

# Pertraction of Cations in a Hybrid Membrane System Containing Soluble Polymeric Ionophores

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**ABSTRACT:** A hybrid membrane system composed of two insoluble cation-exchange membranes (Nafion) and a liquid membrane in between was studied. A series of organic and aqueous liquid membranes containing soluble polymers as macromolecular ionophores (macroionophores) was prepared and tested. The pertraction (membrane-transport) characteristics of poly(ethylene glycol) and its ionizable derivatives, including as poly[poly(oxyethylene) phosphate] (PPOEP) and di-[ $\omega$ -methoxy poly(oxyethylene)] phosphate, were measured and are discussed as dependent on the composition and molecular mass of a macroionophore. The liquid membrane composed of PPOEPs dissolved in dichloroethane combined the cation-exchange properties with neutral coordination functionalities introduced by the poly(oxyethylene) backbone of this ionophore. The overall fluxes, facilitation factors, and the membrane system selectivity were measured in the carrier-mediated pertraction of transient metal cations ( $\text{Cu}^{2+}$ ,  $\text{Zn}^{2+}$ ,  $\text{Mn}^{2+}$ ,  $\text{Co}^{2+}$ , and  $\text{Ni}^{2+}$ ). PPOEP could facilitate the pertraction of  $\text{Zn}^{2+}$  and  $\text{Cu}^{2+}$  over  $\text{Ni}^{2+}$  and  $\text{Co}^{2+}$ . In the case of an aquatic hybrid membrane system, high but nonselective ionic fluxes were observed. © 2002 John Wiley & Sons, Inc. *J Appl Polym Sci* 84: 99–109, 2002; DOI 10.1002/app.10263

**Key words:** polymer; liquid; membranes; macroionophores; pertraction; separation; ion exchangers; polyelectrolytes

## INTRODUCTION

A selective removal of toxic metals or the recovery of valuable ones from the environment and industrial waste waters can be achieved by the application a variety of separation methods, such as adsorption, ion exchange, precipitation, solvent extraction, and numerous membrane techniques. Compared with the predominating solvent-ex-

traction technology, liquid membrane (LM) transport (pertraction) and Donnan dialysis (an ion-exchange dialysis exploiting solid polyelectrolyte membranes) markedly reduce the amount of involved reagents and, thus, respective operational costs. The development of proper liquid membrane technology is, however, limited by the instability and short lifetime of some LM systems, for example, the supported liquid membranes.<sup>1</sup> On the other hand, the functionalized polymer membranes (typically, the membranes with attached sulfonic groups) are easy to handle but sometimes exhibit low selectivity towards different cations of the same valence. To combine the high selectivity of LMs with the properties of

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polymeric ion-exchange membranes, the hybrid membrane systems were designed and experimentally evaluated as new, stably working, and selective membrane devices.<sup>2–5</sup> In the simplest case, the multimembrane hybrid system for the pertraction of metal cations is composed of two cation-exchange membranes and a liquid membrane layered in between. These two components, that is, the polymer and LMs, should allow interfacial coupling of respective ionic fluxes by an ion-exchange reaction or complexation between the mobile carrier molecules (ionophores) in a LM and ion-exchange groups attached to the polymer backbone of the LM-adjacent membranes. In addition, polymer chemistry contributes to the LM area by supplying some new reagents, which by analogy to the low-molecular-weight ionophores (LM carriers), are classified as macroionophores (macromolecular carriers). The macroionophores are represented by various soluble polymers that are able to bind and selectively transport target substances throughout liquid membranes. The respective studies can be related to the first article by Shultz et al.,<sup>6</sup> which described such macroionophores as  $\alpha,\omega$ -poly(cycloalkane)diyls. The polymers containing long segments (at least five to six units) of 2,5-tetrahydrofurandiyl, 2,6-tetrahydropyrandiyl, and 2,4-bicyclo(3.2.1)-3-oxaoctanediyl were therein reported to bind methylene blue and cations of varying sizes (e.g.,  $\text{Li}^{2+}$ ,  $\text{K}^+$ ,  $\text{Ba}^{2+}$ ). Novak and Grubbs<sup>7</sup> synthesized poly(7-oxabornene) of the ionophoric properties towards  $\text{K}^+$  and  $\text{Cs}^+$  (but not  $\text{Li}^+$ ) and, surprisingly, toward large polyaromatic dyes (methylene blue, rhodamine 6G). It was reported that the binding properties of the previous polymers resulted from their helical conformation and their ability to interact with inorganic cations similarly to crown ethers. Analogous properties of poly[(1  $\rightarrow$  6)-2,5-anhydro-3,4-di-*O*-ethyl-D-glucitol] were described by Hashimoto et al.<sup>8</sup> On the other hand, Burger and Seebach<sup>9</sup> studied the transport properties of biomimetic poly(3-hydroxybutanoic acid) [poly(3-HB);  $n = 28$ ], esterified carboxylic groups] and observed its good ionophoric properties toward alkali and alkaline-earth metal cations, despite an open-chain character of poly(3-HB) and a lack of geometry suitable for the complexation of metal cations. Ikeda et al.<sup>10</sup> reported on the ionophoric properties of liquid polybutadiene as the component of the supported LM revealing excellent transport ability towards  $\text{Hg}^{2+}$  over  $\text{Ca}^{2+}$ ,  $\text{Zn}^{2+}$ ,  $\text{Cd}^{2+}$ , and  $\text{Ag}^+$  nitrates. Recently, Ishida and colleagues<sup>11</sup> described the properties of oligobenzo-

xazine (soluble in various solvents) as the ionophore of properties comparable to these shown by calixarenes in respect to alkali and alkaline-earth metal cations. Also, the transport of some organic substances was achieved with the use of macroionophores. In addition to the results concerning methylene blue and rhodamine mentioned previously, it was proven by Kakuchi et al.<sup>12</sup> that poly[(1  $\rightarrow$  6)-2,5-anhydro-3,4-di-*O*-methyl-D-glucitol] enables the enantioselective transport of some racemic methyl amino esters. Yahaya et al.<sup>13</sup> reported on the carrier properties of liquid functionalized polyorganosiloxanes when used in the supported LMs as transporters of lactic acid and its ethyl ester. By analogy to the ionisable low-molecular-weight carriers (e.g., carboxylated crown ethers), the application of some hydrophobic and amphiphilic polyelectrolytes as the LM components can alternatively be taken into account. Such studies can relate to the first article by Varoqui and Pefferkorn<sup>14</sup> on the application of a hydrolyzed copolymer of maleic anhydride with vinyl hexadecyl ether (weight-average molecular weight =  $3 \times 10^5$ ) as the  $\text{Na}^+/\text{H}^+$  transport mediating ionophore. Another carboxylated polymer (i.e. carboxylated polystyrene) was used for transporting some amino acids by Ersoz et al.<sup>15</sup> In our laboratory, similar investigations concerning the application of poly(alkylene phosphates)<sup>16</sup> and poly[poly(oxyethylene) phosphate]s (PPOEPs)<sup>16,17</sup> as transporters of transient metal cations through the bulk and emulsion LMs were carried out. Moreover, water soluble organic polyphosphates,<sup>18–20</sup> sodium poly(vinyl sulfonate), and branched polyethylenimine<sup>21</sup> were used by some authors for preparing new hybrid aqueous LMs for the separation of metal cations or organic anions. The most promising macroionophores can, however, be synthesized on the basis of poly(ethylene glycol) (PEG) as an easily available and cheap polymer with properties parallel to the 18-crown-6 ether macrocycle. Actually, PEG and its derivatives have been used as extractants for various metal ions<sup>22–24</sup> (i.e., starting from PEG300, which is composed of six to seven oxyethylene units, the PEG chain has adequate length for chelating metal cations). Simultaneously, as shown by Okada,<sup>25</sup> the respective complex formation constants are dependent on the PEG degree of polymerization. The efficiency of PEG as the component of emulsion LMs<sup>26</sup> and the corresponding comparison of PEG and its phosphoric acid derivatives were reported elsewhere.<sup>17,27</sup>

Having reviewed a number of articles concerning the properties of soluble polymers as extractants and macroionophores, we point to the following arguments for their application:

1. The pseudocavity created by a macroionophore can be tailored to fit cations by variation in the degree of polymerization.
2. The macroionophore can be separated from any liquid phase and then recycled after a standard filtration treatment.
3. Specifically, the application of PEG with different molecular masses seems encouraging because of its low cost and commercial availability. In comparison, crown ethers are often difficult to synthesize and rather expensive.
4. PEGs are nontoxic, and thus, these polymers can be used in all the membrane processes applied in pharmacy or in the food industry.
5. The polymer can be modified to obtain a variety of macroionophores with carboxylic, phosphate, or phosphodiester acidic groups, which can improve the respective transport properties and enable the pH-driven transports.
6. Finally, PEGs and their derivatives are soluble in aqueous and organic media, which allows the construction of new aquatic LM systems.

Regarding the previous arguments, we constructed and present herein a membrane system composed of soluble and insoluble polymers as components activating the membrane process of pertraction. The main task of this study was to test the LMs containing such macroionophores as PEG2000, PPOEP, and di- $[\omega$ -methoxy poly(oxyethylene) phosphate] (DMPOEP) with regard to their ability to transport divalent metal cations. To evaluate the competitive pertraction behavior of PPOEPs and PEG, a series of pertraction processes was carried out with the most frequently encountered transition-metal cations (Zn, Mn, Cu, Co, and Ni) as components of various industrial waste waters.

## EXPERIMENTAL

### Macroionophores

#### *Polyphosphates of PEG2000: PPOEPs*

Poly(*H*-phosphonate)s of PEG for PPOEPs synthesis were prepared according to the procedure

described in detail by Penczek and colleagues<sup>28</sup> PEG2000 (20 g or 0.01 mol), 1.32 g (0.012 mol) of dimethyl *H*-phosphonate and a catalytic amount of sodium (about 0.005 g) were placed in a vacuum distillation apparatus equipped with a magnetic stirring bar and a large Rotaflo stopcock separating the distillation flask from the condenser. During the reaction time (about 30 h), the reaction mixture was stirred, the temperature was gradually increased to 180°C, and the pressure was decreased to 0.02 mm Hg. When the viscosity of the reaction mixture significantly increased and stirring was no longer possible, the mixture was dissolved in dry CH<sub>2</sub>Cl<sub>2</sub> and oxidized to polyphosphate with N<sub>2</sub>O<sub>4</sub> according to the previously described procedure.<sup>29</sup> Crude PPOEP was purified by ultrafiltration from water solution with an Amicon ultrafiltration stirred cell, with a Diaflo membrane (molecular mass cutoff = 3000) and was finally dried under vacuum.

#### *Phosphate of Monomethoxy Ether of PEG2000: DMPOEP*

Monomethoxy ether of PEG2000 (20 g), 5.5 g (0.05 mol) of dimethyl *H*-phosphonate, and a small grain of sodium were placed in a vacuum distillation apparatus equipped with a magnetic stirring bar. The mixture was stirred for 4 h at 80°C/500 mm Hg with distillation off CH<sub>3</sub>OH and, thereafter, was stirred for 10 h at 140°C at the same pressure. Then, the temperature was increased to 170°C, and the pressure was decreased to 0.02 mm Hg. At this stage of the reaction, dimethyl *H*-phosphonate was formed by transesterification. *H*-phosphonate of PEG was then oxidized to phosphate according to a procedure described elsewhere.<sup>29</sup> Crude DMPOEP, after dissolution in water, was purified by ultrafiltration (membrane with a molecular mass cutoff of 1000) and finally dried under vacuum.

#### *PEG2000*

The polymer was purchased from Fluka Chemie (Switzerland) and used as received.

### Membranes and Solutions

The perfluorinated cation-exchange membrane Nafion-120 (DuPont, Wilmington, DE) was selected for the construction of the multimembrane hybrid system (MHS) because of its good stability in contact with the 1,2-dichloroethane phase of a LM. This ionomeric membrane is composed of a

perfluoroethylene backbone with pendant sulfonic acid groups. The membrane contains 0.85 eq of sulfonic acid groups per 1 kg of a dried polymer sample, as determined by standard potentiometric titration.<sup>30</sup> The thickness of the membrane measured with a micrometer was 0.023 cm. Water content in the Nafion membrane in its acidic form was evaluated by comparison of the mass of polymer in its swollen and vacuum-dried form. The resulting value of 26 wt % corresponded with approximately 44 vol % of water in the swollen membrane. Before transport experiments, the membrane samples for the MHS were soaked several times in 1 mol/dm<sup>3</sup> sulfuric acid solution and then washed in distilled water to achieve pure H<sup>+</sup> ionic form.

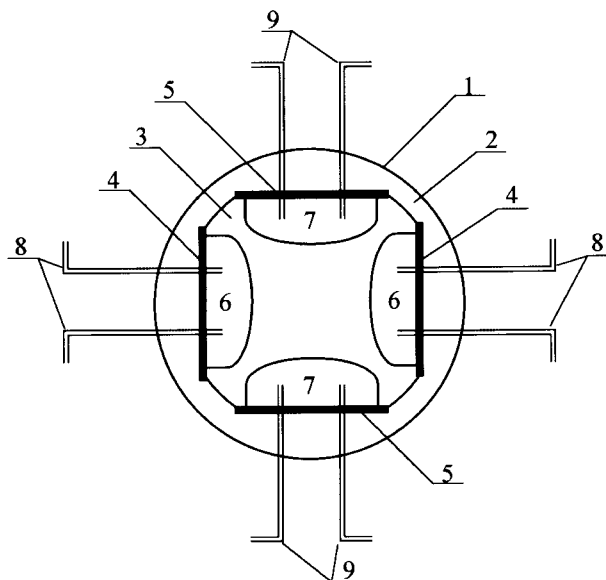
The bulk liquid membranes (BLMs) were prepared by dissolution of the appropriate amount of PPOEP, DMPOEP, or PEG in 1,2-dichloroethane (DCE; purchased from POCh, Gliwice, Poland, reagent grade) or in twice distilled water. The average molecular mass of PPOEP (with POE2000) was 31,000 or 14,700, which corresponded with the average degree of polymerization (DP<sub>n</sub>), 14.8 and 7.5, respectively. The average molecular mass of DMPOEP was 4126. Both polymers contained POE2000 units with a DP<sub>n</sub> of approx. 45.5. To compare different polymers as macroionophores, the BLM solutions with each polymer of the concentration 12 g/dm<sup>3</sup> were prepared. To study the dependence of pertraction rates on the macroionophore concentration, the PPOEP solutions of concentrations ranging from 4 to 480 g/dm<sup>3</sup> were applied.

At zero-time of the pertraction experiment, the membranes forming the MHS were always in their hydrogen form. For each transport run, a fresh LM was prepared, whereas the Nafion-120 membranes were reconverted into their hydrogen form.

The multicomponent feed solution (source phase) was prepared by dissolution of a weighed amount of CuSO<sub>4</sub>, ZnSO<sub>4</sub>, MnSO<sub>4</sub>, CoSO<sub>4</sub>, and NiSO<sub>4</sub> (POCh, reagent grade) to the concentration of  $2 \times 10^{-3}$  mol/dm<sup>3</sup> each. A solution of sulfuric acid (Chemana, Toru, Poland, reagent grade) of the concentration 0.1 mol/dm<sup>3</sup> was used as a stripping solution.

#### Pertraction Cell and Operation Conditions

The pertraction experiments were carried out with laboratory equipment described in detail elsewhere.<sup>4,27</sup> The feed and stripping solutions



**Figure 1** Horizontal cross-section of a multi-window hybrid membrane pertractor: (1) glass vessel, (2) agitated LM, (3) head made of Teflon, (4) feed and (5) stripping interface Nafion membranes, (6) feed and (7) stripping solution, and (8) feed and (9) stripping solution input and output.

were circulated through the contact cells ( $\sim 1$  cm<sup>3</sup>) of the pertractor and contacted with a LM through the respective Nafion membranes, as presented in Figure 1. A feed volume (350 cm<sup>3</sup>), and a stripping solution of volume 150 or 50 cm<sup>3</sup> were pumped at the flow rate 2.5 cm<sup>3</sup>/min by a multichannel peristaltic pump (Minipuls 3 Gilson). The exposed area of the feed and strip side contacting Nafion membranes was 5.85 cm<sup>2</sup>. A LM of volume 25–30 cm<sup>3</sup> was agitated with a magnetic bar at 300–350 rpm (Heidolph MR 2000 magnetic stirrer). The experiments were carried out at  $25 \pm 1^\circ\text{C}$  over a time sufficient to attain quasi-stationary conditions for ionic fluxes. The external aqueous solutions were sampled (0.5–1 cm<sup>3</sup>) in time, and the concentration of each metal was determined by means of absorption spectrophotometry (Varian, SpectrAA20) with standard deviations ranging from 0.5–3%. Because of coupling the metal and hydrogen cation fluxes (cations transferred in the opposite directions in equivalent amounts) and the limited volumes of the solutions, the feed pH changed in time, typically from 5.5 to 3. The feeds, however, were not buffered to avoid competition of other solutes to the cation-exchange sites of the Nafion membranes and the LM components.

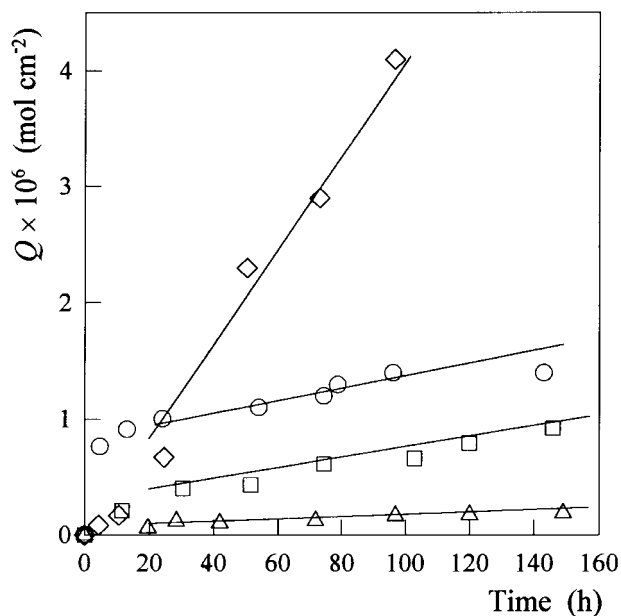
## Characterization

The pertraction results were analyzed with cumulative  $Q = f(t)$  curves, where  $Q$  denotes the number of metal moles transported through  $1 \text{ cm}^2$  of the cation-exchange membrane and stripping solution interface. Under quasi-stationary conditions, this dependence becomes near-linear, which allows one to calculate the fluxes (pertraction rates, stripping rates) as the slope of the linear part of the  $Q = f(t)$  plot:

$$J = \Delta Q / \Delta t \quad \text{with} \quad dJ/dt \approx 0 \quad (1)$$

A weighed least-square linear regression analysis was applied to determine the flux ( $J$ ) values with the standard deviations resulting from atomic absorption spectrometry determinations as respective statistical weights. Only the data that correspond with the squared linear regression coefficient  $r^2 > 0.9$  were accepted. To evaluate the separation characteristics for the MHS, the separation coefficients, as defined by eq. (2), were calculated:

$$\alpha_{\sum M_j}^{M_k} = \frac{[M]_{k,s} \sum_{j \neq k} [M]_{j,f}}{[M]_{k,f} \sum_{j \neq k} [M]_{j,s}} \quad (2)$$



**Figure 2** Cumulative transport curves for the MHS with a bulk DCE membrane and macroionophores: ( $\diamond$ ) PPOEP-14700, ( $\circ$ ) DMPOEP, ( $\square$ ) PEG, and ( $\triangle$ ) the blank system.

**Table I** Comparison of Macroionophore Efficiency in a Multimembrane Hybrid System

Macroionophore	Overall Flux: $J \pm SD$ (mol/cm <sup>2</sup> s)	FF
PPOEP-14700	$(1.3 \pm 0.1) \times 10^{-11}$	73
DMPOEP	$(1.2 \pm 0.2) \times 10^{-12}$	7
PEG2000	$(1.2 \pm 0.2) \times 10^{-12}$	7
No carrier	$(1.8 \pm 0.3) \times 10^{-13}$	1

where  $[M]$  is the M cation concentration and  $k$  denotes the species to separate over remaining  $j$  species. Symbols  $f$  and  $s$  denote the feed and stripping solution, respectively. The value of a separation coefficient higher than 1 indicates the separation effect; that is, the stripping solution is enriched in  $k$  species relatively to  $j$  species when compared to the feed solution. To evaluate the effect of the carrier on the pertraction phenomena, the facilitation factors (FF) were calculated as the ratio

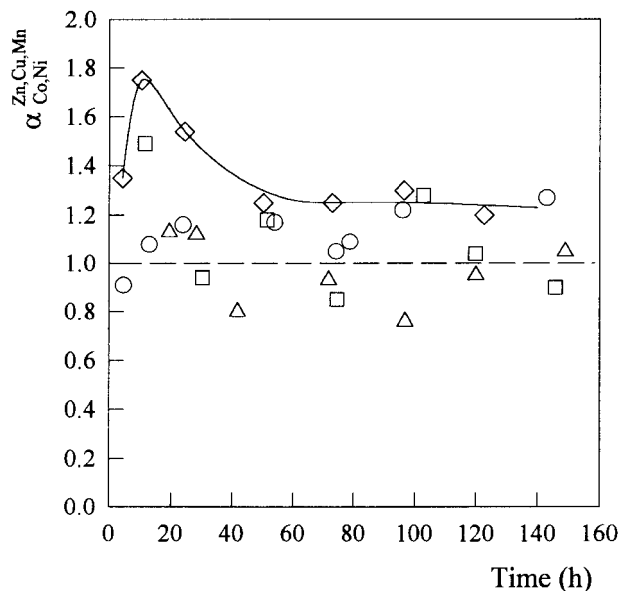
$$FF = J_c / J_b \quad (3)$$

where  $J_c$  and  $J_b$  denote the flux observed in the presence of the carrier and in the blank system (without any carrier), respectively.

## RESULTS AND DISCUSSION

### Dependence of Pertraction on Macroionophore Composition

To compare the carrier properties of PPOEP, DMPOEP, and PEG, the bulk liquid membranes containing the same amount ( $12 \text{ g/dm}^3$ ) of the polymer in DCE were prepared and tested in the MHS. The experimental results are presented in Figure 2 as the total (all metal cations) cumulative curves  $Q = f(t)$ . The corresponding curves show an interesting difference between PPOEP-14700 and DMPOEP, which can be regarded both as a part of the PPOEP chain or as an ionic derivative of respective glyme (PEG methyl ether). The values of overall fluxes presented in Table I indicate a much lower efficiency of DMPOEP in the pertraction process when compared to PPOEP. To some degree, this effect can be explained by general properties of glymes, which were reported to be less effective donor systems than diols.<sup>31</sup> Consequently, as proven by Buncel

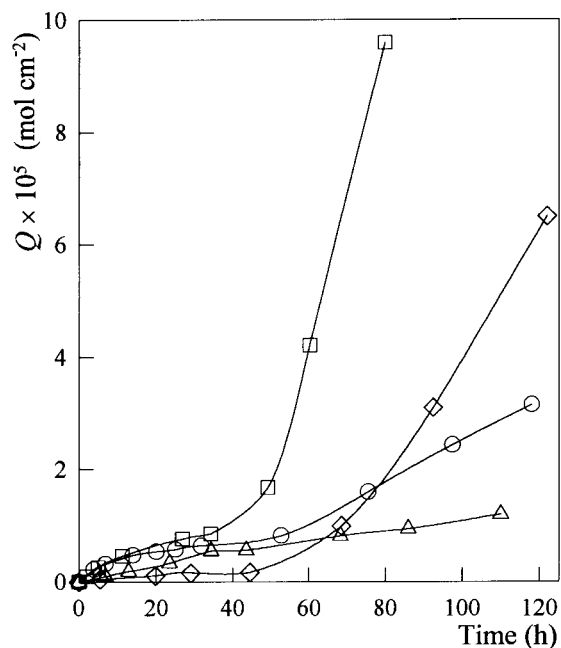


**Figure 3** Separation coefficient of  $\text{Zn}^{2+}$ ,  $\text{Cu}^{2+}$ , and  $\text{Mn}^{2+}$  over  $\text{Ni}^{2+}$  and  $\text{Co}^{2+}$  in the MHS with ( $\diamond$ ) PPOEP-14700, ( $\circ$ ) DMPOEP, ( $\square$ ) PEG, and ( $\triangle$ ) the blank system.

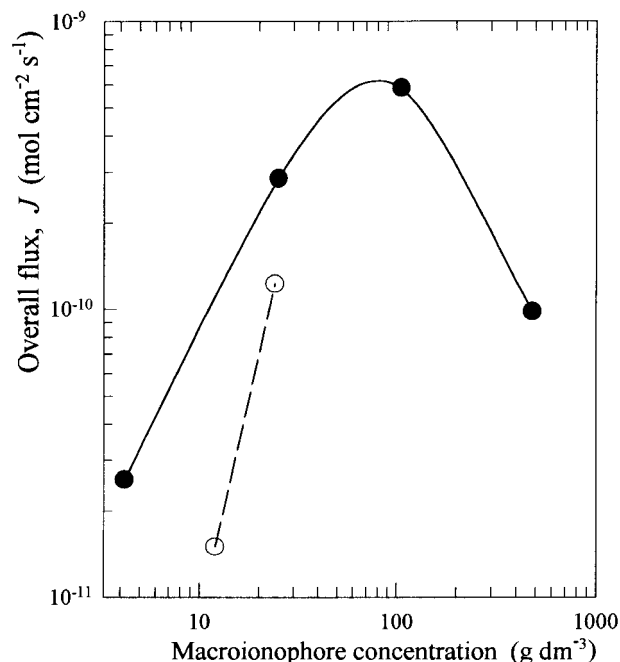
and colleagues,<sup>32</sup> the stability constants for glyme complexes are lower than these of oligoglycols. However, the presence of an ionic phosphodiester group introduces some additional carrier properties that finally allow attainment of a result comparable with the one observed for pure PEG as a macroionophore. This can be concluded from the values of the FFs for the pertraction process calculated from eq. (3) and listed in Table I. In calculations, the blank flux equal to  $1.8 \times 10^{-13}$  mol/cm<sup>2</sup> s as the mean value from the experiments repeated after each series of transport runs was used. This value is in accordance with that reported by Izatt et al.<sup>33</sup> for a simple BLM made of DCE and evaluated to be less than  $1 \times 10^{-12}$  mol/cm<sup>2</sup> s. In fact, FF values observed for the macroionophores varied from 7 to 73, indicating that PPOEP polymer was the best reagent to use in the LM.

From a number of articles,<sup>34–37</sup> it can be concluded that metal cations have the ability to organize flexible PEG chains; that is, PEG or POE chains can wrap the ions in a helical fashion. It means that, contrary to 18-crown-6 ether, PEG can recognize and differentiate cations of a diameter lower than the cavity diameter of its macrocyclic analog. In the case of PPOEPs, this property can be additionally modified by the presence of phosphodiester groups, according to their own

cation-exchange selectivity order. The inspection of data concerning the transport rates of particular cations (see later) allowed us to conclude that it is possible to attain the separation between  $\text{Cu}^{2+}$ ,  $\text{Zn}^{2+}$ ,  $\text{Mn}^{2+}$ , and  $\text{Ni}^{2+}$  and  $\text{Co}^{2+}$ . The respective separation coefficients ( $\alpha_{\text{Co,Ni}}^{\text{Zn,Cu,Mn}}$ ), as dependent on time of transport, are presented in Figure 3. These results show that this separation effect is attainable in the case of PPOEP and becomes rather weak in the case of DMPOEP or PEG itself. Qualitatively, the separation order  $\text{Zn}^{2+}$ ,  $\text{Cu}^{2+}$ ,  $\text{Mn}^{2+} > \text{Ni}^{2+}$ ,  $\text{Co}^{2+}$  seems to be in accordance with the theoretical prediction from the Irving–Williams order<sup>38</sup> suggesting the following sequence:  $\text{Zn} < \text{Cu} > \text{Ni} > \text{Co}$ . In fact, the order  $\text{Cu(II)} > \text{Zn(II)} > \text{Ni(II)}$  was observed experimentally<sup>39</sup> in the case of acyclic polyether dicarboxylic acids (i.e. in the case when the formation of the pseudo-18-crown-6 structure, based predominantly on an induced-fit mechanism, is responsible for the cation recognition). Thus, one can conclude that the presence of phosphorus-containing ion-exchange groups induces the properties typical for the polyether chain of PEG. Their role seems to correspond with the concept of the access mechanism in bifunctional polymer resins as postulated by Alexandratos and Quillen<sup>40</sup> and observed by us in the case of sim-



**Figure 4** Cumulative transport curves the MHS containing PPOEP-31000 of different concentrations in the BLM: ( $\triangle$ ) 4.2, ( $\diamond$ ) 25, ( $\square$ ) 105, and ( $\circ$ ) 480 g/dm<sup>3</sup>.



**Figure 5** Dependence of quasi-stationary overall fluxes on the macroionophores concentration for the MHS with a BLM containing (●) PPOEP-31000 and (○) PPOEP-14700.

pler POE bisphosphates.<sup>27</sup> According to this mechanism, the main role of the ionic group is to supply a cation at the proximity of PEG pseudocyclic structures and to assure electroneutrality of the formed complex.

#### Pertraction with PPOEPs as Macroionophores

The results illustrating the efficiency of two macroionophores differing only in their molecular mass (i.e., PPOEP-31000 and PPOEP-14700) are presented in Figures 4 and 5 and Table II. The cumulative transport curves drawn in Figure 4 indicate a rather complex character of the pertraction phenomena in the studied system because of the multi-ionic composition of the feed and resulting transport competition phenomena. Nevertheless, quasi-stationary conditions were obtained, and the respective fluxes were calculated and plotted in Figure 5 as dependent on the macroionophore concentration. Depending on the carrier concentration and its molecular mass, the fluxes varied from  $1 \times 10^{-11}$  to  $6 \times 10^{-10}$  mol/cm<sup>2</sup> s for concentrations in the range from 4 to 480 g/dm<sup>3</sup>. Because PEG2000 exhibits properties parallel to 18-crown-6 type ionophores, the overall fluxes from Table II can be compared with those

reported by Izatt et al.<sup>41</sup> for the competitive transport of Cd(SCN)<sub>2</sub> and Zn(SCN)<sub>2</sub> from 0.05M feed solution with the use of bis-(1-hydroxyheptylcyclohexano)-18-crown-6 in phenylhexane (0.05 mol/dm<sup>3</sup>), where the overall flux of Zn and Cd was  $4.34 \times 10^{-11}$  mol/cm<sup>2</sup> s. Similar results (i.e., fluxes ranging from  $1 \times 10^{-11}$  to  $5.6 \times 10^{-10}$  mol/cm<sup>2</sup> s) were reported<sup>42</sup> for the transport of divalent metal cations (Ca<sup>2+</sup>, Sr<sup>2+</sup>, Ba<sup>2+</sup>) when mediated by dibenzo-18-crown-6 in a BLM.

The dependence of fluxes and FFs on the macroionophore concentration (Fig. 5) showed a maximum along the concentration axis. The simplest explanation for this phenomenon is the opposite influence of the polymeric carrier concentration on the fluxes as the factor increasing the LM permeability and simultaneously decreasing this permeability because of higher viscosity of the LM solution. Alternatively, it is possible to explain lowering the fluxes at very high polymer concentrations (480 g/dm<sup>3</sup>) by the formation of gel-like structures that can reduce the mobility of a macroionophore in the LM phase. The results concerning POEs terminated at both ends with phosphonium ion endgroups (di-ionic poly-EO), presented by Kubisa and Biedron,<sup>43</sup> also support this possibility. These polymers showed predominant intramolecular aggregation (cyclization) of terminal ionic groups in dilute solutions and predominant intermolecular aggregation at higher concentrations, which leads to cross-linked networks. On the other hand, the fluxes for PPOEP-31000 normalized to 1 mol of acidic group (see Table II, the carrier transport efficiency) were very similar. This suggests that the main factor determining the flux value was the presence of ionic groups in PPOEP and their overall concentration in the LM.

The separation ability of the studied system is characterized by the plots in Figures 6 and 7, where the results concerning the cumulative curves for particular cations and respective separation coefficients are drawn as a function of time. These results correspond with the pertraction in the system with a BLM containing PPOEP-31000 of the concentration 480 g/dm<sup>3</sup>. Any special qualitative differences in the shape of separation curves were observed for other pertraction experiments. The results presented in Figure 7 prove that under stationary conditions, the fluxes showed the order: Zn, Cu, Mn > Ni, Co, as suggested previously. The curves were highly differentiated in the nonstationary-state transport regime (0–40 h), where the order could be addition-

**Table II** Transport Characteristics for MHS Pertraction with PPOEP-Type Macroionophores

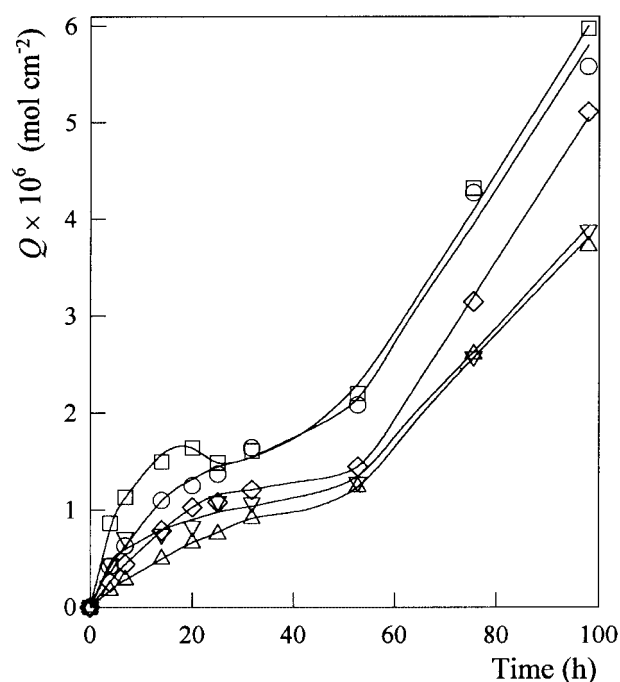
Macroionophore	Concentration in the BLM (g/dm <sup>3</sup> )	Overall Flux: $J \pm SD$ (mol/cm <sup>2</sup> s)	Transport Efficiency (mol/cm <sup>2</sup> s mol <sub>PPOEH</sub> )	FF
PPOEP-31000	4.2	$(2.6 \pm 0.3) \times 10^{-11}$	$(5.2 \pm 0.6) \times 10^{-7}$	142
PPOEP-31000	48	$(2.8 \pm 0.4) \times 10^{-10}$	$(4.9 \pm 0.7) \times 10^{-7}$	1583
PPOEP-31000	105	$(5.9 \pm 0.8) \times 10^{-10}$	$(4.7 \pm 0.6) \times 10^{-7}$	3261
PPOEP-31000	480	$(9.8 \pm 0.2) \times 10^{-11}$	$(1.7 \pm 0.03) \times 10^{-8}$	547
PPOEP-14700	12	$(1.2 \pm 0.3) \times 10^{-11}$	$(6.9 \pm 2) \times 10^{-8}$	68
PPOEP-14700	24	$(1.2 \pm 0.2) \times 10^{-10}$	$(3.5 \pm 0.6) \times 10^{-7}$	683

ally differentiated to  $Zn > Cu > Mn > Ni > Co$ . The values of separation coefficients drawn versus time seen in Figure 7 indicate that PPOEP allowed achievement of a preferential transport ( $\alpha > 1$ ) of  $Zn^{2+}$  and  $Cu^{2+}$ , with a discrimination of  $Co^{2+}$  and  $Ni^{2+}$  ( $\alpha < 1$ ), and a neutral behavior towards  $Mn^{2+}$  ( $\alpha \approx 1$ ).

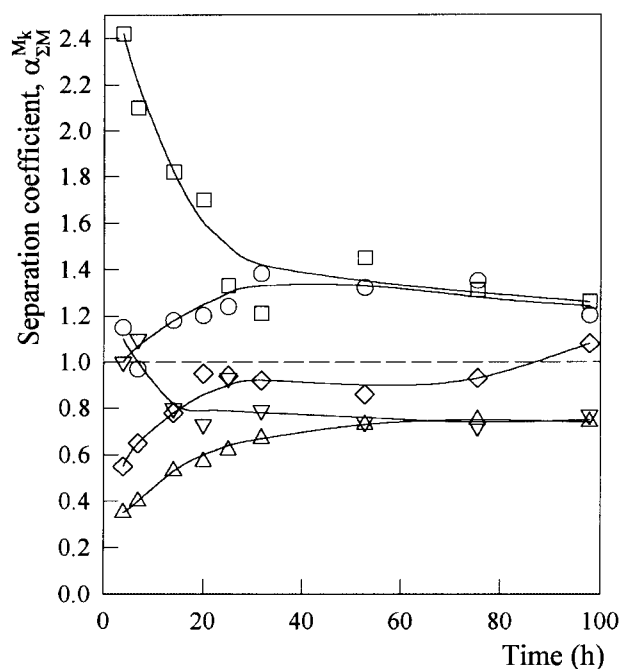
#### Aqueous Hybrid Membrane System

The amphiphilic character of PPOEP allowed construction of a hybrid membrane system with an aqueous LM. The use of water-soluble polymers in LM systems is a relatively new idea aimed for the

solution of the problems of membrane biomimetics<sup>18,19</sup> or preparation of some new membranes of practical importance.<sup>20,21</sup> The application of polyelectrolytes for this purpose is possible on condition that the external, additional polymer membranes (porous or functionalized) are impermeable for the macroionophore. This can be achieved by the establishment of a proper relation between the molecular mass of the macroionophores and the membrane pores (cutoff) and/or by exploitation of the Donnan exclusion of charged species from the ion-exchange membrane in the case of ionic carriers (this study). The total cumulative transport curves corresponding with the pertraction experiments

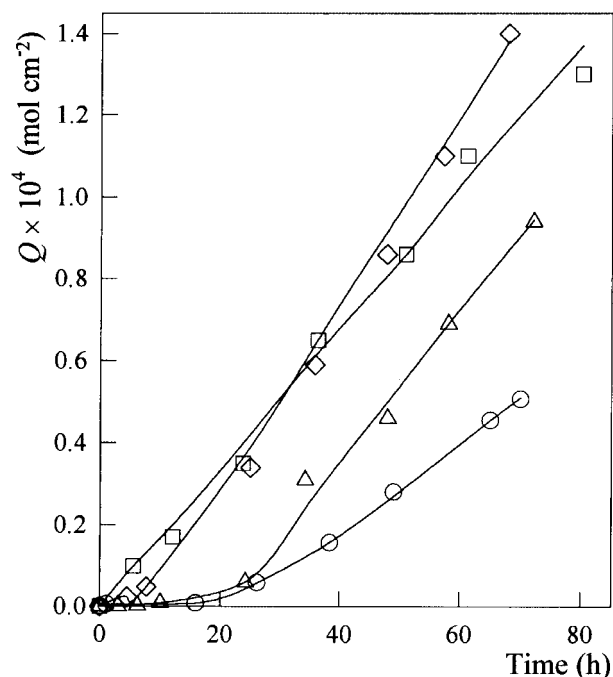


**Figure 6** Cumulative transport curves for ( $\square$ )  $Zn^{2+}$ , ( $\circ$ )  $Cu^{2+}$ , ( $\diamond$ )  $Mn^{2+}$ , ( $\nabla$ )  $Ni^{2+}$ , and ( $\triangle$ )  $Co^{2+}$  pertracted in the MHS with a BLM containing 480 g/dm<sup>3</sup> of PPOEP-31000.



**Figure 7** Separation coefficients for ( $\square$ )  $Zn^{2+}$ , ( $\circ$ )  $Cu^{2+}$ , ( $\diamond$ )  $Mn^{2+}$ , ( $\nabla$ )  $Ni^{2+}$ , and ( $\triangle$ )  $Co^{2+}$  pertracted in the MHS with a BLM containing 480 g/dm<sup>3</sup> of PPOEP-31000.





**Figure 8** Cumulative transport curves for the pertraction of metal cations in the MHS with an aquatic LM containing 12 g/dm<sup>3</sup> of (◇) PPOEP-14700, (○) DM-POEP, (□) PEG, and (△) the blank system.

performed with PPOEP-14700, DMPOEP, and PEG2000 are presented in Figure 8. From these plots, a significant difference between the systems with PPOEP and PEG is visible. The numerical data in Table III prove that the presence of PEG resulted in diminishment of the pertraction rate in comparison to the blank system ( $FF < 1$ ). The FF value observed for PPOEP was, however, very low ( $FF = 1.4$ ) when compared to the parallel results of the experiments with the DCE BLM (see Table I). Simultaneously, the system was practically nonselective with regard to the separation among particular cations; that is, all separation coefficients ( $\alpha$ ) were very close to 1. From these results, one can

conclude that the possible permeation of water from external solutions through hydrophilic cation-exchange membranes (osmotic flow) into any organic LM would result in a substantial increase of the effective fluxes and a loss of the ability to separate cations. Consequently, in the case of an aqueous BLM, the system will behave as a system of Donnan dialysis (ion-exchange dialysis through cation-exchange membranes) rather than pertraction through the BLM. By this observation, we can explain an increase in the transport ability of the system in time with a decreased selectivity (compare Figs. 6 and 7) as a typical property of the LMs made of DCE. The results concerning the aquatic membrane system can be compared with the results reported by Eyal and Kislik<sup>21</sup> for Cu<sup>2+</sup> and Cd<sup>2+</sup> permeated in the hybrid membrane system with the LM containing sodium poly(vinyl sulfonate) as the macroionophore. The previous authors reported fluxes ranging from  $3.2 \times 10^{-10}$  to  $6.2 \times 10^{-10}$  mol/cm<sup>2</sup> s (i.e., permeability coefficients equal to approximately  $1.6$ – $3.1 \times 10^{-6}$  cm/s), which are similar to our results, which varied from  $3.2 \times 10^{-10}$  to  $6.2 \times 10^{-10}$  mol/cm<sup>2</sup> s (permeability coefficients =  $2.9$ – $6.9 \times 10^{-5}$  cm/s). The results presented in this study show that the phenomenon of the free diffusion of salts from the feed through Nafion-120 and the aquatic LMs cannot be neglected, and the resulting flux is comparable to that in the presence of the carriers. Consequently, the FF values were very close to 1, which indicates scarce facilitation effect for this kind of pertraction.

## REMARKS ON MECHANISM OF PERTRACTION

Reaction–diffusion phenomena, which underlie the pertraction process in a LM containing a carrier, form a closed loop capable of pumping cations from external aqueous solutions. This gen-

**Table III** Characteristics of Pertraction in an Aquatic Hybrid Membrane System with Different Macroionophores

Macroionophore	Overall Flux: $J \pm SD$ (mol cm <sup>-2</sup> s <sup>-1</sup> )	FF	Mean Separation Coefficient $\alpha_{Co, Ni}^{Zn, Cu, Mn} \pm SD$
PPOEP-14700	$(6.9 \pm 0.4) \times 10^{-10}$	1.4	$1.01 \pm 0.04$
DMPOEP	$(4.7 \pm 0.3) \times 10^{-10}$	0.9	$1.02 \pm 0.02$
PEG2000	$(2.9 \pm 0.2) \times 10^{-10}$	0.6	$0.98 \pm 0.02$
No carrier	$(5.0 \pm 0.3) \times 10^{-10}$	1	$0.97 \pm 0.04$

eral mechanism can be additionally classified as a big or small carousel,<sup>44</sup> depending on the dominating mechanism of interfacial phenomena. If a carrier is insufficiently hydrophobic (e.g., PEG and its derivatives), it can leave the LM phase. Consequently, the process of cation uptake and release can occur in the aqueous external phases contacted to the hydrophobic LM. This mechanism is called a “big carousel” as opposed to a “small carousel,” which functions with the reactions occurring exclusively on or at the LM surface. The small carousel mechanism is allowed when a carrier is confined to the LM phase, as in the case of the MHS presented in this article. This was achieved by contact of the LM with a solid hydrophilic polymer protecting the permeation of the carrier into the bulk aqueous feed or stripping solutions. With regard to the properties of macroionophores, it should be emphasized that PPOEPs have an important advantage over PEGs because the pertraction of metal cations from the aqueous phase into the organic LM does not require concomitant extraction and transport of an anion providing the electroneutrality of the complex. Moreover, as postulated previously,<sup>27</sup> the ionic groups in PPOEPs facilitate the transfer of exchanged metal cations into the proximity of recognition centers formed by the polyether units. However, due to the properties of POE units in the PPOEP macromolecule, the pertraction of ion pairs (characteristic for any neutral acyclic or macrocyclic carrier) is still possible to the degree controlled by free salt diffusion through the external ion-exchange polymer membranes. It is also possible that POE units interact directly with counterions of sulfonic groups in the cation-exchange membrane, as it was observed in the chromatography of PEGs on cation-exchange resins.<sup>25</sup> This effect can alternatively lead to enhancement of the interfacial ion-exchange processes or to partial immobilization (retention) of POE units on the surface of the cation-exchange membrane. The first effect should be characteristic for low-molecular-mass PEGs and the second one to those of high molecular mass. However, in the case of PEG solution contacted with the Nafion membranes, the compound should show the lower complexation ability because of steric hindrances. In this view, the presence of ionic groups in PPOEPs seemed the main factor enhancing an effective pertraction in the studied system.

On the other hand, pertraction is at least a three-step process including the sorption, diffusion, and desorption at the opposite interface. Thus, the pro-

cess occurring at the stripping (receiving) interface of the transport cannot be neglected when one interprets pertraction results. Approximately, the stripping process can be regarded as the sorption of cations by the cation-exchange membrane from a solution (LM) containing ionic (PPOEP) or nonionic (PEG) components. The first case is rather simple because the liquid phase can be treated as a liquid exchanger and the process of double ion-exchange can be exploited as an appropriate model. The second case can be partly interpreted by taking into account the studies of Dietz et al.<sup>45</sup> concerning the influence of some neutral crown ethers on the ion-exchange behavior of alkaline-earth metal cations. Namely, the effect of cation-exchange enhancement was not observed in the case of higher-molecular-weight (or hydrophobic) crown ethers. Consequently, the presence of a similar reagent (PEG) in a LM can change the kinetics of cation release because of strong binding. In turn, this can effectively change the ion-exchange selectivity sequence normally exhibited by the cation-exchange resin membrane. Thus, the parallel sequence of the transport selectivity order, when PPOEPs and PEGs are used, could not be expected, although it was possible. Also, this effect could explain  $FF < 1$  observed somewhat in the presence of PEG in a LM.

## CONCLUSIONS

The application of soluble macroionophores in an active collaboration with insoluble polyelectrolyte membranes can be considered an alternative for the use of macrocyclic ligands polymerized or physically immobilized on porous support polymers. The idea of a multimembrane hybrid systems leads to the development of new continuous separation processes and an alleviation of the toxicity of certain low-molecular macrocyclic carriers replaced herein by their macromolecular analogs. The macroionophores, such as PPOEP, can be regarded to behave like a bifunctional macroligand that cooperatively recognizes cations according to the properties of its polyether chain and the properties of attached, ionizable, ion-exchange groups. The mechanism of complexation for the divalent metal cations and PPOEPs is thought to involve an initial attachment of a cation to the phosphodiester anionic group followed by the formation of pseudocyclic structures according to the specific properties of POE units. The supreme action of cation-exchange groups was deduced

from the preferential transport of  $Zn^{2+}$ , which was hard to observe in the case of PEG itself.

Taken together, the presented results demonstrate that PEG and its acidic phosphororganic derivatives can facilitate the pertraction of divalent cations, and this process is enhanced by the presence of poly(phosphodiester) structure of the macromolecular carrier. A well-defined molecular mass of PEG and POEPs and their ability to form pseudocyclic structures can be regarded as an efficient basis for the design of some new membrane transport systems.

The ion-exchange membranes used in the MHS performed as the cation-exchange material between external solutions, the components of a LM, and the porous material enabling free diffusion of salts to the LM interface. Obviously, the last phenomenon could be highly hindered by the co-ions exclusion Donnan effect. Replacement of the sulfonic acid polymer membranes with other membranes with specific properties could enhance the separation if required.

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