plasticizer preparation

Figures 1 and 2 illustrate the structure of the basic polymer, in addition to the carriers that are used in the process of generating the polymer inclusion membrane.

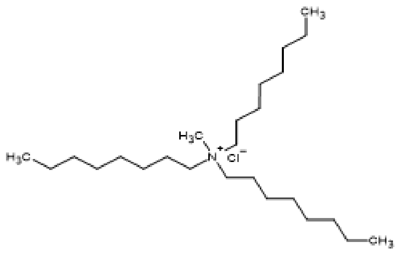

Figure 1: Aliquat 336

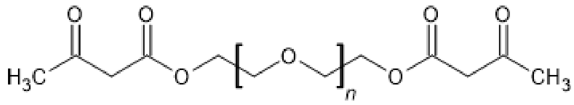

Figure 2: Oxo-crown, n = 1, 2, 3 for ligands I_a, I_b, I_c respectively

Process of ligand synthesis (I_a, I_b, And I_c)

First, 0.66 mole of diethylene glycol and 2 mol of ethyl acetoacetate were well mixed together isotope-capped flask. Subsequently, the concoction was allowed to simmer at a slow temperature of 1800^0C for four to six hours. The surplus ethyl acetoacetate was removed by distillation at a lower pressure in order to minimize any possible breakdown that may occur at 1800^0C. A dark residue that was greasy in appearance, known as I_a, was removed from the distillation flask [4]. This residue was the pure acetoacetic diester of diethylene glycol. Using an FT-IR Bruker Tensor 27 Spectrophotometer that was working in the transmission mode and spanning the spectral range from 4000-800 cm^{-1}, the IR spectroscopy was used to check the purity of these compounds for the purpose of determining their composition. The ligands do not provide any visible signal at 3500 cm^{-1}, which indicates that the esterification process has been completed. Sharpness of the signal is another indicator that may be used to determine the purity of the sample. A selection of the infrared's distinctive frequencies is listed below:

1. Ligand I_a: 1710 and 1725 cm^{-1} (C=O, diketone), 3500 cm^{-1} (-OH).
2. Ligand I_b: It extends to 3420 cm^{-1} (-OH), 1750 and 1720 cm^{-1} (diketone, C=O), and 1660 cm^{-1} (enol, C=O)
3. Ligand I_c: 3440 cm^{-1} (-OH), 1745 and 1720 cm^{-1} (diketone), 1655 cm^{-1} (enol, C=O)

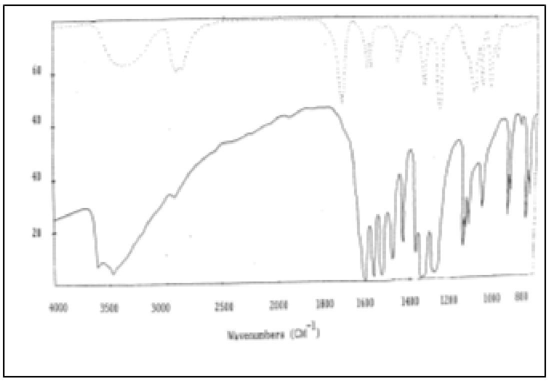

Figure 3: K (Pic) I_c

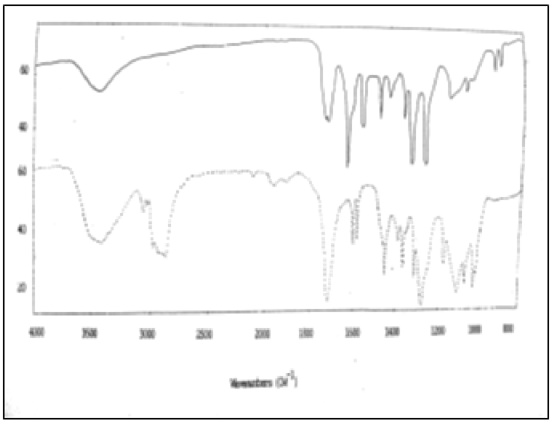

Figure 4: Na (Pic)I_b

The ligands I_b and I_c, which are acetoacetic diesters of tri and tetra ethylene glycols, respectively, were artificially produced by using a method that was very similar [5]. The ligands I_a, I_b, and I_c are represented by the numbers n = 1, 2, and 3, respectively, in this context. These numbers also serve to highlight the chemical reactions that occur throughout the process that was previously discussed.

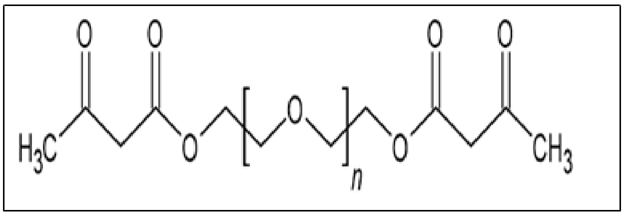

Figure 5: Oxo-crown, with n equal to 1, 2, and 3 for ligands I_a, I_b and I_c all in that order

RESULTS AND DISCUSSION

Modifications in the Concentration of Carrier

Polymer inclusion membranes primarily use amine-based chemicals with a high molecular weight, weak basic compounds, and ammonium salts as Aliquat 336 as carriers. These basic carriers create an ion pair with the anion during the feed phase, acting as an anion exchanger. Consequently, a positive charge on the carrier is required. The intended recipients include a wide range of species, from anions and heavy metals to organic molecules. One common carrier in the manufacturing of polymer inclusion membranes is Aliquat 336. Reason being the fact that it is both convenient and adaptable.

The kind of carrier present in the membrane, as well as the concentration of that carrier, is one of the most important factors that determines the manner in which metal ions are carried by membranes. There has been research that have been carried out to establish that metal ions are unable to be transported under conditions when carriers are not used. One of them is the membrane, which comes initially. In 2008, research on carrier and metal transport was carried out with the use of CTA base polymer and NPOE plasticizer. Aliquat 336 was not used in this study. According to the findings of this investigation, the membrane that included Aliquat 336 delivered the greatest results. In their study, Radzyminska-Lenarcik and colleagues [6] evaluated transfer of ions including zinc, cobalt, alongside nickel utilizing a 1 M 1-heptylimidazole carrier as well as without a carrier. They discovered that the carrier performance was superior to the other methods. As is well knowledge, the manner in which metal ions are transported is significantly influenced by the kind of carrier as well as the concentration of the carrier.

This assertion is backed up by the research carried out by Kolev and colleagues. The membranes that were created with in their study, [7] examined the effects of varying doses of D_2EHPA carrier and found that metal transport increased with increasing concentrations. This is exactly what our study indicates.

Table 1: The influence of as a function of carrier concentration and J_m value of the Cu^{2+} cation

Carrier Conc. (10^{-4} M)	Metal transported in moles after				$J_m \times 10^7$ mol/hours
	12 hours	24 hours	36 hours	48 hours	
0.5	1.7×10^{-5}	2.1×10^{-5}	2.7×10^{-5}	3.4×10^{-5}	9.325
1.0	2.2×10^{-5}	2.8×10^{-5}	3.7×10^{-5}	4.6×10^{-5}	12.4
1.5	2.9×10^{-5}	3.9×10^{-5}	4.8×10^{-5}	5.3×10^{-5}	16.15
2.0	3.4×10^{-5}	4.5×10^{-5}	5.2×10^{-5}	5.9×10^{-5}	18.625

Table 2: The influence of as a function of carrier concentration and J_m value of the Zn^{2+} cation

Carrier Conc. (10^{-4} M)	Metal transported in moles after				$J_m \times 10^7$ mol/hours
	12 hours	24 hours	36 hours	48 hours	
0.5	0.02×10^{-6}	0.09×10^{-6}	0.3×10^{-6}	0.8×10^{-6}	0.07
1.0	0.09×10^{-6}	0.4×10^{-6}	0.7×10^{-6}	1.2×10^{-6}	0.168
1.5	0.2×10^{-6}	0.9×10^{-6}	1.2×10^{-6}	1.9×10^{-6}	0.312
2.0	0.8×10^{-6}	1.2×10^{-6}	1.6×10^{-6}	2.1×10^{-6}	0.507

Table 3: The effect of carrier concentration on the J_m value of the Ni^{2+} cation

Carrier Conc. (10^{-4} M)	Metal transported in moles after				$J_m \times 10^7$ mol/hours
	12 hours	24 hours	36 hours	48 hours	
0.5	0.2×10^{-7}	0.7×10^{-7}	1.4×10^{-7}	1.7×10^{-7}	0.029
1.0	0.8×10^{-7}	1.2×10^{-7}	1.8×10^{-7}	2.1×10^{-7}	0.052
1.5	1.2×10^{-7}	1.9×10^{-7}	2.2×10^{-7}	2.6×10^{-7}	0.073
2.0	1.5×10^{-7}	2.2×10^{-7}	2.8×10^{-7}	3.2×10^{-7}	0.089

Table 4: The movement of the cation by means of the membrane

Cation	$J_m \times 10^7$ mol/hour Carrier Conc. (10^{-4} M)			
	0.5	1.0	1.5	2.0
Cu^{2+}	9.325	12.4	16.15	18.625
Zn^{2+}	0.07	0.168	0.312	0.507
Ni^{2+}	0.029	0.052	0.073	0.089

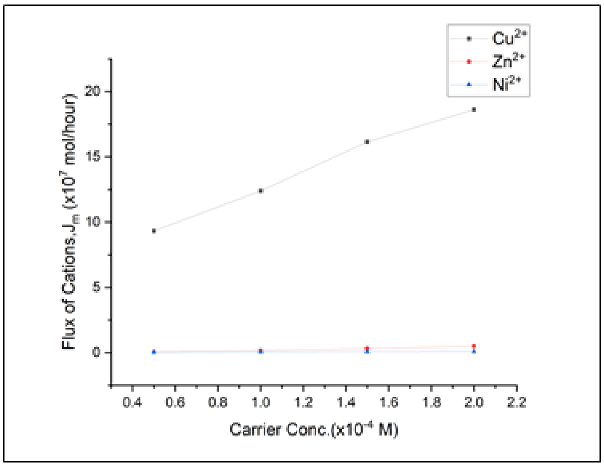

Figure 6: Diagram illustrating the Flux of Cations (Cu^{2+}, Zn^{2+}, Ni^{2+}) v/s Carrier Conc.

Additionally, membranes constructed with Aliquat 336 at different concentrations were used in order to study the transportation of metals. According to what we learned from this study, the rate of metal transport increased in proportion to the concentration of the Aliquat 336. [8] There was a correlation between the concentration of Aliquat 336 and an increase in carrying performance and fluxes, which was discovered.

Comparative Analysis of the Effectiveness of Synthesized Carriers and Commercial Carriers (Aliquat 336) in the Field of Metal Ion Distribution

Table 5: Using Aliquat 336 at a number of different concentrations to create Flux of Metal Ions

Carrier Concentration ($\times10^{-4}$ M)	Cu^{2+} Flux ($J_m \times 10^7$ mol/h)	Zn^{2+} Flux ($J_m \times 10^7$ mol/h)	Ni^{2+} Flux ($J_m \times 10^7$ mol/h)
0.5	9.325	0.070	0.029
1.0	12.400	0.168	0.052
1.5	16.150	0.312	0.073
2.0	18.625	0.507	0.089

The effectiveness of transporting copper, zinc, and nickel across polymer inclusion membranes was investigated using both synthetic carriers (I_a, I_b, and I_c) and the commercial carrier Aliquat 336 [9]. The components were transported via inclusion membranes made of polymer. The results show clearly that Aliquat 336 is far more efficient in transporting metal ions in comparison to the carriers that were created to carry them. At a carrier concentration of 2.0×10^{-4} M, Aliquat 336 attained the maximum flow for Cu^{2+}, which was 18.625×10^{-7} mol/h. This was followed by Zn^{2+}, which demonstrated a flux of 0.507×10^{-7} mol/h, and Ni^{2+}, which demonstrated a flux of 0.089×10^{-7} mol/h. Aliquat 336 has a strong complexation and transport capabilities, as shown by the fact that the flux values rose in a consistent manner with increasing carrier concentrations. Synthesized carriers, on the other hand, exhibited somewhat lower flux rates, which indicated that their transport performance was restricted. These findings were further corroborated by scanning electron microscopy (SEM) research, which revealed that Aliquat 336 enabled a more uniform and smooth membrane architecture, which in turn promoted improved ion flow across the membrane [10]. Therefore, Aliquat 336 was shown to be a carrier that is more efficient and selective for the purpose of removing heavy metal ions using PIMs.

Studies of Selectivity Using Model Samples

The chemical composition of the carrier, which may contain acetoacetic diesters, the structural characteristics of the membrane matrix, and the concentration of heavy metal ions like Cu^{2+}, Ni^{2+}, and Zn^{2+} have a significant impact on the performance of polymer inclusion membranes (PIMs) for these ions. coordination behavior of the target metal ions. While acetoacetic diesters of diethylene and triethylene glycols have proven effective for the extraction and transport of alkali and alkaline earth metals—such as sodium, potassium, magnesium, and calcium—due to their favorable ionic radii and coordination preferences, they are less suitable for transition metals like copper, nickel, and zinc. This limitation arises from the distinct coordination requirements and complexation behavior of heavy metals, which are not adequately met by the donor atoms and molecular geometry offered by these particular diesters.

1. **The chemistry of coordination and the size of ions**

The ethylene glycol acetoacetic diesters, when mixed with alkali, have the ability to induce the formation of highly effective coordination complexes, such as potassium and sodium ions, as well as alkaline earth metals, such as calcium and magnesium ions. On the other hand, these ions are larger and less polarizable in comparison to heavy metals. A stable complexation may be achieved by the interaction of the ions with the oxygen atoms of the diester, which are responsible for donating electrons. The ionic radii of the transition metals Cu^{2+}, Ni^{2+}, and Zn^{2+} are lower than those of the alkali and alkaline earth metals, and their charge density is larger. Because of these characteristics, stronger and more specific ligands are required. For example, molecules that include nitrogen or sulfur, as well as ligands with donor atoms that are highly polarizable, are examples of such ligands. There is a possibility that acetoacetic diesters, which include oxygen-donating groups, may not possess sufficient power or specificity for these heavy metal ions. [11]

2. **Descriptions of the properties of binding sites**

The carbonyl (C=O) and ether (-O-) groups that are most often found in acetoacetic diesters may form complexes with alkali and alkaline earth metals, which are softer and less polarizable. However, because of their increased polarizability and greater covalent interaction potential, ligands with softer donor atoms, such as phosphorus (P), nitrogen (N), or sulfur (S), are often preferred by heavy metal ions like Cu^{2+}, Zn^{2+}, and Ni^{2+}. This makes them better suited for complexation with these metals. [12]

3. **Lipophilicity and the process of solvent**

Given that heavy metal ions like to form hydrated complexes in aqueous media, it may be challenging to dissolve them in the acetoacetic diester carrier that is included inside the PIM. This is one of the reasons why the extraction and transportation of heavy metal ions is restricted. Because sodium, potassium, magnesium, and calcium ions are able to efficiently interact with the acetoacetic diester and have hydration spheres that are less visible, they are able to transport substances more effectively. [13]

4. **Effects of Steric**

With regard to the flexibility of their ethylene glycol chains, acetoacetic diesters are capable of producing coordination cavities that are larger in size. These cavities are either too large or not suitable for the lower ionic radii of heavy metals such as Cu^{2+}, Zn^{2+}, and Ni^{2+}, which results in the formation of complexes that are either very weak or extremely unstable. Alkali and alkaline earth metals are more suited to the coordination cavity that acetoacetic esters offer. This is due to the fact that they are larger and less polarizing with respect to acetoacetic esters. [14]

CONCLUSION

It is concluded that during the course of the comparative investigation of created and commercially available carriers in PIMs, it became abundantly evident that Aliquat 336 outperformed the ligands I_a, I_b, and I_c that were synthesized in terms of the efficiency with which they transported metal ions. Aliquat 336 obtained the greatest transfer rates, notably for Cu^{2+}, despite the fact that the flux values for Cu^{2+}, Zn^{2+}, and Ni^{2+} all rose as the carrier concentration increased. The results were validated by scanning electron microscopy (SEM) research, which demonstrated that Aliquat 336 enhanced ion mobility by exhibiting a smoother and more uniform membrane architecture. During the course of the research, the researchers came to the conclusion that Aliquat 336 is a very effective and selective carrier in order to purge wastewater of heavy metal ions and other environmental applications. Although the synthesized carriers were functional, they displayed decreased performance, which highlights the efficiency and dependability

Various pharmaceutical transporters like Aliquat 336 in membrane-based separation techniques.

References

1. Almeida, M. I. G. S.; Cattrall, R. W.; Kolev, S. D. Recent Trends in Extraction and Transport of Metal Ions Using Polymer Inclusion Membranes (PIMs). J. Membr. Sci. 2012, 415–416, 9–23. https://doi.org/10.1016/j.memsci.2012.06.006.

2. Nghiem, L.; Mornane, P.; Potter, I.; Perera, J.; Cattrall, R.; Kolev, S. Extraction and Transport of Metal Ions and Small Organic Compounds Using Polymer Inclusion Membranes (PIMs). J. Membr. Sci. 2006, 281 (1–2), 7–41. https://doi.org/10.1016/j.memsci.2006.03.035.

3. Kaczorowska, M. A. The Use of Polymer Inclusion Membranes for the Removal of Metal Ions from Aqueous Solutions—The Latest Achievements and Potential Industrial Applications: A Review. Membranes 2022, 12 (11), 1135. https://doi.org/10.3390/membranes12111135.

4. Muktibodh, S. Systematic Transport Investigation on Alkali and Alkaline Earth Metal Ions Using Selected Linear Oxo-Crown Ethers across Organic Liquid Membrane. Int. J. Sci.& Res. 2015, 4 (10), 1001–1006.

5. Hanada, T.; Firmansyah, M. L.; Yoshida, W.; Kubota, F.; Kolev, S. D.; Goto, M. Transport of Rhodium (III) from Chloride Media across a Polymer Inclusion Membrane Containing an Ionic Liquid Metal Ion Carrier. ACS Omega 2020, 5 (22), 12989–12995. https://doi.org/10.1021/acsomega.0c00867.

6. Radzyminska-Lenarcik, E.; Maslowska, K.; Urbaniak, W. Removal of Copper (II), Zinc (II), Cobalt (II), and Nickel (II) Ions by PIMs Doped 2-Alkylimidazoles. Membranes 2021, 12 (1), 16. https://doi.org/10.3390/membranes12010016.

7. Kolev, S. D.; Baba, Y.; Cattrall, R. W.; Tasaki, T.; Pereira, N.; Perera, J. M.; Stevens, G. W. Solid Phase Extraction of Zinc(II) Using a PVC-Based Polymer Inclusion Membrane with Di(2-Ethylhexyl)Phosphoric Acid (D2EHPA) as the Carrier. Talanta 2009, 78 (3), 795–799. https://doi.org/10.1016/j.talanta.2008.12.047

8. Kebiche-Senhadji, O.; Tingry, S.; Seta, P.; Benamor, M. Selective Extraction of Cr(VI) over Metallic Species by Polymer Inclusion Membrane (PIM) Using Anion (Aliquat 336) as Carrier. Desalination 2010, 258 (1–3), 59–65. https://doi.org/10.1016/j.desal.2010.03.047

9. Lenarcik, B.; Barszcz, B. Stability and Structure of Transition-Metal Complexes of Azoles in Aqueous Solutions. Part 21. A Comparison of the Complex-Forming Capacity of 1,2-Dimethylimidazole with That of Other 1,3-Diazoles. J. Chem. Soc., Dalton Trans. 1980, No. 1, 24. https://doi.org/10.1039/dt9800000024.

10. Gaazo, J. Plasticity of the Coordination Sphere of Copper(II) Complexes, Its Manifestation and Causes. Coord. Chem. Rev. 1976, 19 (3), 253–297. https://doi.org/10.1016/S0010-8545(00)80317-3

11. Radzyminska-Lenarcik, E.; Maslowska, K.; Urbaniak, W. Removal of Copper (II), Zinc (II), Cobalt (II),

and Nickel (II) Ions by PIMs Doped 2-Alkylimidazoles. Membranes 2021, 12 (1), 16. https://doi.org/10.3390/membranes12010016.

12. Pyszka, I.; Radzyminska-Lenarcik, E. New Polymer Inclusion Membrane in the Separation of Nonferrous Metal Ion from Aqueous Solutions. Membranes 2020, 10 (12), 385. https://doi.org/10.3390/membranes10120385.

13. Zante, G.; Boltoeva, M.; Masmoudi, A.; Barillon, R.; Trébouet, D. Supported Ionic Liquid and Polymer Inclusion Membranes for Metal Separation. Sep. Purif. Rev. 2022, 51 (1), 100–116. https://doi.org/10.1080/15422119.2020.1846564.

14. Radzyminska-Lenarcik, E.; Ulewicz, M. Polymer Inclusion Membranes (PIMs) Doped with Alkylimidazole and Their Application in the Separation of Non-Ferrous Metal Ions. Polymers 2019, 11 (11), 1780. https://doi.org/10.3390/polym11111780.