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Impact of Metal Source phase concentration and thickness on transportation of heavy metals (Cu^{2+}, Ni^{2+}, Zn^{2+}) through polymer inclusion membrane using Aliquat 336

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Abstract: The purpose of this research is to explore the transport behavior of via polymer inclusion membranes (PIMs) containing Aliquat 336 as a carrier for heavy metal ions (Cu^{2+}, Ni^{2+}, Zn^{2+}). Polyvinyl chloride (PVC) serves as the primary polymer in this investigation, with 2-NPOE serving as the plasticizer. Membranes were made with various polymer weights added to them to see how the thickness of the membrane impacts the flow of metal ions. Furthermore, the effect of the source phase metal ion concentration on transport efficiency was also studied. Using scanning electron microscopy (SEM), the membrane's morphology was examined. Membrane homogeneity, minimal surface roughness, and partial polymer melting were all verified by this method. The results showed that higher-thickness membranes significantly reduced transport rates, while thinner-thick membranes enabled a higher ion flux. Additionally, it was common for the transport rates of all three metal ions to rise when the concentration of metal ions in the source phase increased. Ni^{2+} and Zn^{2+} had the next-highest flow levels, behind Cu^{2+}. The findings show that PIMs with Aliquat 336 are suitable for the efficient and selective transport of, and also provide practical insight into how to change membrane characteristics for better separation performance. heavy metals.

Keywords: Microscopy, Membrane, Aliquat, Polymer, Metal

INTRODUCTION

The formation of a PIM that contains polymers does not need the incorporation of a plasticizer in order to achieve the achievement of the physical trapping of a carrier inside a polymer network. One of their particular advantages is that it is simple to synthesize them, they are excellent in immobilizing carriers, they are versatile, and they have high mechanical qualities. They are regarded as an excellent alternative to supported liquid membranes (SLMs), which are characterized by the process of impregnating a polymeric film with a liquid phase that includes both the solvent and the carrier [1]. The physical features of PIMs make them suited for a broad variety of applications that go beyond the standard processes for extracting metal ions and tiny organic molecules. This is despite the fact that both kinds of membranes have some commonalities. The creation of optodes and catalyzers, the conversion of energy and passive sampling, the detection of speciation, the pretreatment of samples, and the manufacture of metal nanoparticles are some examples of these. However, this particular list is not exhaustive. PIMs, on the other hand, continue to have a great deal of concerns that have not been solved and need more study. This is evident from the extensive variety of subjects that were discussed in the most recent "Polymer Inclusion Membranes" special issue in

Membranes.

Scientists and the concerned public are increasingly apprehensive about metal pollution in industrial effluents and outflow streams. Moreover, they possess the capacity to amass and adversely affect living organisms, in addition to impacting water quality [2]. Metals manifest in several forms. The nodules located on the ocean bottom exhibit an extraordinarily high concentration of copper, nickel, and cobalt. Despite nickel's reputation as a relatively innocuous metal, prolonged exposure may result in significant health repercussions, including physiological disorders, allergic reactions, and maybe cancer. In summary, these metals are essential for life, however they may induce toxicity at certain quantities. Therefore, it is essential to reclaim and process these metals. Moving metal ions from water-based solutions requires enhancement via more efficient and selective methodologies. Membrane procedures are economical and adaptable, since they may concurrently perform extraction and stripping processes. The study demonstrates Composite cation-exchangers or hybrid cation-exchanging nanofibers for the concentration of heavy metal transport were produced [3].

EXPERIMENTAL

Materials and substances

As a basic polymer, polyvinyl chloride (PVC), metal picrates, synthetic ligands (as a carrier), Aliquat 336 (a carrier that is commercially available), 2-NPOE (as a plasticizer), and diethylene glycol and ethyl acetoacetate were used for the production of ligands, while chloroform and tetrahydrofuran were utilized as solvents [4]. All of these compounds were of an analytical quality, and they were purchased from Sigma-Aldrich in the region of the United States.

Individually, stock solutions (in M) of nickel, copper, and zinc were generated by making use of AR grade salts of $NiSO_4.6H_2O$, $CuSO_4.6H_2O$, and $ZnSO_4.H_2O$.

It was determined that distilled water was used to produce metal solutions. After being washed with distilled water, the glassware that is used to make stock solutions is then dried in an oven that is heated to 105^0C in order to remove any moisture that may still be present.

Preparation of membranes

To create a homogeneous solution, the necessary quantities of poly vinyl chloride, carrier, and plasticizer will be dissolved in tetrahydrofuran solvent while being constantly agitated by magnets. This process will continue until the target solution is reached. After that, the solution will be placed the contents of a glass funnel-lined petri dish that has a diameter of 9.0 cm [5,6]. Doing so will ensure that the solvent evaporates slowly, protecting against dust contamination in the future. The organic solvent may now be allowed to evaporate. at room temperature for a period of twenty-four hours. Following this, the membrane that was created will be peeled onto the glass plate. In appearance, the PIM has the appearance of thin layers that are uniform and translucent.

Figure 1. Stirring the Polymer Inclusion Membrane mixture

Figure 2. Prepared PIM

Evaluation of Scanning Electron Microscope

The morphology of the membrane was investigated via the use of scanning electron microscopy, and pictures were obtained through the use of a VEGA II SBH electron microscope that was manufactured by TESCAN. There is no heterogeneity in the shape of the membrane [7]. Using the look of the cell membrane under scanning electron microscopy (SEM), surface as well as the cross section of the membrane was investigated. The presence of lumps in the PIM surface cross section of PVC, as seen in the picture, is indicative of partial polymer melting inside the material. Crystallization of carriers may occur in the membrane on occasion throughout the course of the procedure. Certain photographs have a greater degree of roughness on the film that is caused by the carrier process.

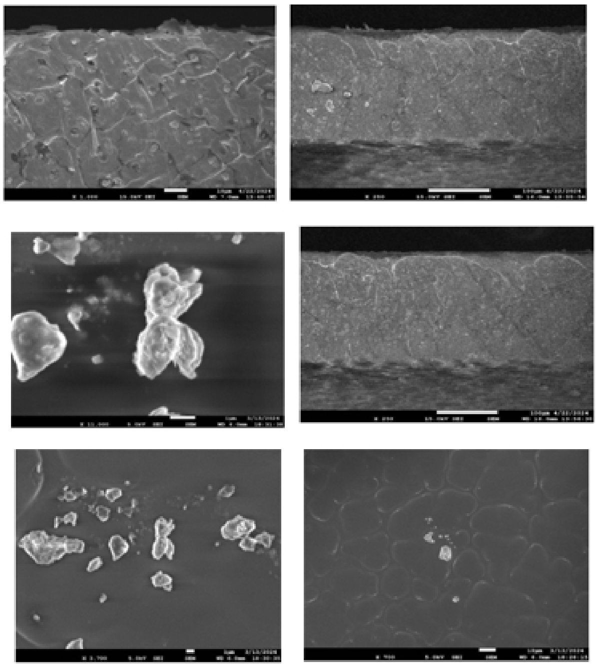

Figure 3. Polymer (PVC), plasticizer (2-NPOE), and a carrier that is commercially available (Aliquat 336) are the components that make up the PIM in the SEM pictures.

RESULTS AND DISCUSSION

Mechanism of Transportation

The capacity of Aliquat 336 to extract metallic species is based on a sort of ion-exchange process that involves the production of an ion-pair that, owing to its size or charge, ought to be able to navigate through the membrane [8]. This mechanism is the foundation for Aliquat 336's ability to extract metallic species. An anionic version of the metallic species is the one that should be used in this scenario. Furthermore, it has been shown that copper (II) quickly forms complexes with chloride, resulting in the formation of chloro-metal complexes that are negatively charged and can be extracted using the Aliquat 336 via the anion-exchange mechanism.

- **A reaction of complexation occurring on the feed side: -**

When copper ions in water react with the carrier (Aliquat 336) on the feed side, a complex known as Cu (II)-Aliquat 336 is produced-

$$Cu^{2+}_{aq} + 2(R_3N^+Cl^-_{org}) \leftrightarrow [CuCl_4]^{2-}_{org} + 2R_3N^+_{org}$$

- **The process of the compound becoming diffused via the membrane: -**

The formation of the $[CuCl_4]^{2-}$ combination occurs during the feeding phase, and it permeates the cell membrane. This study emphasizes a concentration gradient-driven mechanism rather than a chemical reaction.

- **The release of copper ions (II) at the receiving side: -**

Cu (II) ions are subsequently liberated from the $[CuCl_4]^{2-}$ complex under varying circumstances, such as pH or the presence of a stripping agent that may compete with Aliquat 336 for Cu (II) binding [9]. The reaction may proceed as follows in acidic circumstances:

$$[CuCl_4]^{2-}{}_{org} + 2H^{+}{}_{aq} \leftrightarrow Cu^{2+}{}_{aq} + 4Cl^{-}{}_{aq} + 2R_3N^{+}Cl^{-}{}_{org}$$

- **Aliquat 336 was able to be revived inside the membrane: -**

Upon The process is advanced because to the reabsorption of Aliquat 336 in the membrane, which allows for the attraction of more Cu (II) ions from the feed side and the release of Cu (II) ions. A metal-carrier complex was formed at the feed-membrane interface as a result of a reversible interaction between Cu (II) ions and the carrier agent Aliquat 336, which was the overall transport mechanism. Subsequently, this compound spread across the membrane phase. The Cu (II) ions were transferred from the feed solution to the receiving phase in a selective and directed manner when they reached the membrane-receiving interface and were released into the receiving solution by decomplexation. [10].

The Impact of the Thickness of the Membrane on Transport

The movement of metal ions over PIM of varying thicknesses was investigated and carried out. The thickness of the membrane was varied by adjusting the weight of the polymer that was put to the petri dish (400 mg, 450 mg, 500 mg, and 550 mg, 600 mg, and 650 mg, respectively). This was done in order to get the desired results. A representation of the cations flow as a function of membrane thickness may as seen in Table 1.

Table 1. The impact of cell membrane thickness on cation J_m values

Weight of Polymer (PVC) in mg	Cu (II) flux (in M)	Zn (II) flux (in M)	Ni (II) flux (in M)
400	5.9×10^{-5}	2.1×10^{-6}	3.2×10^{-7}
450	5.1×10^{-5}	1.9×10^{-6}	2.8×10^{-7}
500	4.5×10^{-5}	1.6×10^{-6}	2.2×10^{-7}
550	3.6×10^{-5}	0.8×10^{-6}	1.8×10^{-7}
600	2.8×10^{-5}	0.2×10^{-6}	1.2×10^{-7}
650	1.5×10^{-5}	0.09×10^{-6}	0.8×10^{-7}

From the data shown in this table, it is evident that the cations flow reduces as the membrane thickness increases. At a weight of 300 mg of polymer, there was absolutely no formation of a membrane [11,12]. When the polymer weight reached 350 mg, it was difficult to eliminate the membranes from the petri dish since they were incredibly thin and sensitive. This made the process difficult. These membranes were subjected to further transport tests, which resulted in the rupture of the membrane being seen [13].

When the polymer weight surpasses 650 mg, the transport mechanism across the membrane either decelerates or ceases entirely due to the increased membrane thickness.

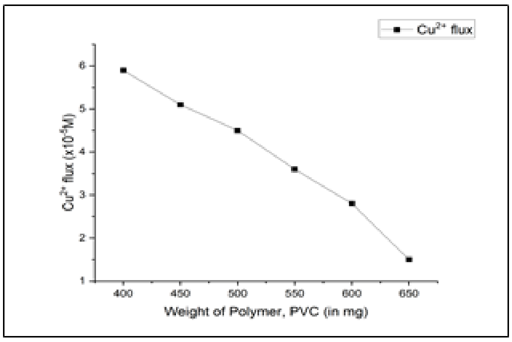

Figure 4. Relationship between Cu^{2+} flow plot and polymer weight

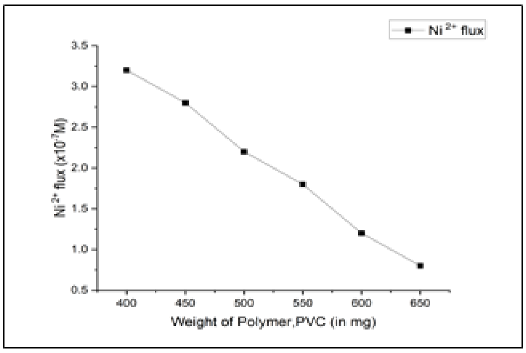

Figure 5. Relationship between flux of Ni^{2+} plot and polymer weight

Polymer inclusion membranes (PIMs) of various thicknesses were used to study how membrane dimension affects metal ion transport. During casting, polymer mass in Petri dishes was adjusted to manage membrane thickness. Membranes of various thicknesses were made using 400 mg to 550 mg of polymer for comparative experimental study.

Alteration in the Concentration of the Metal Source Phase

Taking into consideration this shift, a change in the concentrations of metal salts has also been observed [14,15]. This is done in order to evaluate the efficiency of the conveyance. It is typically the case that the J_m value rises as the concentration of metal salt rises, despite the fact that there is no discernable pattern. In addition, the transport profile does not change in the opposite direction for carriers that include any cation.

Table 2. How the J_m value of the metal source phase changes as its concentration changes Cu^{2+} cation

Metal Salt Conc. in source phase (10^{-4} M)	**Metal transported in moles after**				**J_m x 10^7 mol/hours**
	12 hours	**24 hours**	**36 hours**	**48 hours**	
1.5	1.9 x 10^{-5}	2.4 x 10^{-5}	2.9 x 10^{-5}	3.7 x 10^{-5}	10.375
2.0	2.1 x 10^{-5}	2.8 x 10^{-5}	3.5 x 10^{-5}	4.2 x 10^{-5}	11.875
2.5	2.7 x 10^{-5}	3.1 x 10^{-5}	4.1 x 10^{-5}	4.8 x 10^{-5}	14.175
3.0	3.4 x 10^{-5}	4.5 x 10^{-5}	5.2 x 10^{-5}	5.9 x 10^{-5}	18.625

Table 3. How the J_m value of the metal source phase changes as its concentration changes Zn^{2+} cation

Metal Salt Conc. in source phase (10^{-4} M)	**Metal transported in moles after**				**J_m x 10^7 mol/hours**
	12 hours	**24 hours**	**36 hours**	**48 hours**	
1.5	0.05 x 10^{-6}	0.08 x 10^{-6}	0.5 x 10^{-6}	0.9 x 10^{-6}	0.095
2.0	0.07 x 10^{-6}	0.3 x 10^{-6}	0.9 x 10^{-6}	1.5 x 10^{-6}	0.183
2.5	0.5 x 10^{-6}	0.8 x 10^{-6}	1.2 x 10^{-6}	1.8 x 10^{-6}	0.361
3.0	0.8 x 10^{-6}	1.2 x 10^{-6}	1.6 x 10^{-6}	2.1 x 10^{-6}	0.507

Table 4. How the J_m value of the metal source phase changes as its concentration changes Ni^{2+} cation

Metal Salt Conc. in source phase (10^{-4} M)	Metal transported in moles after				J_m x 10^7 mol/hours
	12 hours	24 hours	36 hours	48 hours	
1.5	0.4 x 10^{-7}	0.6 x 10^{-7}	0.9 x 10^{-7}	1.5 x 10^{-7}	0.0285
2.0	0.9 x 10^{-7}	1.5 x 10^{-7}	1.8 x 10^{-7}	2.1 x 10^{-7}	0.0575
2.5	1.2 x 10^{-7}	1.7 x 10^{-7}	2.4 x 10^{-7}	2.8 x 10^{-7}	0.0735
3.0	1.5 x 10^{-7}	2.2 x 10^{-7}	2.8 x 10^{-7}	3.2 x 10^{-7}	0.089

Table 5. The movement of the cation by means of the membrane

Cation	J_m x 10^7 mol/hour Metal Source Phase Conc. (10^{-4} M)			
	1.5	2.0	2.5	3.0
Cu^{2+}	10.375	11.875	14.175	18.625
Zn^{2+}	0.095	0.183	0.361	0.507
Ni^{2+}	0.0285	0.0575	0.0735	0.089

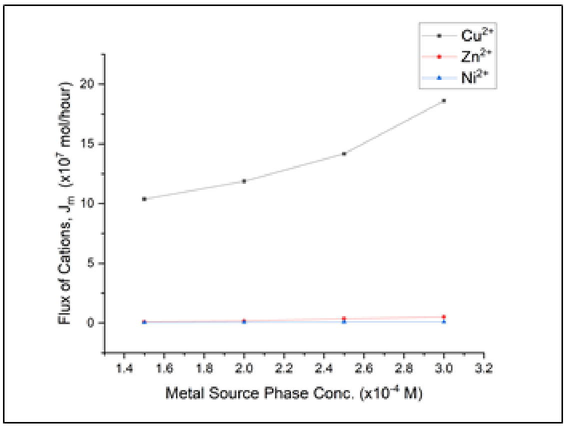

Figure 6. Flux of Cations (Cu^{2+}, Zn^{2+}, Ni^{2+}) shown as a Plot against the Concentration of Metal Salts

CONCLUSION

Across the use of Aliquat 336, this research highlights the significant impact that the thickness the effectiveness of heavy metal transport across polymer inclusion membranes (PIMs) depends on the membrane's properties and the concentration of metal ions in the source phase. That was a while ago shown via experiments that the ion flow is inversely related to the thickness of the membrane. Thinner membranes allow for quicker transport since they have a shorter diffusion route length and a lower resistance profile. On the other hand, thicker membranes restrict the flow of ions, which results in dramatically reduced flux rates. Transport almost completely stops at the maximum thickness that was examined by the researchers. In the process of regulating transport behavior, how many metal ions are present in the real source phase is an extremely important contributing factor. When concentrations are increased, the driving force for diffusion is increased, which ultimately results in an improvement in the efficiency of transport across the membrane. Cu^{2+} consistently demonstrated the greatest flow among the ions that were examined, which is indicative of a significant affinity for Aliquat 336 and a more advantageous complexation–decomplexation pathway. Zn^{2+} and Ni^{2+} then came next with much slower transport rates, which showed that they had weaker interactions with the cargo and membrane matrix. Based on the combined findings, it seems that adjusting membrane design is vital for enhancing the functionality of PIMs, which in metal ion separation processes. This is especially true when it comes to managing the thickness of the membrane and the level of concentration of the source phase. The use of Aliquat 336 as a carrier shows a high level of selectivity, particularly for Cu^{2+}, which validates the possibility for targeted heavy metal retrieval for use in the field of treatment of wastewater and recycling of resources. It is recommended that future research investigate the long-term stability of membranes, alternate carriers, and the circumstances of wastewater in the actual world in order to broaden the scope of this technology's usefulness.

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