

COMPARISON BETWEEN LIQUID MEMBRANE AND POLYMER INCLUSION MEMBRANE FOR THE EFFECTIVE TRANSPORT OF SODIUM AND MAGNESIUM IONS

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Abstract

The escalating demand for environmentally sustainable and cost-efficient methodologies for the removal of toxic metal ions from contaminated aquatic environments and the retrieval of valuable noble metal ions from various waste matrices, often relegated to the status of secondary sources, has precipitated a surge in the exploration of techniques rooted in polymer inclusion membranes (PIMs). PIMs, characterized by their multifaceted advantages encompassing the simultaneous extraction and back-extraction capabilities, exceptional stability, and high reusability, can be tailored to specific target analytes by judicious selection of carriers, polymers, and plasticizers in their formulation. Nonetheless, the efficacy and selectivity of the membrane process hinge on a plethora of factors, including membrane composition, the chemical attributes of the metal ions subject to removal, and the compositional makeup of the aqueous feed solution. Consequently, concerted research endeavors are consistently directed towards the systematic development of novel PIMs with the aim of augmenting these critical parameters. The current investigation is focused on the comparative analysis of liquid membranes and polymer inclusion membranes in the context of their efficacy for the facilitated transport of sodium and magnesium ions.

Keywords: PIMs, liquid membrane, heavy metal ions, waste water treatment.

Introduction

The escalating generation of industrial wastewater, sludges, and hazardous waste materials, particularly from industries such as electroplating, the oil and gas sector, steel manufacturing, and the chemical industry [1,2,3], presents a formidable environmental challenge. These byproducts frequently contain toxic heavy metals, and their improper disposal poses significant risks to various ecological components, including aquatic ecosystems, agricultural produce, and human health [4,5]. To address this pressing environmental concern, a group of separation methods, known for their eco-friendliness and energy efficiency, has gained prominence: membrane techniques [6,7]. The evolution of membrane technology over recent decades has resulted in the development of materials that offer not only high efficiency but also selectivity, a critical attribute for industrial applications [8]. A membrane, typically a thin layer, has been defined as a permeable or semi-permeable phase, which can be solid, liquid, or a solvent-swollen gel, serving as a barrier between two adjacent phases, usually gas or liquid. This membrane controls the exchange of substances between these phases [9,10]. Membrane processes can be categorized in various ways, including by the types of membranes used (natural or synthetic, organic or inorganic, isotropic or anisotropic, etc.) and the exerted driving force (equilibrium- or non-equilibrium-based membrane processes, pressure-driven and non-pressure-driven processes, etc.) [9,10]. Liquid membranes, particularly polymer inclusion membranes (PIMs), have garnered increasing attention due to their unique properties. PIMs incorporate a liquid phase within the polymeric network of a base polymer [11]. These functionalized membranes offer numerous advantages, including the ability to conduct

simultaneous extraction and back extraction, excellent stability, high reusability, simplicity, relatively low costs in membrane processes, and minimal organic solvent consumption (especially compared to classical extraction methods) [12,13]. Their versatility makes them suitable for a variety of applications in analytical chemistry, with particular efficacy as an extraction medium for the removal of diverse substances, such as pharmaceuticals, organic contaminants, and various anions and cations from aqueous solutions [11,12,13,14,15].

In the context of this study, we aim to contribute to the understanding of sustainable and efficient methods for heavy metal removal by conducting a comparative analysis of liquid membranes and PIMs in their selective transport of sodium and magnesium ions. This research strives to advance the current knowledge base and potentially provide innovative solutions to the critical issue of industrial wastewater management and the reduction of hazardous metal emissions into the environment.

Experimental

Chemical and reagents

Aliquat 336 was procured from Sigma-Aldrich (USA), while the polymers CTA and PVC were acquired from Fluka (Bern, Switzerland). Chloroform (for CTA) and tetrahydrofuran, THF (for PVC), both sourced from Panreac (Barcelona, Spain), were employed in the study; all chemicals were of analytical reagent grade and utilized in their as-received state.

Membrane preparation

The preparation procedure for Polymer Inclusion Membranes (PIMs) utilizing cellulose triacetate (CTA) or polyvinyl chloride (PVC) as foundational polymers (refer to Figure 1a,1b for the chemical structures of these polymers) has been previously elucidated [17,18]. In summary, 200 mg of CTA or 400 mg of PVC was dissolved in 20 mL of either chloroform or THF, respectively. Subsequently, the corresponding quantity of the ionic liquid was introduced into the solution and stirred magnetically for 2 hours. Following this, the solution was poured into a flat-bottom glass Petri dish measuring 9.0 cm in diameter, placed horizontally, and loosely covered. The solvent was left to evaporate at room temperature overnight, resulting in the formation of a film that was then peeled off from the Petri dish.

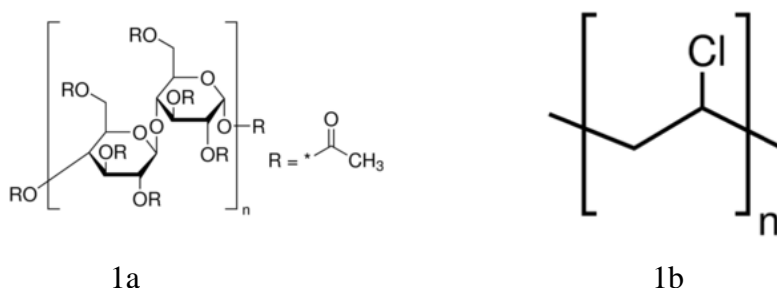


Figure 1: chemical structure of 1a cellulose triacetate (CTA); and (1b) polyvinyl chloride (PVC).

Fourier transformed infrared spectrometry (FT-IR)

Infrared spectra were obtained using an FT-IR Bruker Tensor 27 Spectrophotometer operating in the transmission mode, covering the spectral range from 4000 to 400 cm^{-1} .

SEM Analysis

Details about membrane morphology were acquired through the utilization of scanning electron microscopy (SEM), with images captured using a VEGA II SBH electron microscope manufactured by TESCAN. To ensure the acquisition of a clear cross-sectional image,

conductive for the analysis of the internal Polymer Inclusion Membrane (PIM) morphology, sample preparation involved freezing the membrane under liquid nitrogen, swiftly followed by fracturing. Subsequently, the samples were affixed to an aluminum support using a C graphite double scotch and then coated with a 15 nm gold layer via sputtering.

Liquid liquid membrane extraction and PIMs extraction of Na and Mg ions

The Na and Mg ion-selective lipophilic macrocycle employed as a carrier was synthesized as previously documented [19]. Materials were procured from Sigma-Aldrich Corporation (USA, owned by Merck) and were utilized without additional purification, except where specifically indicated. Solvents were subjected to drying and purification according to established protocols [20]. In the context of liquid-liquid extraction procedures, aqueous solutions of metal salts (6 mL) were subjected to extraction with equivalent volumes (6 mL) of crown ether in dichloromethane. To maintain consistent liquid phase volumes during extraction, the solvents were pre-saturated before measurements. For ensuring uniform phase contact efficacy during the extraction process, two-phase mixtures were contained within glass vials and agitated at 300 rpm using an IKA KS 130 (IKA®-Werke GmbH & Co. KG, Germany) shaker. To assess the metal salt content in the organic phase, dichloromethane was separated from the aqueous phase via a separatory funnel. The resulting organic phase was further agitated with 5×2 mL of a 10 m/m% aqueous acetic acid solution to eliminate cations, and the resultant aqueous phase was subjected to evaporation under reduced pressure until a constant weight was achieved.

In transport studies, the source phase comprised an aqueous solution of Na and Mg ions (2 mL), while the receiving phase was either 6 mL of double-distilled water or buffered aqueous solution. The liquid membrane (LM) was formulated by dissolving the crown ether in 12 mL of an apolar solvent, characterized by a relatively high density in comparison to water. The use of an apolar organic membrane served to prevent membrane leakage, allowing only carrier-mediated transport of metal salts. The metal ions were in significant excess during the transport process. Stirring of the membrane phase during the transport experiments was carried out continuously using a polytetrafluoroethylene-coated magnetic stirring bar, with dimensions of 10 mm length and 4 mm diameter. The material transfer surface area of the transport apparatus utilized was $7.07 \times 10^{-4} \text{ m}^2$. The preparation of source phases involved dissolving metal salts in double-distilled water, unless otherwise stated. Additional experiments were conducted with buffered aqueous phases ($\text{KH}_2\text{PO}_4/\text{Na}_2\text{HPO}_4$, pH = 7.0) to compare the outcomes. However, no significant differences were observed, signifying that varied pH levels in the salt solutions did not impact the measurement results.

For membrane regeneration and to quantify the total amount of Pb^{2+} within the membrane, the bulk phase was isolated from the source phase using a separatory funnel. The organic phase was subsequently agitated with 5×2 mL of a 10 m/m% aqueous acetic acid solution to eliminate cations. Regeneration involved drying the organic phase over magnesium sulfate, filtration, and evaporation. The carrier's purity was verified using thin-layer chromatography (TLC) on silica gel, employing a methanol and dichloromethane mixture (1:10) as an eluent ($R_f = 0.75$). To determine the total amount of Na and Mg ions within the membrane, the combined aqueous phases were evaporated and dried to a constant weight before analysis. The investigations were carried out at adjusted temperatures of 10 ± 0.5 or 15 ± 0.5 or 20 ± 0.5 °C as indicated in each instance, employing air-tempering equipment. All data presented were obtained from the average of a minimum of three replicate measurements.

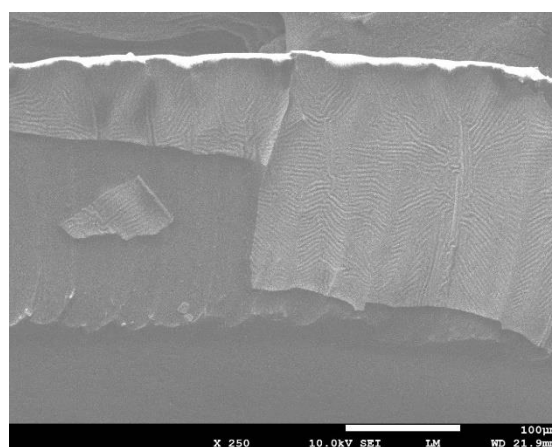
Quantification of the extracted and transported quantities was conducted through weight measurements. For sample preparation, the receiving phase was evaporated under reduced pressure, dried to a constant weight, and the mass of the solid residue was determined using a Mettler Toledo XS105 microanalytical balance (Mettler Toledo, USA) to the nearest 0.1 mg. The errors associated with the transported amounts of metal salts were less than ± 1.0 mg and

were calculated based on at least three independent measurements. In all cases, membrane leakage was less than 1.0%.

For sample composition analyses, the elemental masses of the residue were determined using inductively coupled plasma optical emission spectroscopy (ICP-OES). Subsequently, 5 mL sample solutions were prepared from the residues. The solutions were acidified with 50 μ L nitric acid (63%) and diluted with distilled water before determining the element concentrations via the ICP-OES method. The sample solutions were analyzed in simultaneous, multielement mode using a Labtest Plasmalab ICP-spectrometer (Labtest Equipment Company, USA) equipped with a 40-channel Paschen-Runge vacuum polychromator and photomultiplier detectors, utilizing a 27 MHz argon plasma. The instrument settings involved forward power set at 1.3 kW, sample introduction utilizing a "OneNeb" nebulizer (Agilent Technologies, USA), cyclonic spray chamber, and Gilson peristaltic pump (Gilson Company, USA) operating at a 1 mL/min sample flow rate. The observation height was set at 13.5 mm, and an integration time of 5 seconds was employed. The limit of quantitation for Mg was 0.0005 mg/L (wavelength: 279.553 nm), and for Na, it was 0.19 mg/L (wavelength: 589.592 nm).

Results

Infrared (IR) spectroscopy served to elucidate the chemical distinctions among the examined membranes. The Fourier-transform infrared (FTIR) spectra, depicted in for PIMs, largely exhibit characteristic bands of the individual constituents constituting the membrane, as previously noted [18]. Notably, consistent bands appeared across all membrane compositions: the 1235 cm^{-1} band, attributed to the TOMA group in Aliquat 336, and the absorption bands at 1747 and 1041 cm^{-1} , indicative of the C=O and C-O-C groups within the CTA polymer, respectively. Furthermore, distinct bands related to the accompanying anion of the quaternary ammonium group were discernible. Specifically, the absorption band at 2048 cm^{-1} corresponds to the $-\text{N}-\text{C}-\text{S}$ of the thiocyanate anion, while the intense band in the 1300–1400 cm^{-1} range is associated with the stretching bands of the nitrate group. These findings, coupled with the absence of band displacement compared to the pure components, suggest the entrapment of the ionic liquid (IL) within the polymeric matrix without undergoing chemical alterations. This implies the unimpeded capacity of the IL to interact freely with the species in solution.



a

Figure 2: Cross section of PIM

SEM was used to determine the appearance of the membrane surface and cross section obtained image are shown in fig. 2. Fig 2 shows cross sections PIM surface of PVC contains lumps and this show may incomplete melting of the polymer. Moreover in SEM image of surface and

cross section of the investigated membrane lumps were found because of incomplete melting of PVC. Some images show roughness of the film surface due to containing carrier (roughness was more visible). Carrier some time crystallize in the membrane during process. Membrane is dense and homogenous with agglomeration.

Heavy metal ions are a primary focus of environmental research due to their significant role as pollutants with potential health implications upon accumulation within biological systems. Among these, lead compounds, prevalent in various industrial sectors such as metallurgy, construction, and energy, remain prominent contaminants. In liquid membrane studies, the lipophilic macrocycle demonstrated reversible complex formation with Na and Mg ions, establishing a 1:1 complex-stoichiometry, allowing swift metal ion separation by enhancing solubility of heavy metal salts in the organic phase. However, significant variability in the extraction results and the loss of selectivity under competitive conditions rendered the selector molecule unsuitable for conventional liquid-liquid extraction-based heavy metal ion separation.

Conversely, in Polymer Inclusion Membranes (PIMs), a notably enhanced effectiveness was observed. PIMs exhibited heightened sensitivity to the presence of protic polar solvents, facilitating the transport of Na and Mg ions. Notably, the transport through dynamically stirred PIMs displayed a weak dependency on counterions, suggesting potential efficacy in manipulating ionic balance to enhance transport efficiency through the use of precipitating agents or an acidic receiving phase as shown in table 1. This underscores the pivotal role of the membrane-receiving phase interface in the transport process, given the significant impact of metal ion-carrier complex accumulation within the membrane on ion-flux. Consequently, the selection of an appropriate receiving phase stands as a crucial factor for effective separation. Altering the carrier-to-Na and Mg ion ratio, as well as adjusting the acidity or alkalinity of the receiving phase, resulted in increased transport efficiency. Moreover, the observed optimum temperature within the studied range suggests the process's reversibility, emphasizing the dynamic influence of temperature, pH, and carrier concentration on the efficiency of the separation process.

Table 1: metal transport (in moles)

Cations	12 hours	24 hours	36 hours	48 hours	$J_m * 10^7$ mol/ hours
Na ⁺	$0.8 * 10^{-5}$	1.40E-05	2.020E-05	2.900E-05	63
Mg ²⁺	1.20E-05	2.050E-05	3.550E-05	5.04E-06	10.26

Conclusion

Polymer inclusion membranes (PIMs) offer a myriad of advantages over traditional liquid membrane systems, including notably high diffusion coefficients, superior selectivity stemming from their underlying chemical retention mechanisms, cost-effectiveness, and low energy consumption. Furthermore, PIMs exhibit heightened chemical stability and mechanical robustness when juxtaposed with prevalent alternatives, such as emulsion liquid membranes (ELMs) and supported liquid membranes (SLMs). The Polymer Inclusion Membranes (PIMs) are composed of a polymer matrix coupled with an extracting agent or carrier, designed to extract or transport specific chemical species (ions or molecules) from aqueous solutions. Additionally, these membranes typically incorporate plasticizers, which serve to enhance the overall properties of the membranes. PIMs manifest as thin, pliable, and durable films, fabricated through the dissolution of the polymer, carrier, and plasticizer in a suitable solvent, followed by a gradual solvent evaporation process.

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Supplementary data

