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## TRANSPORT OF PERRHENATE ANIONS ACROSS PLASTICIZER MEMBRANES WITH BASIC ION CARRIERS

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Transport experiments across polymer inclusion membranes (PIMs) are presented. The physical immobilization of trioctylamine (TOA) or methyltrioctylammonium chloride (TOMACl) as the ion carriers and *o*-nitrophenyl octyl ether as the plasticizer in cellulose triacetate as the support were used to prepare polymer inclusion membranes. The competitive transport of  $\text{ReO}_4^-$  ions from nitrate aqueous solutions through a PIM with TOA or TOMACl was investigated. The effect of the pH of the source aqueous phase on  $\text{ReO}_4^-$  transport from nitrate solution was studied. The higher efficiency of  $\text{ReO}_4^-$  removal was observed with use of the basic carrier, TOMACl. The selectivity of competitive oxoanions transport from the source phase decreases as follows:  $\text{ReO}_4^- > \text{NO}_3^- > \text{SO}_4^{2-}$ . This order of permeability correlates well with the energy of transported anions hydration.

*key words: polymer inclusion membranes, oxoanions, separation, perrhenate*

### INTRODUCTION

The selectivity and removal of toxic metal cations from water has frequently been addressed in membrane separation systems. Toxic metal anions have not received significant attention. There are specific reasons why anion receptors are more challenging to design than cation receptors (Gale, 2003).

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Anion separations are important for a number of reasons. Some anions, when introduced into the environment in sufficient quantities, pose health risks to humans and animals (Vandergrift et al., 1992). Fertilizers, feedlots, livestock waste and human waste from highly populated areas produce large amounts of nitrates, phosphates and sulfates.

Another important target of metal anion separation is technetium. Nuclear wastes contain radioactive  $^{99}\text{Tc}$ , which is often present in solution as pertechnetate (Manahan, 1994). It would be desirable to remove the radioactive pertechnetate from nuclear wastes at the reprocessing plant. Also, radioactive  $^{99}\text{Tc}$  and  $^{188}\text{Re}$  are generated in isotonic solutions as pertechnetate or perrhenate for use in medical diagnostic and therapeutics (Brix et al., 2001a). Furthermore, non-radioactive perrhenate is often used as a model anion to simulate binding of radioactive pertechnetate, since the perrhenate anion has the same charge and a similar radius as pertechnetate (Brix et al., 2001b). Permeability was higher for the oxoanions than for halide anions although hydration energies for the monovalent oxoanions are comparable to those of the halides, while hydration energies of the other oxoanions are higher.

Transport of anions was attenuated significantly in a number of cases, and very high selectivity for perrhenates was observed. Perrhenates transport was selective over the divalent anions. The selectivity for perrhenate over the divalent metal cations was also observed (Gardner et al., 2006).

Recently, ion exchange methods such as solvent extraction (Kasikov et al., 2007; Zhou et al., 1999), liquid membrane transport (Gardner et al., 2006) and polymer inclusion membrane (Marcus, 1991) in separation of perrhenate anions were presented. Marcus (1991) observed anion transport selectivity in PIM transport for  $\text{ReO}_4^-$  over  $\text{NO}_3^-$ . This trend in anion transport selectivity follows the trend of calculated hydration energy values.  $\text{NO}_3^-$  has a higher hydration energy and is transported slower than  $\text{ReO}_4^-$ , which has a lower hydration energy. Lamb et al., (2008) showed that  $\text{ReO}_4^-$  is selectively transported over  $\text{NO}_3^-$ . In the presence of  $\text{K}^+$  and  $\text{Na}^+$ ,  $\text{ReO}_4^-$  transport is promising, while  $\text{Pb}^{2+}$  promotes  $\text{NO}_3^-$  removal. Kudo et al. (2007) determined equilibrium constants for the formation of  $\text{Na}^+\text{-ReO}_4^-$ -crown ether complex. Kopunec et al., (Kopunec et al., 1998) showed that the extraction constant for  $\text{Ph}_4\text{P}^+\text{-ReO}_4^-$  ion pair is several times higher than that for  $\text{Ph}_4\text{As}^+\text{-ReO}_4^-$ .

This paper describes the competitive transport of perrhenate, sulfate and nitrate anions from aqueous solutions through PIMs with the basic carries tri-n-octylamine (TOA) and methyltrioctylammonium chloride (TOMACl). The influence of ion carriers and pH of source phase on the transport efficiency is reported. The separation of  $\text{ReO}_4^-$ ,  $\text{NO}_3^-$ ,  $\text{SO}_4^{2-}$  from acidic aqueous solutions across PIM with TOMACl was also studied.

## MATERIALS AND METHODS

### REAGENTS

Inorganic chemicals such as sodium perrhenate, sodium hydroxide, sulfuric and hydrochloric acids were of analytical grade and were purchased from POCh (Gliwice, Poland). Organic reagents, such as cellulose triacetate (CTA), *o*-nitrophenyl octyl ether (ONPOE), tri-*n*-octylamine (TOA), methyltrioctylammonium chloride (TOMACl) and dichloromethane were also of analytical grade and were purchased from Fluka and used without further purification. Aqueous solutions were prepared with double distilled water with a conductivity of  $0.1 \mu\text{S cm}^{-1}$ .

### PREPARATION OF POLYMER INCLUSION MEMBRANES

A solution containing cellulose triacetate as the support, *o*-nitrophenyl octyl ether as the plasticizer, and tri-*n*-octylamine or methyltrioctylammonium chloride as the ionic carrier in dichloromethane as the organic solvent was prepared. A specified portion of this organic solution was poured into a glass Petri dish consisting of a 9.0 cm glass ring attached to a glass plate with cellulose triacetate-dichloromethane glue. The dichloromethane was evaporated overnight, and the resulting membrane was separated from the glass plate by immersion in cold water. Two samples of membrane were cut out from the same membrane for duplicate transport experiments.

### TRANSPORT STUDIES

Transport experiments were carried out in a permeation cell in which the membrane film ( $4.9 \text{ cm}^2$  effective surface) was tightly clamped between two compartments. The aqueous receiving phase was a  $0.10 \text{ mol dm}^{-3}$  aqueous solution of sodium hydroxide ( $50 \text{ cm}^3$ ). Transport was conducted at a room temperature (23 to 25  $^{\circ}\text{C}$ ) and both the source and receiving aqueous phases were stirred at 600 rpm with synchronous motors. Samples ( $0.010 \text{ cm}^3$ ) of the aqueous receiving phase were removed periodically via a sampling port with a syringe and analyzed to determine the concentrations of  $\text{ReO}_4^-$ ,  $\text{NO}_3^-$  and  $\text{SO}_4^{2-}$ . The source phase acidity was monitored using a pH meter (multifunctional pH meter, CX-731 Elmetron, with combine pH electrode, ERH-136, Hydromet, Poland). The kinetics of the transport process through the polymer inclusion membrane is described by a first-order reaction in respect to metal ion concentration (Danesi, 1984):

$$\ln(c/c_i) = -kt \quad (1)$$

where  $c$  is the metal ion concentration ( $\text{mol dm}^{-3}$ ) in the source phase at a given time;  $c_i$  is the initial  $\text{ReO}_4^-$  concentration in the source phase;  $k$  is the rate constant ( $\text{s}^{-1}$ ); and  $t$  is the transport time (s).

To calculate the  $k$  value, a plot of  $\ln(c/c_i)$  versus time was made. The rate constant value for the duplicate transport experiment was the averaged, and the standard deviation was calculated. The permeability coefficient ( $P$ ) was calculated as follows:

$$P = -(V/A)k \quad (2)$$

where  $V$  is the volume of aqueous source phase, and  $A$  is the area of membrane.

The initial flux ( $J_i$ ) was calculated as follows:

$$J_i = Pc_i \quad (3)$$

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

$$RF = \frac{c_i - c}{c_i} \cdot 100 \% \quad (4)$$

A capillary electrophoresis system with an ultraviolet (UV) detector (Capel-105, Russia) was used to determine the concentrations of perrhenate, sulfate, nitrate, and chloride anions. The electrophoretic buffer consisted of  $5.0 \cdot 10^{-3}$  M chromium(VI) oxide,  $2 \cdot 10^{-2}$  M diethanolamine, and  $1.65 \cdot 10^{-3}$  M methyltrioctylammonium chloride (from Fluka), at a voltage of 17 kV. The detection limits in this method for the  $\text{ReO}_4^-$ ,  $\text{NO}_3^-$ , and  $\text{SO}_4^{2-}$  anions were  $0.10 \pm 0.02$ ,  $0.15 \pm 0.05$  and  $0.20 \pm 0.03$   $\text{mg/dm}^3$ , respectively.

## RESULTS AND DISCUSSION

At first, the influence of ion carriers TOA or TOMACl immobilized in cellulose triacetate membrane on perrhenate anions transport was studied. Blank experiments in the absence of the carrier yielded no significant flux across PIM with support and plasticizer only. In previous studies on chromium(VI) transport across PIM, we observed that tertiary amines, such as TOA, also have plasticizing properties (Kozlowski and Walkowiak, 2002, 2005). The polymeric inclusion membranes investigated contained 77 wt. % CTA and 23 wt. % ion carrier. As source and receiving phases, 0.10 M  $\text{HNO}_3$  and 0.10 M NaOH aqueous solutions were used, respectively. The results shown in Fig. 1 demonstrate transport of perrhenate anions from 0.10 M nitric acid across the PIM containing TOA or TOMACl. The transport conditions were set up for a high excess of  $\text{NO}_3^-$  over  $\text{ReO}_4^-$ .

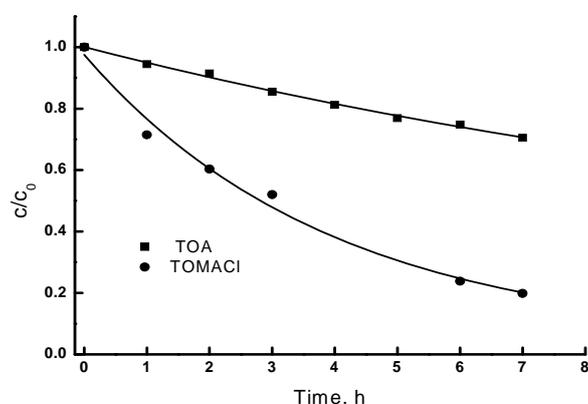


Fig. 1. Kinetics curves of perrhenate anions transport across PIM with TOA and TOMACl  
 PIMs: 77 wt. % CTA, and 23 wt. % ion carrier; source phase: 0.0050 M  $\text{ReO}_4^-$  in 0.10 M  $\text{HNO}_3$ ;  
 receiving phase: 0.10 M NaOH

The recovery factors (RF) of nitrate anions for transport with TOA and TOMACl after seven hours were equal to 5.0 % and 3.0 %, respectively. Fig. 1 shows an exponential decrease of  $\text{ReO}_4^-$  concentration in the source phase versus time. The kinetics of the  $\text{ReO}_4^-$  transport across the membrane is described by the first order. For transport across PIM with TOMACl and TOA, the fluxes were equal to 3.5 and 0.7  $\mu\text{mol}/\text{m}^2\text{s}$ , respectively.

Perrhenate removal was observed only in membranes with support (CTA) and ion carriers (TOA or TOMACl). We also applied polymer inclusion membranes containing the typical plasticizer, *o*-nitrophenyl octyl ether. The influence of source phase acidity on  $\text{ReO}_4^-$  transport through PIM was studied. PIM composition was 40 wt. % of cellulose triacetate as the support, 25 wt. % of tri-*n*-octylamine or methyltrioctylammonium chloride as the ion carrier, and 35 wt. % of *o*-nitrophenyl octyl ether as the plasticizer. These membranes containing ONPOE as the plasticizer showed much faster transport of  $\text{ReO}_4^-$  anions. The effect of perrhenate initial fluxes values on pH of source phase is shown in Fig. 2. Comparison of the perrhenate transport across PIM with TOA and TOMACl indicates that the transport rate is twice as high for quaternary ammonium salt (TOMACl), which is a more basic carrier. The results in Fig. 2 show the linear decrease of perrhenate transport flux (in log-log scale) with the pH increase values from 1 to 5. The initial transport flux value achieved for TOMACl at pH 1.0 was equal to 11.68  $\mu\text{mol}/\text{m}^2\text{s}$ .

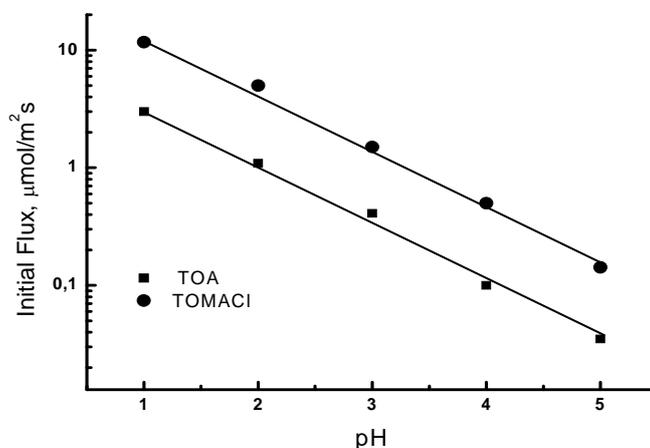


Fig. 2. Initial flux values vs. pH of the source phase. Membrane:  $0.8 \text{ cm}^3$  ONPOE / 1.0 g CTA, 1.0 M carriers (TOA, TOMACI); source phase:  $5 \cdot 10^{-3} \text{ M ReO}_4^-$ ,  $\text{H}(\text{Na})\text{NO}_3 \text{ I}=0.1 \text{ M}$

Finally, competitive transport of perrhenate, nitric and sulfuric anions from acidic solutions was performed. As the aqueous source phase the solution containing  $5 \cdot 10^{-4} \text{ M ReO}_4^-$  in  $0.05 \text{ M HNO}_3$  and  $0.05 \text{ M H}_2\text{SO}_4$  was used. The used membrane contained: 1.0 M carrier (TOMACI) and  $0.8 \text{ cm}^3$  ONPOE/1.0 g CTA. As the receiving phase, 0.1 M NaOH was applied. The dependence of recovery factors (RF) for perrhenate, nitrate and sulfate anions vs. time in transport across PIM with TOMACI as ionic carrier is shown in Fig. 3.

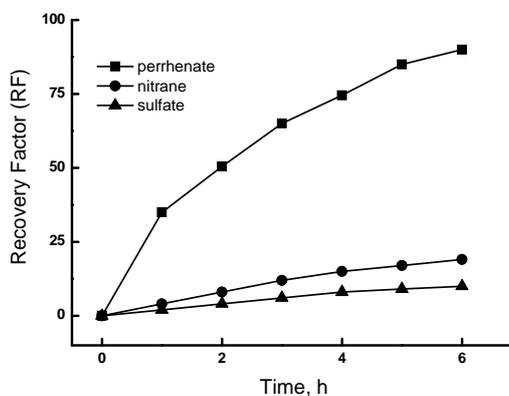


Fig. 3. Recovery factor (RF) vs. competitive transport of perrhenate, nitrate and sulfate on PIM with TOMACI. PIM: 1.0 M TOMACI,  $0.8 \text{ cm}^3$  ONPOE / 1.0 g CTA; source phase:  $5 \cdot 10^{-4} \text{ M ReO}_4^-$  in  $0.05 \text{ M HNO}_3$  and  $0.05 \text{ M H}_2\text{SO}_4$ ; receiving phase:  $0.10 \text{ M NaOH}$

As can be seen from Fig. 3, the selectivity order of transport through PIM with TOMACI was as follows:  $\text{ReO}_4^- > \text{NO}_3^- > \text{SO}_4^{2-}$ . The removal of perrhenate was

higher than that of sulfate and nitrate anions in spite of the high excess of  $\text{NO}_3^-$  and  $\text{SO}_4^{2-}$  anions. For these transport conditions the selectivity coefficients for perrhenate/nitrate and perrhenate/sulfate were: 11.1 and 8.2, respectively. The hydration energy of  $\text{SO}_4^{2-}$ ,  $\text{NO}_3^-$  and  $\text{ReO}_4^-$  anions were  $-1103 \text{ kJ mol}^{-1}$ ,  $-314 \text{ kJ mol}^{-1}$  and  $-240 \text{ kJ mol}^{-1}$ , respectively (Gardner et al., 2006). Hydration energy was highest for  $\text{SO}_4^{2-}$ , and lowest for  $\text{ReO}_4^-$  anions. There is the correlation between selectively sequence of anions transported,  $\text{ReO}_4^- > \text{NO}_3^- > \text{SO}_4^{2-}$ , and hydrophobicity. The highest transported anions are perrhenates, which are the least hydrated.

## CONCLUSIONS

Perrhenate anions can be effectively separated from aqueous solutions containing high excess of sulfate and nitrate anions by polymer inclusion membrane transport with basic ion carrier, such as TOMACl. For both TOA and TOMACl, the initial fluxes decreased as the pH of the source phase increased. For competitive transport, the removal of sulfates and nitrates is lower than that of perrhenates, in spite of the high excess of  $\text{NO}_3^-$  and  $\text{SO}_4^{2-}$  anions. The selectivity order sequence for anions fluxes transported across the polymer inclusion membrane with TOMACl was  $\text{ReO}_4^- > \text{NO}_3^- > \text{SO}_4^{2-}$ . This correlates well with the hydrophobicity of these anions.

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W pracy opisano badania laboratoryjne dotyczące selektywnego wydzielania anionów nadrenianowych z roztworów azotanowych przez polimerowe membrany inkluzyjne zawierające w roli przenośników jonów trioktyloaminę lub chlorek metyloktioamoniowy oraz trioctan celulozy jako matrycę. Określono również wpływ pH fazy zasilającej na efektywność transportu  $\text{RO}_4^-$  przy użyciu polimerowej membrany inkluzyjnej zawierającej w/w przenośniki jonów, plastyfikator, tj. eter *o*-nitrofenylooktylowy, immobilizowane do matrycy z trioctanu celulozy. Wykazano, że chlorek metyloktioamoniowy z roztworów silnie kwaśnych efektywnie transportował aniony nadrenianowe niż trioktyloamina. Zbadano również konkurencyjny transport oxoanionów przez plastyfikowaną membranę zawierającą chlorek metyloktioamoniowy i eter *o*-nitrofenylooktylowy. Z porównania szybkości transportu wynika, że malała ona w szeregu  $\text{ReO}_4^- > \text{NO}_3^- > \text{SO}_4^{2-}$ . Selektowność badanego układu membranowego powiązано z procesem dehydratacji anionów selektywnie transportowanych przez membranę zawierającą czwartorzędową sól amoniową

*słowa kluczowe: nadreniany, separacja, polimerowe membrany inkluzyjne*