

Utilization of Cellulose-Triacetate-Blended Membranes for Carrier-Mediated Transport of Some Metal Ions

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ABSTRACT: In this study, cellulose triacetate was used as a suitable base polymer for polymer-blended membranes for ion sensing and separation. Polymer-blended membranes were prepared with the solvent casting technique in the presence of mixed plasticizer and a metal ion carrier known as an *ionophore*. 7-Dodecyl-8-hydroxyquinoline and *N,N'*-diphenylethyl Kemp's triacid diamide, in addition to the newly synthesized 8-[*N*-acetyl-*O*-(4-*tert*-butyl benzyl)-*L*-tyrosylamino] quinoline, were used as representative examples for ionophores. The membranes were evaluated through the transport of copper and lead ions into 0.1M nitric acid as the receiving phase. The concentrations of the investigated metal ions in both phases were assayed by atomic absorption spectrometry. From this study, it can be concluded that the efficiency of the membrane, either as an ion-transporting or as an ion-extracting candidate, is controlled by the amount of the immobilized ionophore, the immobilization time within the membrane matrix while in contact with the receiving phase, the nature of the ionophore-metal ion complex, and so on. The carrier-mediated transport mechanism was also investigated. © 2001 John Wiley & Sons, Inc. *J Appl Polym Sci* 82: 2008–2015, 2001

Key words: polymer membranes; ionophores; carrier-mediated transport; ion sensing and separation; cellulose triacetate; sensor; diffusion; FTIR

INTRODUCTION

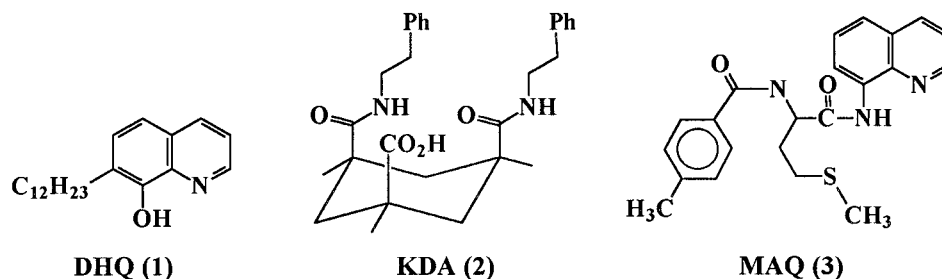
Membrane technology is regarded as one of the most promising technologies in the sensing and separation of chemical species. Consequently, the use of functional membranes has recently been studied extensively.^{1–6} Metal ion extraction, through complexation with an organic soluble ligand known as an *ionophore*, is a process widely used in the hydrometallurgy industry for the separation, purification, and recovery of many metals. It is now being applied to environmental problems to reduce the emissions of heavy met-

als.^{7–9} Considerable attention has been paid to the extraction and transport of heavy metal ions through liquid membranes by synthetic ionophores.¹⁰ Some heavy metal ions are invaluable as so-called noble metals, whereas some are harmful and cause serious environmental problems. Therefore, besides their industrial significance, the effective separation and recovery of these metals by ionophores are regarded as key technologies that can resolve these problems.¹¹ Scheme 1 shows some examples of such ionophores.^{3,4,12,13}

Although a number of natural and artificial ionophores are known, the development of new ones for practical use is still an active field.^{14–20} Hence, many amide and imide compounds have been synthesized for this purpose.^{21,22} Cellulose triacetate (CTA)-based membranes, which con-

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Scheme 1 Some representative examples of known ionophores.

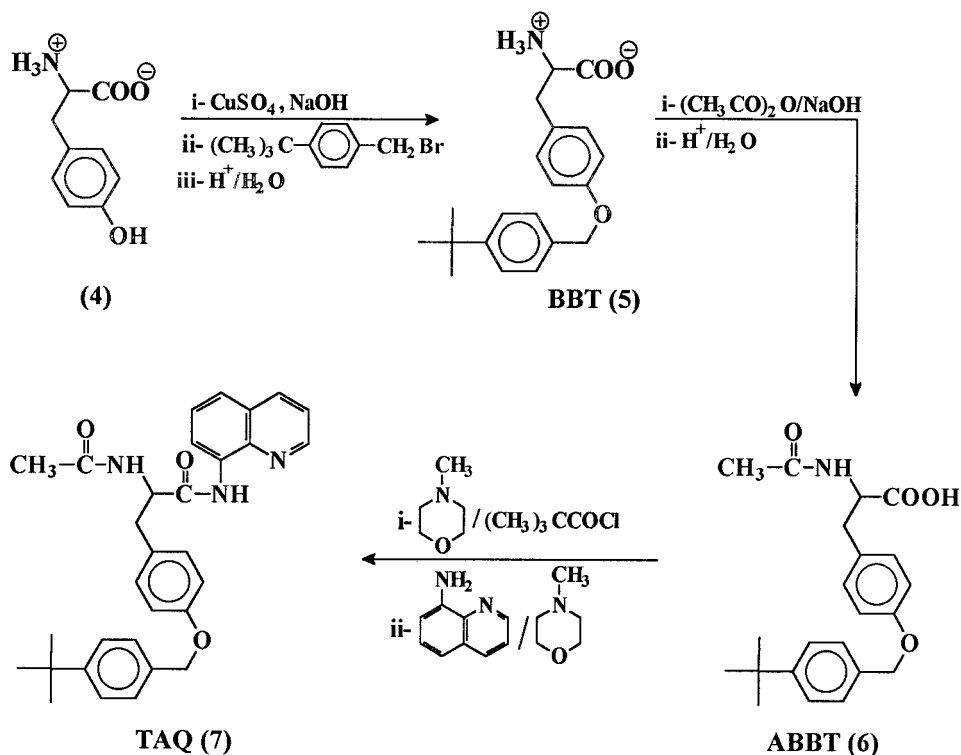
tain a mixture of two kinds of organic liquids as plasticizers, have been found to be quite effective for the transport of some transition and rare-earth metal ions.^{1,23}

This study's goal was the synthesis of the new organic compound 8-[*N*-acetyl-*O*-(4-*tert*-butylbenzyl)-*L*-tyrosylamino] quinoline TAQ (7) to be investigated as an ionophore in comparison with some already known ionophores such as 7-dodecyl-8-hydroxyquinoline [DHQ (1)] and *N,N'*-diphenylethyl Kemp's triacid diamide [KDA (2)]. The synthesis of 7 is represented in Scheme 2. Cu^{+2} and Pb^{+2} as acetate salts were used as examples for the transition metal ions. Both the

source and the receiving phases were assayed by atomic absorption spectrometry.

EXPERIMENTAL

All materials were supplied by Aldrich (Milwaukee, WI) and were used without further purification. Metal ion concentrations were determined by a Shimadzu AA-680/G V-5 atomic absorption spectrometer (Kyoto, Japan). Fourier transform infrared (FTIR) and $^1\text{H-NMR}$ spectra were recorded by a Mattson 5000 FTIR spectrometer (Cambridge, UK) and a Bruker ASX 400 400 MHz



Scheme 2 Synthesis of 7.

instrument (Karlsruhe, Germany), respectively. CTA was purified through a dissolution/precipitation technique prior to use. The thickness of the membrane was measured by means of a Mitutoyo (Kyoto, Japan) No. 293-521-30 digital micrometer. All melting points were uncorrected and were determined by a Stuart (Staffordshire, UK) melting point apparatus SMP-2.

Synthesis of 7

Preparation of *O*-(4-*tert*-butylbenzyl)-*L*-tyrosine [BBT (5)]²⁴

An aqueous solution (20 mL) of 1.25 g of $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ was added to a solution of 2.0 g of *L*-tyrosine 4 in 20 mL of 2*N* NaOH. The reaction mixture was warmed gently for 15 min and left to cool. A mixture of 150 mL of methanol and 20 mL of 2*N* NaOH was added to the separated precipitate; 1.3 g (1.1 mL) of 4-*tert*-butylbenzyl bromide at room temperature was then added, and the mixture was stirred for 1 h. The separated 5-copper complex was cleaved by acidification with dilute HCl and stirred for 15 min. The product was then extracted with ethyl acetate, washed with water, NaHCO_3 solution, and again with water and finally dried over anhydrous MgSO_4 . Evaporation of the ethyl acetate solution led to the production of an oil that solidified over time (~24 h). It was recrystallized from ethyl acetate/petroleum ether to afford colorless fine needles [melting point (mp) = 116.5°C, decomp.; yield = 2.4 g, 82%], which gave a negative test with FeCl_3 for the phenolic OH group of 4. The formation of the C—O—C bond was determined from the absorptions at 1240 and 1040 cm^{-1} , which are characteristic for the aryl alkyl ether group.^{25a} This is, of course, in addition to the absorption bands characterizing the α -amino acids at 3100–2600, 1610, 1513, 1480, 540, and 515 cm^{-1} caused by the ($^+\text{NH}_3$ —) N—H bond, at 1600–1590 cm^{-1} as a shoulder, and at 1415 cm^{-1} caused by the carboxylate group.^{25b}

ELEM. ANAL. Calcd for $\text{C}_{20}\text{H}_{25}\text{NO}_3$ (327.42): C, 73.37%; H, 7.70%; N, 4.28%. Found: C, 72.98%; H, 7.54%; N, 4.32%.

Acetylation of 5

A mixture of 1.3 mL of 3*N* NaOH and 40 mL of water was added to 1.05 g of 5 and stirred for 30 min until the mixture was homogeneous. A mixture of 0.46 g of acetic anhydride and 1.3 mL of 3*N* NaOH was then added dropwise. The reaction

mixture was stirred for 1 h at room temperature and was then acidified with about 5 mL of 1*N* HCl. The reaction mixture was then extracted with ethyl acetate, washed twice with water, and dried over anhydrous MgSO_4 . The evaporation of ethyl acetate under reduced pressure led to the production of an oil that solidified over time (~24 h) into fine needle crystals (mp = 196–199°C, decomp.; yield = 0.85 g, 72%). The chemical structure was confirmed as *N*-acetyl-*O*-(4-*tert*-butylbenzyl)-*L*-tyrosine [ABBT (6)]. FTIR (KBr) showed absorption at 1726 cm^{-1} , which corresponded to C=O of the free carboxylic group, in addition to a new peak at 1640 cm^{-1} for the carbonyl group, formed by the acetylation of the amino group of 4. Also, absorption at 3460 and 1515 cm^{-1} , which correspond to the N—H bond, in addition to absorption at 1245 cm^{-1} which resulted from the interaction between N—H bending and C—N stretching, were observed.^{25c}

ELEM. ANAL. Calcd for $\text{C}_{22}\text{H}_{27}\text{NO}_4$ (369.46): C, 71.52%; H, 7.37%; N, 3.79%. Found: C, 71.38%; H, 7.26%; N, 3.62%.

Amidation of 6

6 (426 mg) and *N*-methyl morpholine (102 mg) were dissolved in 10 mL of dry tetrahydrofuran (THF), and 121 mg of pivaloyl chloride was added dropwise while the mixture was stirred at –10 to –15°C under inert atmosphere. The solution was stirred further for 1 h at –5°C, and then a mixture of 2.3 g of 8-aminoquinoline and 1.6 g of *N*-methyl morpholine in 5 mL of dry THF was added in one portion, while the temperature was kept between 0 and –5°C. The reaction mixture was continuously stirred overnight at room temperature. Afterwards, the reaction mixture was diluted with 200 mL of chloroform and washed with water, 5% NaHCO_3 solution, water again, and finally with saturated salt solution. Drying over anhydrous Na_2SO_4 and evaporation under reduced pressure resulted in the formation of a colorless material that was recrystallized from ethyl acetate and confirmed as 7 (mp = 185–187°C, decomposed; yield = 0.27 g, 48%). FTIR (KBr) showed a shifted absorption peak of the free carboxylic group to 1710 cm^{-1} caused by amidation. In addition, the quinoline derivative showed absorption at 800 and 710 cm^{-1} caused by the pyridine ring^{25d} and at 870, 1540, and 3330 cm^{-1} caused by the trisubstituted benzene ring with three adjacent hydrogen atoms.^{25e}

ELEM. ANAL. Calcd for $C_{31}H_{33}N_3O_3$ (495.62): C, 75.13%; H, 6.71%; N 8.48%. Found: C, 74.68%; H, 6.52%; N, 8.38%.

$^1\text{H-NMR}$: 1.3 (9H, s, *t*- CH_3), 2.2 (3H, d, CH_3), 3.5 (5H, m, CH_2 and CH), 6.95, 7.15, 8.1 (6H, d, quinoline), 7.4 (4H, m, CH-aromatic), 8.8 (2H, dd, NH).

Membrane Preparation

The membrane was prepared according to a method described earlier.^{1,23} A solution of 50 mg CTA, 75 μmol of the ionophore, 150 mg of 2-nitrophenyl octyl ether, and 100 mg of tri-*n*-butylphosphate in 10 mL of chloroform was cast in a glass culture dish (flat bottom and 6 cm in diameter). The solution was slowly air dried at room temperature. Afterwards, it was dried in a vacuum oven at 35°C for 2 days. The membrane of 40–42 μm thickness was cut into pieces 3 cm in diameter, which were suitable for use in the transport experiment.

Transport Experiment

For the metal ion transport studies, a two-compartment U-tube-type glass cell was used. The CTA membrane was fixed between the two compartments of the cell. To the first compartment, designated as the source phase compartment, was added 200 mL of 0.2 mM of the metal acetate dissolved in an acetic acid/sodium acetate buffer solution of pH 5.9. The receiving phase, contained in the second compartment, was 200 mL of 0.1M HNO_3 . The two phases were stirred in a thermostated bath at 25°C for 48 h. The samples for analysis were collected at definite time intervals and prepared for assaying by atomic absorption spectrometry. The investigated metal ions, Cu^{+2} and Pb^{+2} , were assayed at wavelengths of 324.8 and 217.0 nm, respectively. The data represented in this study are the means of three replicates.

RESULTS AND DISCUSSION

The efficiency of a certain membrane to perform either transport or extraction of a certain metal ion is controlled by different factors. Common to these systems is the problem of the membrane solvent and carrier being lost to the aqueous phases, which limits the long-term integrity of the membrane. Among the factors affecting the carrier loss from the membrane to the aqueous phases are the nature of the membrane, such as

its porosity and the plasticizers added; the ability of the carrier to form a complex with the metal ion under investigation; the hydrophilicity of the carrier, reflecting its ability to be dissolved into one of the aqueous phases; the molecular (crystalline) size of the metal ion carrier complex, which affects its diffusion through the membrane to the receiving phase; and the solubility and stability of the carrier or its metal ion complex against pH in the aqueous acidic medium. There are some other factors that can affect, more or less, the loss of the carrier, such as the order of the carrier molecules within the membrane. Hence, the rate of ion transport within the membrane is not the only way to evaluate the membrane for ion transport or extraction, but the time spent by the carrier, within the membrane in an effective form, is of great importance, too.

Among different classes of compounds that can be used as metal ion carriers, there are the compounds that contain acyl amino groups in addition to the 8-aminoquinolyl amido groups that are effective in the complexation of some metal ions.¹² Therefore, 7 was synthesized as a model compound for such ionophores, containing both groups and also the *O*-alkyl derivative, which enhances the order of the molecules within the polymer matrix. The chemical structure of the newly synthesized 7 was proven by FTIR and $^1\text{H-NMR}$ spectroscopy. On the other hand, 8-*N*-(4-methylbenzoyl)-*S*-methyl-*L*-methionyl amino) quinoline [MAQ (3)] was also synthesized but it could not be used in this study because it was insoluble in the membrane composition, which led to a nonhomogeneous film. It may be possible to obtain a homogeneous film under different conditions of the plasticizer type, the membrane material, the casting solvent, and so on.

There is a previous report on the transport of different metal ions through liquid membranes in which the transport of the metal ions was achieved only under the effect of the pH difference between both the source and the receiving phases as equimolar concentrations of the metal ions in both sides were used. This was the case, for both single metal ion transport and mixed metal ion transport in studying the membrane selectivity.¹² In this case, the transport process was influenced by the pH difference in addition to the difference of the metal ion concentration on both sides. Also, the investigation considered only the single metal ion transport in which the metal ions were Cu^{+2} and Pb^{+2} .

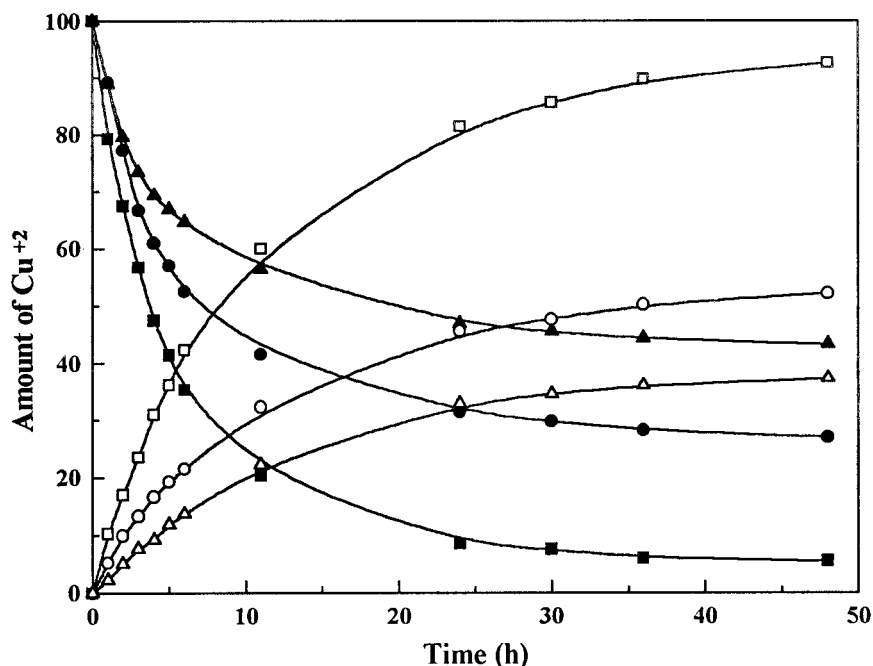


Figure 1 Time dependence of the amount of Cu^{+2} , as a percentage of 0.2 mM concentration, transported from the source phase (solid symbols) to the receiving phase (open symbols) through CTA-blended membranes containing (■, □) 1, (●, ○) 2, and (▲, △) 7 as ionophores.

Cu^{+2} Ions

Figure 1 describes the dependence of the amount of Cu^{+2} on the contact time. A marked increase in the amount of Cu^{+2} with the contact time in the receiving phase and a marked decrease in the source phase was noticed. This reflected the ability of the membranes to be used as transporting membranes for Cu^{+2} ions. Generally, the membrane had similar behavior apart from the ionophore that was used as the metal ion carrier. Comparison of the investigated membranes, in the sense of the decrease or increase of the amount of the metal ion in both the source and the receiving phases, respectively, led to the conclusion that the capability of these membranes to transport Cu^{+2} ions is in the following apparent order:

$$1 > 2 > 7$$

From the data represented in Figure 2, it is clear that the total amount of Cu^{+2} in both the source and the receiving phases was less than 100% of the 0.2 mM concentration of Cu^{+2} in the source phase. This difference represents the complexed amount of Cu^{+2} immobilized by the mem-

brane with the carrier. The simplest mechanism for the transport process is the formation of a complex between the metal ion to be transported and the immobilized ionophore through the contact between the source phase and the membrane, followed by diffusion of the complex through the membrane up to the receiving phase into which the metal ion will be dissolved. A similar mechanism was reported before for liquid membranes.⁴ If this mechanism is applicable in this case, the amount of the membrane-immobilized metal ion would have increased up to a certain value and then levelled off. Figure 2 shows that this was not the case, and the amount of the immobilized metal ion increased up to a certain value, after which it stepped down at different rates. This means that the metal ion transport process is not a simple diffusion process that leads to downloading only the metal ion into the receiving phase, but it is also controlled by the other factors mentioned previously, such as the solubility of the metal ion-ionophore complex in the aqueous acidic medium of the receiving phase. This leads to more or less dissolution ability of the complex from the membrane into the receiving phase. Consequently, as the dissolution increases, the

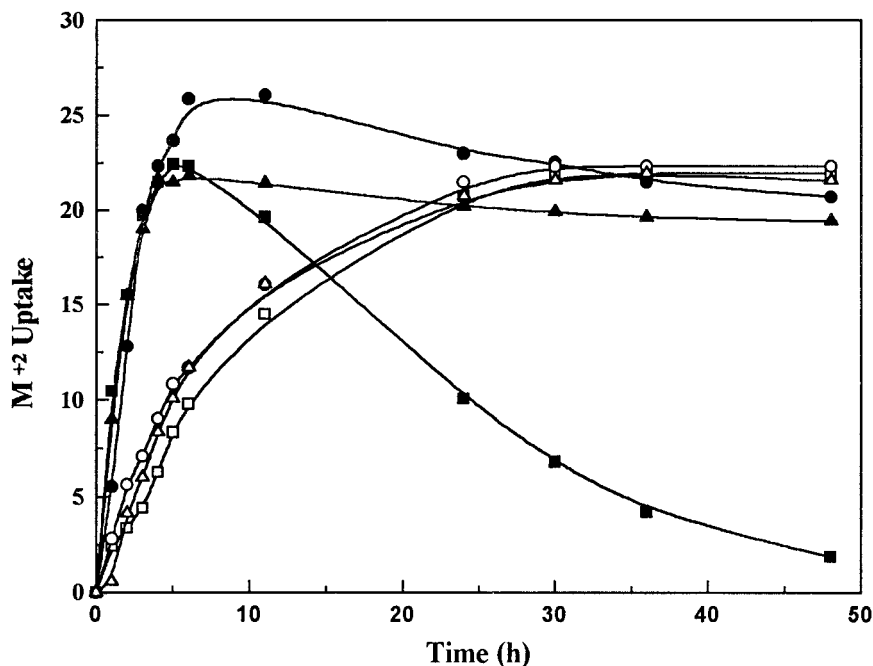


Figure 2 Time dependence of the amount of M^{+2} , as a percentage of 0.2 mM concentration, in the case of Cu^{+2} ions (solid symbols) and Pb^{+2} (open symbols) taken up by CTA-blended membranes containing (■, □) 1, (●, ○) 2, and (▲, △) 7 as ionophores.

amount of the metal ion and the membrane-immobilized ionophore decrease to a minimum, and the efficiency of the membrane is minimized. Also, the stability of the complex against the contact time plays an important role in the lifetime of the metal ion–ionophore complex in the membrane during the contact with the receiving phase.

The net effect of all these factors results in the behavior represented in Figure 2, and the amount of the membrane-immobilized complex formed in the presence of 1, 2, or 7 reached its maximum within 4–11 h and then decreased. The efficiency of the membrane, either as an ion-transporting or as an ion-extracting agent, was controlled by the amount of the immobilized ionophore and the immobilization time within the membrane matrix while in contact with the receiving phase. Therefore, the membrane containing 1 was the least effective one because it had the shortest lifetime in the matrix. On the other hand, although the amount of the metal ion taken up by the membrane containing 2 as an ionophore reached to a higher value than that containing 7; the latter one reached its maximum in a shorter time with little change after that recorded. This means that the membrane containing 7 would be effective for a longer time and, hence, can be considered more

efficient. The investigated ionophores can be arranged according to the immobilization time and immobilized amount in the following order:

$$7 \geq 2 > 1$$

Pb^{+2} Ions

Figure 3 shows that, when Pb^{+2} was used as the metal ion to be transported or extracted, the investigated membranes behaved in a similar way to that of Cu^{+2} . As a result of the differences between Cu^{+2} and Pb^{+2} characteristics, the amount of Pb^{+2} , as a percentage of 0.2 mM concentration, in both the source and the receiving phases were not sharply changed in comparison with that of Cu^{+2} . This means that the ion-extracting ability of such membranes toward Pb^{+2} is higher than their ion-transporting ability. The efficiency of the membranes then can be arranged in the following order:

$$7 > 2 > 1$$

This behavior can be attributed to the larger molecular size of Pb^{+2} and its complex that leads to low mobility and, consequently, a low diffusion

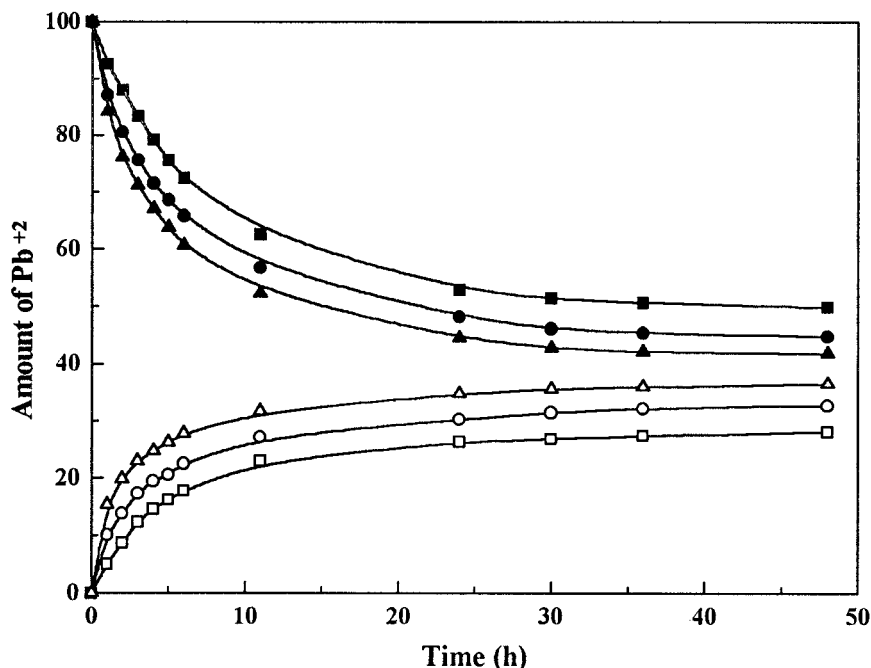


Figure 3 Time dependence of the amount of Pb^{+2} , as a percentage of 0.2 mM concentration, transported from the source phase (solid symbols) to the receiving phase (open symbols) through CTA-blended membranes containing: (■, □) 1, (●, ○) 2, and (▲, △) 7 as ionophores.

rate through the membrane. Also, it is known that the solubility of Pb^{+2} salts is lower than that of Cu^{+2} , which leads to a marked lower diffusion rate of Pb^{+2} salts and their complexes through the membrane and, consequently, to lower metal ion transport ability in comparison with Cu^{+2} under the same conditions.

Figure 2 shows also that there was no significant difference between the investigated ionophores in the sense of effect on the amount of Pb^{+2} in both the source and the receiving phases. Also, the investigated ionophores can be arranged in the following order according to the immobilization time and the amount of the immobilized ionophore:

$$2 \geq 1 \geq 7$$

In conclusion, 7-blended CTA membranes may be used as ion-transporting or as ion-extracting agents for Cu^{+2} and Pb^{+2} , respectively. Considering the improved efficiency and if it would make a practical difference in membrane-separation performance, it could be the main target in other supplementary work in cooperation with some specialists in the field of such applications.

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