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Separation of silver(I) and copper(II) by polymer inclusion membranes with aza[18]crown-6 derivatives as ion carriers

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ABSTRACT

In the presented work, we analyzed transport properties of novel polymer inclusion membranes (PIMs) containing a cellulose triacetate polymer matrix, *o*-nitrophenyloctyl ether as plasticizer and macrocyclic exchangers N-(diethylthiophosphoryl)-aza[18]crown-6 and N-(diethyloxophosphoryl)-aza[18]crown-6 as specific carriers toward silver(I) ions. The study was specifically focused on the transport properties of Ag(I) at conditions simulating industrial wastewaters. We analyzed the impact of several parameters on Ag(I) transport process such as: the carrier content in the PIM and strip phases composition. We concluded that efficient transport processes occur through a PIM containing 0.25 M of crown ethers. The process was very fast and efficient for solutions of initial silver concentration smaller than 10^{-3} mol L^{-1}, for which nearly all of silver was removed within 6 h. The performed experiments proved that Ag(I) transport through the membrane was a facilitated counter-transport process. Additionally, it possessed an excellent long-term integrity and a high selectivity for Ag(I) from Cu(II) ions.

Keywords: Polymer inclusion membrane; Facilitated transport; Silver and copper ions; Aza-crown ethers as carriers

1. Introduction

One of the hazardous waste generators is photographic industry, which includes the manufacturing process, graphic arts, engineering and medicine [1]. Beside silver, the produced waste also contains other heavy metals like iron, zinc, lead, copper, nickel and chromium [2]. In this waste, silver exists mainly as insoluble halide, soluble silver thiosulfate complex, silver ion or elemental silver, depending on the type and the stage of the originating process. The silver content in environmental wastewaters increases with the increasing use of silver compounds and silver-containing preparations in industry and medicine [3]. Silver can enter environment via industrial wastewaters, because it is an impurity in copper, zinc, arsenic and antimony ores [4]. This fact results in the focused attention on potentially toxic nutrients. Thus, separation, concentration and sensitive determination of Ag^+ ions in solution deserves an increasing interest. There are many methods, which have been commercially established to recover silver from photographic wastes, that is, precipitation, electrolysis, ion exchange and reverse osmosis.

Liquid membranes are interesting option for extraction processes due to their several advantages. The molecular diffusion in liquids is generally several orders of magnitude faster than one in solids. Liquid membranes can also be designed to be highly selective for specific solutes, and relatively small quantities of carrier or extractant are needed. Therefore, small amounts of highly selective, relatively expensive agents can be used. Furthermore, a maximum driving force, which avoids the use of multistage processes of liquid extraction,

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can be created. A major disadvantage of liquid membranes, in comparison with polymer inclusion membrane (PIM), is the lack of the long-term stability. Recently, due to their mechanical stability, PIMs provide a more effective separation than supported liquid membrane and bulk liquid membrane systems. The large ratio of surface area to volume observed for PIMs results in their potential use in nuclear and harmful metal waste remediation on an industrial scale.

PIMs are simple in structure; they consist of a polymer, which provides mechanical strength, a carrier molecule, which effectively binds and transports ions across the membrane and a plasticizer, which provides elasticity and acts as a solvent, in which a carrier molecule can diffuse. The carrier molecule acts as a specific receptor and causes the permeability of selective membranes toward target species [5]. The polymer cellulose triacetate (CTA) has many properties that facilitate it to be used as an effective polymer in the production of PIMs. CTAs are thermoplastic polymers consisting of linear polymer chains devoid of cross-links between them. The mechanical strength of films made within these polymers is determined by a combination of intermolecular forces and entanglement process [6].

Lamb et al. [7] have studied the transport of Ag(I) through CTA/*o*-nitrophenyloctyl ether (*o*-NPOE) membranes containing a series of pyridino- and bipyridino-podands. These carriers have hydrophobic palmitoyl tails making them insoluble in aqueous solutions and highly soluble in membranes, thus convening in their excellent homogeneity and stability of membranes. These podands have three pyridine nitrogen atoms in tridentate coordinating positions and reveal strong biding properties toward Ag(I) ions. Thus, only Ag(I) transport from a perchlorate solution at the presence of Cd(II), Zn(II), Co(II), Ni(II), Pb(II) and Cu(II) to the water receiving phase was observed. A similarly high transport selectivity toward Ag(I) in comparison with Pb(II) and Cd(II) has been observed by Kim et al. [8] for a series of calix[4]azacrown ether derivatives immobilized in CTA-based PIM plasticized with *o*-NPOE. In another study, Kim et al. [9] have also investigated the transport of Ag(I) by PIMs and SLMs using acyclic polyether ligands having diamide end-groups. They have also found highly selective transport of Ag(I) at the presence of Cd(II), Zn(II), Co(II), Ni(II), Pb(II) and Cu(II). In addition, the transport of Ag(I) has been considerably faster in PIMs than in SLMs.

The mentioned studies show that aza-crown ethers bearing phosforyl derivative groups have not been yet used as carrier in making PIMs for silver ion extraction. The present paper concerns the transport studies of Ag(I) and Cu(II) from nitrate aqueous solution across PIM containing cellulose triacetate as support, *o*-NPOE as plasticizer and ethers **1** and **2** as ionic carriers. The impact of reproducibility effect and receiving phase on Ag(I) transport across PIMs are also discussed.

2. Materials and methods

2.1. Reagents

Inorganic chemicals, that is, silver(I) and copper(II) nitrates, were of analytical grade and were purchased from POCh (Gliwice, Poland). The organic reagents, that is, CTA (Mn = 72,000–74,000), *o*-NPOE and dichloromethane, were also of analytical grade; they were purchased from Fluka, Poland and used without further purification.

The phosphorylation of the aza[18]crown-6 affording N-(diethylthiophosphoryl)-aza[18]crown-6 (**1**) or N-(diethyloxophosphoryl)-aza[18]crown-6 (**2**) was performed by the Maeda et al. method [10] – Fig. 1.

2.1.1. Preparation of the PIM

We prepared a solution consisting of a support (CTA), ion carriers (ether **1** or **2**), and a plasticizer (*o*-NPOE) in dichloromethane. A portion of this solution was poured into a membrane mold, that is, a 9.08-cm glass ring adhered to a glass plate with CTA−dichloromethane glue. The organic solvent was allowed to evaporate overnight, and the resulting membrane was separated from the glass plate by immersion in cold water. Next, the prepared membrane was placed in a permeation cell.

2.1.2. Transport studies

The polymeric film was sandwiched between two glass cells (internal diameter of 6.5 cm) and sealed with an O-ring with the aid of a clamp. The membrane area, which was in contact with 50-ml aqueous source and strip phases, was ca. 10 cm^2. The transport cell was kept at 25.0°C ± 0.2°C in a thermostated room. In a typical heavy metal cation transport experiment, the aqueous source phase contained a 10^{-3}-M solution of Ag(I) and Cu(II) in 0.01 M nitric acid at pH 3.5. The aqueous strip phase of an initial pH 5.2 contained a solution of disodium ethylenediaminetetraacetate (EDTA), sodium thiosulfate and nitric acid. During the transport experiment, both aqueous phases were stirred at 600 rpm by custom-made glass rods with propellers. Concentrations of the transported species were monitored by periodic removal of equal volumes of source and strip phases for determination of metal ion concentrations by atomic absorption spectrometer (AAS) spectrophotometer, Unicam Solaar 939, England. The samples were sufficiently small to ensure that the membrane remained covered with the aqueous source and strip phase solutions throughout whole transport experiment. Transport of metal ions was monitored for 6 h. Each experiment was performed in triplicate. The agreement between different runs of a given system was within 95% in all cases.

The permeability coefficient (*P*), according to the mass transfer model described by Danesi [11], is given in Eq. (1):

$$\frac{dC}{dt} = -\frac{A}{V} \cdot P \cdot C \tag{1}$$

The mass balance can be derived by integration of Eq. (1):

$$In\left(\frac{C}{C_i}\right) = -\frac{A}{V} \cdot P \cdot t \tag{2}$$

where C is the metal concentration (mol dm^{-3}) in the source phase at a given time; C_i is the initial metal concentration in the source phase; t is the transport time (s); V is the volume of the aqueous solution in the source phase; and A is the area of the membrane. To calculate P values, we prepared a plot of ln(C/C_i) vs. time. The relationship of ln(C/C_i) vs. time was linear, what was confirmed by high values of the determination coefficient (r^2) 0.9538–0.9996. The initial flux (J_i) was determined using Eq. (3):

$$J_i = P \cdot C_i \tag{3}$$

The selectivity coefficient (S) was defined as the ratio of initial fluxes for $M1$ and $M2$ metal ions:

$$S = J_{i,M1} / J_{i,M2} \tag{4}$$

To describe the efficiency of metal removal from the source phase, the recovery factor (RF) was calculated as follows:

$$RF = \frac{C_i - C}{C_i} \cdot 100\% \tag{5}$$

3. Results and discussion

The reproducibility of Ag(I) transport across PIM with 0.25 M ether **1** and 4.0 cm^3 *o*-NPOE/1.0 g CTA was investigated; the flux of metal ions transported after 6 h, obtained from 10 replicate measurements, was found to be 11.07 ± 0.05 μmol m^{-2} s^{-1}. The blanc experiments, in the absence of carrier, with a support and plasticizer only, yield to no significant flux across PIM.

3.1. Effect of carrier concentration

An organic liquid phase, immobilized into a polymer membrane, can be treated as selective and effective ionic exchanger for the processes of metal ions transport from aqueous solution. In our earlier studies of silver and copper cations separation, it was found that the lariat ether N-(diethylthiophosphoryl)-aza[18]crown-6 (**1**) exhibited very good Ag$^+$ selectivity in competitive transport through immobilized CTA membranes [12]. Therefore, two lariat ethers with geminal diethylthiophosphoryl and diethyloxophosphoryl groups were used as ion carriers for silver cations transport from a source aqueous phase, containing 0.0010 M of Ag(I). Aqueous solution containing 0.1 M HNO_3 served as a strip phase. For the proton-coupled metal ion transport, the metal cation flux was found to be strongly influenced by side arm of lariat ether as well as lariat ether concentration in membrane. In order to analyze the effect of carrier concentration on Ag$^+$ transport, the lariat ethers **1** and **2** of different concentrations (0.01–0.8 M) were used. The calculated, initial flux values are given in Fig. 2.

The results indicated that the transport of Ag(I) increased as the lariat ether concentration increased. However, this effect stopped at a concentration of 0.25 M. When the lariat ether concentration increased from 0.25 to 0.8 M, the transport rate stabilized at constant level, that is, the level of ion carriers saturation in the membranes. Therefore, the carrier concentration was maintained at 0.25 M for further experiments. If mass transport is performed by the diffusion process in the PIM system and lariat ether concentration increases stepwise in particular levels, this fact enhances the viscosity of the organic phase in the membrane. In this case, since the resistance of the membrane against carrier movement is higher, the transport rate of the ion decreases. Therefore, there is an optimum carrier concentration in all plasticized membrane systems, and this concentration needs to be determined experimentally. Similar results were also obtained by Arous [13].

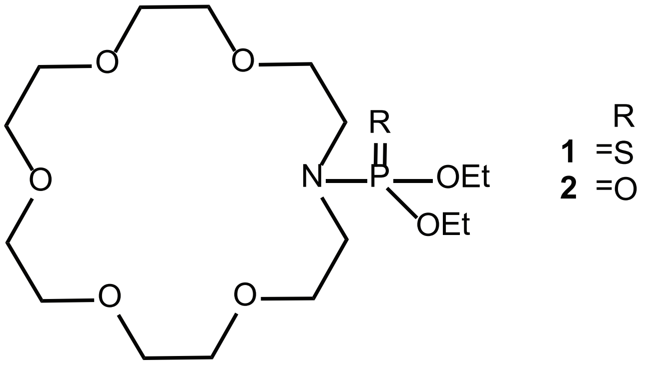

Fig. 1. The structure of the aza-crown ethers derivatives.

3.2. Effect of stripping phase

The effect of the striping phase on Ag(I) transport across PIMs with ethers **1** and **2** was studied using following receiver solutions, that is, 0.1 M $Na_2S_2O_3$, 0.1 M HNO_3 and 0.1 M EDTA.

These experiments indicated that the transport across PIM with **1** and **2** decreased in the following order of strip phases: nitric acid > EDTA > thiosulfate. The *RF* values for Ag(I) transport into 0.1 M HNO_3 as strip solution for ethers **1** and **2** were equal to 90% and 78%, respectively.

It can be observed in Fig. 2 that transported Ag(I) was better recovered from the membrane with ether **1** than with ether **2**. The results shown in Fig. 3 reveal that HNO_3 solution allowed the effective recovery of the metal from the membrane phase. In case of facilitated transport of Ag(I) through PIMs, the efficiency of process was controlled via formation of ion pairs of protonated lariat groups with metal ions. The ion transport properties were also interpreted by an induced-fit mechanism. The ethers **1** and **2** used as ionic carrier for transport of Ag(I) showed preferential formation of metal complexes in membrane. In the experiment, we found that the extraction of **1** and **2**, probably depended not only on their size fit but also on the ion–dipole interaction between thia- and oxo- groups with metal ions. The steric effect of the

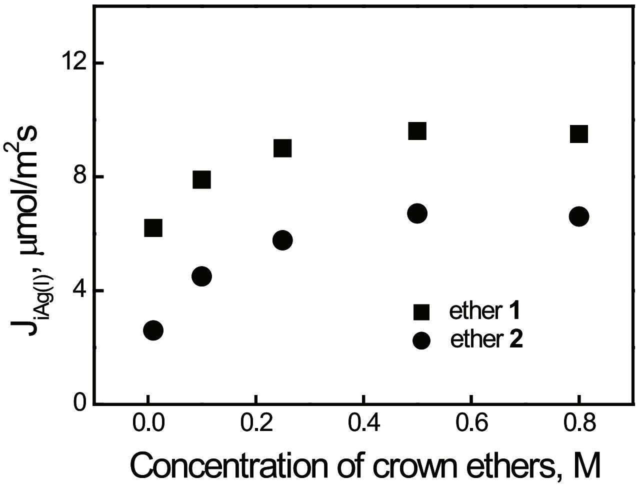

Fig. 2. The effect of carrier concentration on Ag(I) transport across PIMs with aza-crown ethers **1** and **2**.

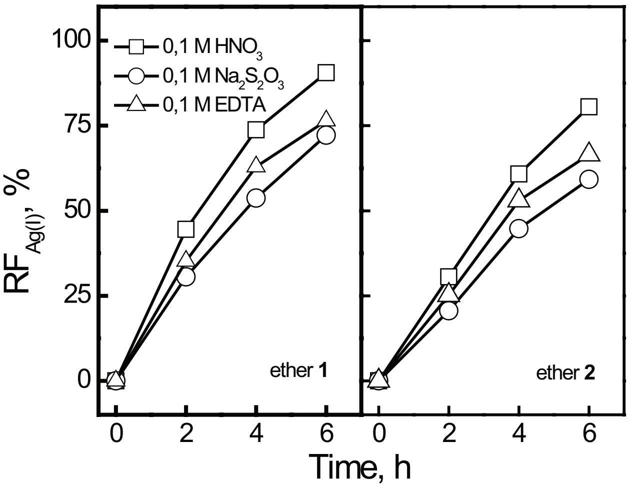

Fig. 3. The *RF* of Ag(I) obtained for differed striping phase in transport through PIM with crown ethers 1 and 2.

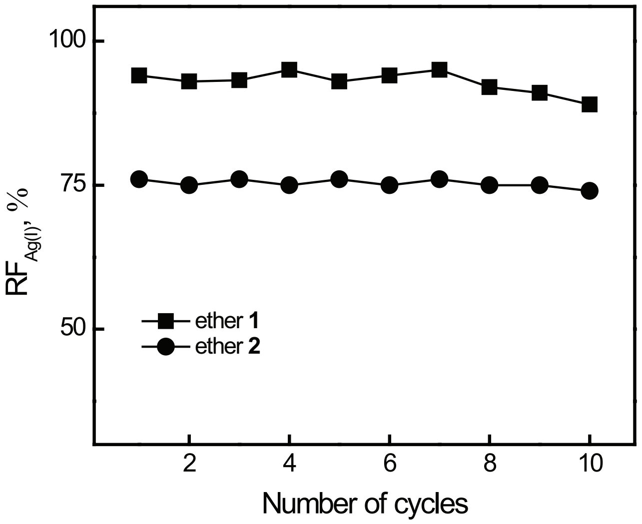

Fig. 4. The *RF* of Ag(I) vs. number of replicate measurements (source phase, 1×10^{-3} M $AgNO_3$ in 0.01 M HNO_3; membrane composition, 4.0 ml *o*-NPOE/1 g CTA, 0.25 M carrier; strip phase, 0.1 M nitric acid).

Table 1
Parameter of competetive transport of Ag(I) and Cu(II) across PIM with crown ether 1 obtained for $Na_2S_2O_3$ and HNO_3 stripping solutions

Metal ions	Strip phase	J_i μ mol m^{-2} s^{-1}	Selective coefficients $S = J_{Ag}/J_{Cu}$	Recovery factor *RF*, %
Ag^+	0.1 M $Na_2S_2O_3$	5.92	Ag > Cu	$RF_{Ag} = 89$
Cu^{2+}		0.11	54	$RF_{Cu} = 6$
Ag^+	0.1 M HNO_3	9.35	Ag > Cu	$RF_{Ag} = 69$
Cu^{2+}		0.08	117	$RF_{Cu} = 1$

cavity, space-regulating effect, and so on had to be also taken into account. Similar behavior has been received by Prof. Bartsch team for the separation of alkali metal cations using ionizable ethers attached to various lariat groups [14].

3.3. Stability of PIMs

In order to investigate the ion transport by the PIMs, we conducted 10 experiments under the same conditions, without changing the membrane, while the source and strip phases were renewed. The results indicated that the transport efficiency of the PIM with ethers 1 and 2 was reproducible. In the case of PIM with 1, the *RF* values were over 90.0% in the first four cycles of the PIM (each cycle, 6 h; Fig. 4). After the eighth cycle, the *RF* values decreased; at the ninth cycle, the *RF* value was 89.85%. The small decrease of the stability of the membrane could have been caused by the partitioning of the carrier between the membrane and the aqueous solution. Additionally, after seven cycles of transport processes, we observed small amount of precipitate metal complexes on the membrane surface (at the source aqueous phase/membrane). However, it did not significantly affect transport rate and stability of metal removal by PIMs. In the case of PIM with ether 2 in the first eight cycles, *RF* values are over 75%; therefore, the prepared PIM with ether 1 seems to be more effective for long-term transport processes.

3.4. Competitive transport of Ag and Cu by PIM with ether 1

In the series of experiments, competitive transport of Ag(I) and Cu(II) ions from acidic aqueous nitrate solutions (source phase), through PIM with 1 into 0.10 M nitric acid or thiosulfate aqueous solutions (strip phases), was studied. It was found that selectivity coefficients Ag^+/Cu^{2+}obtained for PIMs with ether 1 were higher for HNO_3 stripping phase than those obtained for thiosulfate stripping phase being – Table 1.

For 0.0010 M metal ion concentrations, the selectivity coefficients were higher for aqueous nitric acid strip phases than from aqueous thiosulfate (117 for HNO_3 and 54 for $Na_2S_2O_3$). It resulted of very low Cu(II) transport revealed by aqueous nitrate solutions. The results presented in Table 1 show the possibility of very effective Ag(I) and Cu(II) separation from acidic solution into either thiosulfate or nitrate solutions by PIMs with ether 1.

These large separation factors obtained for investigated membrane systems are higher than those reported by Hayashi et al., who separated lead from copper in a PIM transport system with proton-ionizable polyether as a carrier [14], as well than those reported by Sgarlata et al. [15]. Although these papers deal with the separation of some transition metal ions, only Nowik-Zajac et al. [16] have studied the selective separation of Ag(I) and Cu(II) from mixtures using macrocyclic carriers, but their results, however, showed lower selectivity and efficiency. To our knowledge, the discussed experiments are the first report of successful separation of Ag(I) from a source phase solutions containing a mixture of Ag(I) and Cu(II) with a PIM system.

4. Conclusion

The PIMs containing N-(diethylthiophosphoryl)-aza[18]crown-6 (ether 1) and N-(diethyloxophosphoryl)-aza[18]crown-6 (ether 2) as carriers were found to be efficient toward silver ions. On the basis of the obtained results, it can be concluded that Ag(I) transport through PIM with ethers **1** and **2** was described by first-order reaction occurring at membrane interface. When the metal ions were inserted deeper in the ether cavity, the selectivity coefficient Ag^+/Cu^{2+} is higher. The transport using ether **1** showed higher selectivity toward Ag than for Cu, and the maximum values of separation coefficient Ag/Cu for 0.1 M $Na_2S_2O_3$ and for 0.1 M HNO_3 solutions as strip phases were 54 and 117, respectively. The recovery factor for Ag(I) was higher for HNO_3 than $Na_2S_2O_3$ and EDTA solution as receiving phase. Selectivity is also related to the nature of the thia- (P=S) and oxo- (P=O) groups of ethers **1** and **2** forming the carrier as well as attached side arms. The kinetic parameters of this process were determined in the aspect of its effectiveness and selectivity. The extraction ability of ion carrier was not reflected, as expected, by the pKa values. Phosphate lariat ethers have two different donor sites, that is, thia- and oxo- groups which provide weak complementarity and a rugged coordination site. Furthermore, since the P=S group in ether **1** is located at the side arm, when a metal ion complex is formed with the phosphorylated aza[18]crown-6, its complexation is preferred. The repeated transport experiments of PIM indicated its long-term integrity. In the test of long-term stability of PIM with ether **1**, the *RF* of Ag (I) decreased only slightly after seven cycles of transport processes.

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