

Poly[poly(oxypropylene) phosphate] Macroionophores for Transport and Separation of Cations in a Hybrid: Cation-Exchange Polymer and Liquid Membrane System

Romuald Wódzki,¹ Marek Świątkowski,¹ Julia Pretula,² Krzysztof Kałużyński²

¹Faculty of Chemistry, Nicolaus Copernicus University, Gagarina St. 7, 87-100 Toruń, Poland

²Centre of Molecular and Macromolecular Studies, Polish Academy of Sciences, Sienkiewicza St. 112, 90-363 Łódź, Poland

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ABSTRACT: Poly[poly(oxypropylene) phosphate]s (PPOPP, $M_n = 5800, 8100, 10,400$), with different POP units (400, 1200, 2000), were synthesized and applied as cation-selective macroionophores in a multimembrane hybrid system (MHS). The solution of PPOPP in dichloroethane formed the flowing liquid membrane (FLM) circulating between two polymer cation-exchange membranes, and subsequently, between two polymer-made pervaporation (PV) membranes. It was found that the PPOPP macroionophores activate the preferential transport of Zn^{2+} cations from aqueous solutions containing competing Cu^{2+} , Ca^{2+} , Mg^{2+} , K^+ , and Na^+ cations. The following separation orders were observed for PPOPPs with POP-400 and POP-1200: $Zn^{2+} > Cu^{2+} \gg Ca^{2+}, Mg^{2+}, K^+, Na^+$, and for PPOPP with POP-2000: $Zn^{2+} > Cu^{2+}, Ca^{2+} \gg Mg^{2+}, K^+, Na^+$. Always, the particular cations are separated as: Zn^{2+}

$> Cu^{2+}, Ca^{2+} > Mg^{2+}$, and $K^+ > Na^+$. The properties of PPOPPs were compared to respective transport and separation characteristics corresponding to those of respective poly(propylene glycol)s and poly(oxypropylene) bisphosphates. The results of investigation indicate that the bifunctional character of PPOPPs is caused by the presence of ionizable groups and probably pseudocyclic POP structures. By comparing the separation of cations in the simple MHS[FLM] system and the system supported by pervaporation unit [MHS[FLM-PV] it was found that continuous dehydration of an organic FLM improves the system overall performance. © 2004 Wiley Periodicals, Inc. *J Appl Polym Sci* 93: 1436–1445, 2004

Key words: membranes; macroionophores; pertraction; separation of polymers; cations

INTRODUCTION

Liquid membranes, when used as a part of hybrid membrane systems, based on cooperation of their components with cation- or anion-exchange polymer membranes, have been demonstrated to transport and separate various substances including metal cations and inorganic or organic acids.^{1–13} The development of advanced hybrid liquid membrane systems, involving the process of pertraction (liquid membrane transport arranged as extraction–diffusion–back extraction),¹⁴ is strongly influenced by advances in the synthesis of new reagents that would be able to recognize and react specifically and reversibly with separated substances, and thereafter, to transfer them through-out a conventional liquid or polymeric membrane by a diffusion mechanism. On the other hand, searching for new ionophores (liquid membrane carriers) is stimulated also by the biophysics of cellular transport ascribed to the crucial role of various natural ionophores in the regulation of metal cations content in living

organisms.¹⁵ In this context, the development and application of the soluble polymeric carriers (macroionophores) is a challenging problem from both a fundamental and practical point of view, as reported in a number of articles^{6,16–34} and briefly discussed in our previous report.¹³

Moreover, in a number of natural cellular systems, a transported solute when reaching its destination passes and/or is separated by a series of membranes of varied properties. This rather evident—to biophysicists—feature of natural systems was the inspiration for our studies, based on the assumption that high selectivity and stability of membrane systems can be attained probably in the multimembrane systems with a hierarchy of processes mimicking bacterial cell envelopes.¹⁵ From the perspective of our previous reports concerning the properties of poly[poly(oxyethylene) phosphate]s^{13,26,27,32} as the macroionophores, a natural extension of our studies was to synthesize more hydrophobic polymers such as poly[poly(oxypropylene) phosphate]s (PPOPPs) and to test them in the pertraction of typical transient (Zn^{2+} , Cu^{2+}), alkali-earth (Ca^{2+} , Mg^{2+}), and alkaline (K^+ , Na^+) metal cations. Also, as postulated in the previous article,¹³ to eliminate some effects caused by water

Correspondence to: R. Wódzki (wodzki@chem.uni.torun.pl).

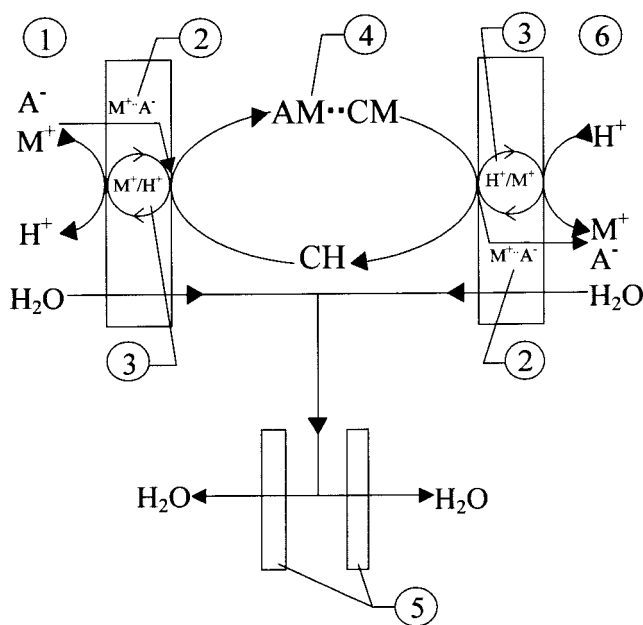


Figure 1 Composition and transport scheme of univalent cations in the MHS[FLM-PV] pertractor: ① feed; ② diffusion of salt through feed and stripping-side cation-exchange membrane; ③ cation-exchange dialysis through feed and stripping-side cation-exchange membrane; ④ countertransport (CH and CM) and/or cotransport (AM·CM) in a liquid membrane; ⑤ pervaporation process and membranes; ⑥ stripping solution.

uptake from external aqueous solutions into a liquid membrane phase, a continuous dehydration of a liquid membrane by water pervaporation method was additionally applied. According to the scheme of the system operation in Figure 1, the overall membrane system constitutes a set of very different membranes such as: a hydrophobic liquid membrane, hydrophilic polymer cation-exchange, and hydrophilic polymer pervaporation membranes. These polymer membranes are expected to support the operation of a liquid membrane with dissolved PPOPP as the macroionophore and liquid exchanger of cations to be transported and separated. Such a system was recently tested and reported to be effective when applying both low molecular weight [e.g., di(1,2-ethylhexyl) phosphoric acid³⁵] and some star-shaped polymer ionophores.³³

EXPERIMENTAL

Macroionophores

Polyphosphates of PPG: poly[poly(oxypropylene) phosphate]s, PPOPPs

Poly(H-phosphonates) of poly(1,2-propylene glycol)s (PPGs) were prepared according to the procedure similar to the one described in detail for the synthesis of poly(H-phosphonates) of poly(ethylene glycol)s

(PEGs).³⁶ A 20-g sample of PPG-400, PPG-1200, or PPG-2000, 20% molar excess of dimethyl H-phosphonate, and a catalytical amount of sodium (~ 0.005 g) were charged to 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, the reaction mixture was stirred, the temperature was gradually increased to 180°C, and the pressure decreased to 0.02 mmHg. The condensation was stopped after about 30 h. After cooling, the viscous reaction mixture containing poly(H-phosphonate) was dissolved in dry CH_2Cl_2 , and thereafter oxidized with N_2O_4 to the corresponding polyphosphate.³⁷ The crude product was purified by ultrafiltration from an aqueous solution using an Amicon stirred ultrafiltration cell (Amicon, Beverly, MA), with Diaflo ultrafiltration membrane (molar mass 1000, cutoff; Amicon) and finally dried under vacuum.

Poly(propylene glycol)s

The polymers of molecular mass 400, 1200, and 2000 were purchased from Fluka Chemie AG (Buchs, Switzerland; pure reagent) and used as received.

Membranes and solutions

The liquid membranes were prepared by dissolving a weighed amount of PPOPPs or PPGs (Table I) in 1,2-dichloroethane to a concentration of 12 g dm^{-3} . In the pertraction cell, the liquid membrane was separated from the feed or stripping aqueous solution by two additional Nafion-117 (Du Pont, Wilmington, DE) cation-exchange membranes (CEMs). These hydrophilic membranes (0.022 cm thickness) are composed of a poly(tetrafluoroethylene) backbone with pendant sulfonic acid groups on perfluorinated ether side chains. After potentiometric titration, the membrane was found to contain 1.05 ± 0.05 equiv of sulfonic groups per 1 kg of swollen polymer in its acidic form.

The Pervap 2201 membrane (Sulzer Chemtech GmbH, Neunkirchen, Germany) was used for constructing the pervaporation module. The membrane has a skin layer made of crosslinked hydrophilic poly(vinyl alcohol), which enables effective sorption of water from a liquid membrane, which it then transports into a vacuum side, according to principles of pervaporation.^{38,39}

A multicationic aqueous feed solution (source phase) was prepared by dissolving a weighed amount of $\text{Zn}(\text{NO}_3)_2$, $\text{Cu}(\text{NO}_3)_2$, $\text{Mg}(\text{NO}_3)_2$, KNO_3 , and NaNO_3 (Polskie Odczynniki Chemiczne, Gliwice, Poland; reagent grade) to a concentration of $0.002 \text{ mol dm}^{-3}$ each. A solution of sulfuric acid (Chemana, Toruń, Poland; reagent grade), at a concentration of 0.5

TABLE I
 Characteristics of Studied (PPOPP) and Compared (POPBP, PPG) Macroionophores

Macroionophore	Symbol	Molecular mass (g)	Degree of polymerization	
			<i>m</i>	<i>n</i>
-[(CH ₂ CH(CH ₃)O) _{<i>n</i>} -P(O)OH] _{<i>m</i>} -	PPOPP-400	5800	12	7
	PPOPP-1200	8100	6	21
	PPOPP-2000	10,400	5	35
(HO) ₂ P(O)-[CH ₂ CH(CH ₃)O] _{<i>n</i>} -P(O)(OH) ₂	POPBP-2000	2160	1	35
-[CH ₂ CH(CH ₃)O] _{<i>n</i>} -	PPG-400	400	1	7
	PPG-1200	1200	1	21
	PPG-2000	2000	1	35

mol dm⁻³, was used as a stripping (receiving) solution.

Pertraction cell and operation conditions

A laboratory pertractor, presented schematically in Figure 2, was composed of two flat CEMs (63.6 cm² each) with a flowing liquid membrane (FLM) between them, and simultaneously between two pervaporation membranes (36.3 cm² each). The FLM was pumped at a flow rate of 150 cm³ min⁻¹ by a Teflon piston pump (OSI, France) throughout the MHS and PV modules connected by tubing made of perfluorinated polymer (Vitonfluran, Ismatec, Glattbrugg, Switzerland). The

parts of a pertractor contacted with the aqueous solutions were made of Plexiglas, whereas those containing dichloroethane-based FLM were made of Teflon. The CEMs were put in contact with the aqueous feed and receiving solution, containing dissolved salts and sulfuric acid, respectively. The solutions (feed: 2.5 dm³; and stripping solution: 50 cm³) were intensively stirred. Periodically, the solutions were sampled, diluted, and the concentrations of particular metal cations were determined by atomic absorption spectrometry (AAS; SpectrAA20, Varian Australia Pty Ltd., Mulgrave, Victoria, Australia). The receiver of the PV unit was connected to a vacuum system operating at the pressure of 5–10 mmHg. Water pervaporated into a receiver was frozen by solid carbon dioxide and its amount was determined by weighing. The experiments were carried out at 25 ± 2°C over the time sufficient to attain quasi-stationary conditions for ionic fluxes.

Characterization

Quasi-stationary fluxes of particular cations (J_M , stripping rates), separation (α), and selectivity (β) coefficients were calculated to characterize the macroionophores and pertraction process. These quantities were calculated using concentrations expressed in equivalents (equiv mol charges) according to the methods applied in the case of ion-exchange membranes⁴⁰ separating and transporting cations of different valences. Under quasi-stationary transport conditions (ensured by a large volume of the feed compared to that of the stripping solution and high concentration of the stripping agent) the strip cumulative curves become nearly linear. Thus, the experimental fluxes (pertraction rates) were calculated as the slopes of the Q_s versus time curves, according to following equation:

$$Q_s = \frac{z_M[M]_{s,t}V_s}{1000A_s} = J_M t + \text{constant (equiv cm}^{-2} \text{ s}^{-1}) \quad (1)$$

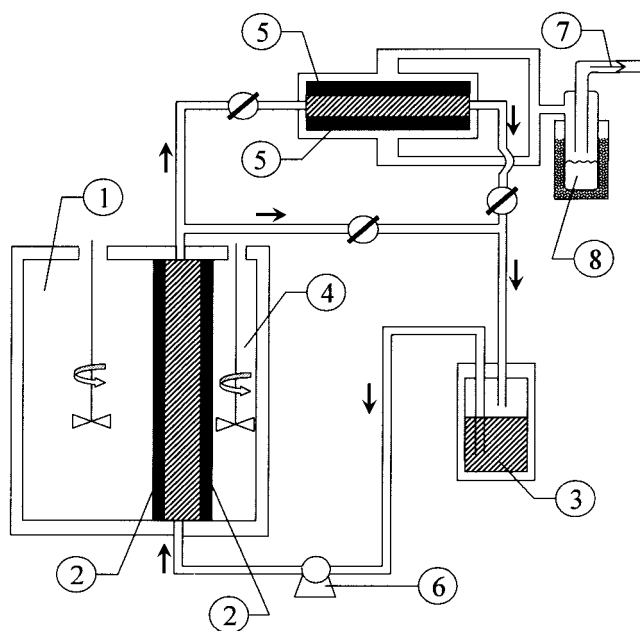


Figure 2 Scheme of the experimental MHS[FLM-PV] system for pertraction of metal cations: ① feed; ② cation-exchange membrane; ③ flowing liquid membrane; ④ stripping solution; ⑤ pervaporation membrane; ⑥ piston pump and tubing; ⑦ vacuum system; ⑧ frozen water.

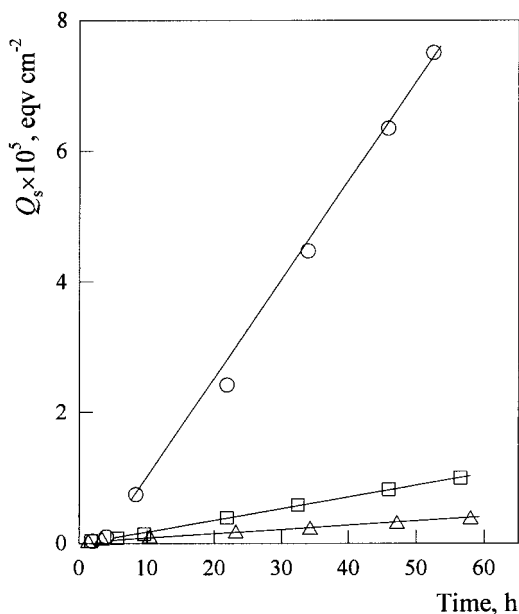


Figure 3 Overall accumulation of cations in the stripping solution of the MHS[FLM-PV] system with: (○) PPOPP-400; (□) PPOPP-1200; and (△) PPOPP-2000 macroionophores.

In eq. (1), Q_s denotes the number of metal equivalents transported into the receiver after the time t through 1 cm² of the stripping CEM area (A_s , cm²), V_s is the volume (cm³) of the stripping solution, and $[M]_{s,t}$ denotes the time-dependent molar concentration of metal (M) species of the valence z_M in the stripping solution (s). A weighed linear regression analysis ($r^2 > 0.9$) was used to determine the J_M value as the slope of $Q_s = f(t)$ line with the statistical weights corresponding to the standard deviations for $[M]_{s,t}$ determined by the AAS method. The pervaporation fluxes of water, expressed in moles of water transported through 1 cm² of the PV membrane, were calculated analogously.

The selectivity coefficients, as defined by the ratio of stationary fluxes of M_k and M_i species [eq. (2)] were used as time-independent (quasi-stationary period only) characteristics for the evaluation of the pertraction process:

$$\beta_k^i = J_i/J_k \quad (2)$$

A practical separation ability of the macroionophore in the MHS[FLM-PV] system was evaluated by calculating the mutual separation coefficients:

$$\alpha_{\sum M}^{M_k} = \frac{z_{M_k}[M]_{k,s,t} \sum_{i \neq k} z_{M_i}[M]_{i,f,t}}{z_{M_k}[M]_{k,f,t} \sum_{i \neq k} z_{M_i}[M]_{i,s,t}} \quad (3)$$

The separation coefficients $\alpha_{\sum M}^{M_k}$ reflect simultaneous changes in the concentration of the feed (f) and strip-

ping solution (s) attributed to the preferential transport of target M_k over other cations M_i .

To characterize the influence of the macroionophores on the liquid membrane properties, the facilitation factor FF was calculated as the ratio of the overall stationary flux (all the species taken into account) observed in the system with (J_c) and without the carrier (J_b , blank system):

$$FF = J_c/J_b \quad (4)$$

RESULTS AND DISCUSSION

According to our previous studies, the performances of hybrid pertractors transporting and/or separating ionic species^{35,41} depend mainly on the composition and transport mechanism allowed by the liquid membrane. As a rule, the overall process requires the ionophore to react reversibly at the respective interface to close the reaction–diffusion loop in a liquid membrane phase. Depending on the chemical composition of the ionophore, two basic processes such as cotransport (symport) and/or countertransport (antiport, exchange diffusion) can be observed. The cotransport, as mediated by the neutral ionophores, makes the pertraction of ion pairs possible, whereas the countertransport is typical for carriers of acidic or basic character and allows the process of equivalent transmembrane exchange cations or anions. Regarding the composition of macroionophore such as PPOPP one can expect its dual transport behavior because of the presence of polyether chains and acidic phosphodiester moieties. The polymeric units of POP should enable the cotransport of cations and anions together in one direction, whereas the ionic acidic groups should enable opposite-directed countertransport of cations (Fig. 1). Alternatively, these two PPOPP components can cooperate in the way such that ionic groups mediate an easy access to those parts of the macroionophore that are responsible for their selective recognition. Such a mechanism was described by Alexandratos et al.⁴² as operating in some functionalized polymeric sorbents, and by other authors^{43–45} as the mechanism mediated by ionizable lariat-type crown ethers in liquid membranes. In view of these considerations the basic aim of our investigation was to verify the following hypotheses:

- It is possible to exploit the properties of PPOPPs as bifunctional macroionophores in the liquid membranes.
- Macroionophores enable the pertraction phenomena comparable to those observed in the case of low molecular compounds, that is, with the uphill transport effects and fluxes sufficient for possible practical applications.

TABLE II
Overall Pertraction Fluxes of Cations and Facilitation Factors for the MHS[FLM-PV]
and MHS[FLM] Systems with Different Macroionophores in FLM

Macroionophore	Overall quasi-stationary flux, $J_M \pm s^a$ (equiv $\text{cm}^{-2}\text{s}^{-1}$)	Normalized overall flux (equiv $\text{cm}^{-2}\text{s}^{-1}\text{mol POOH}^{-1}$)	Facilitation factor, FF
Blank system	$1.3 \pm 0.2 \times 10^{-12}$		1
PPOPP-400	$4.3 \pm 0.1 \times 10^{-10}$	$13.3 \pm 0.3 \times 10^{-8}$	331
PPOPP-1200	$5.1 \pm 0.1 \times 10^{-11}$	$4.2 \pm 0.1 \times 10^{-8}$	39
PPOPP-2000	$1.7 \pm 0.1 \times 10^{-11}$	$2.3 \pm 0.1 \times 10^{-8}$	13
PPG-400	$3.8 \pm 0.3 \times 10^{-12}$		2.9
PPG-1200	$3.2 \pm 0.2 \times 10^{-12}$		2.5
PEG-2000	$3.0 \pm 0.2 \times 10^{-12}$		2.3

^a s, standard deviation.

- The cooperation of different polymer-based membranes, forming a hybrid membrane system, leads to a new class of highly selective and stable membrane systems.

Pertraction process mediated by macroionophores

The main property required from the investigated membrane system is a high rate of cation transportation from the feed to strip (receiving) solution. Quantitatively this can be evaluated from the experimental data presented in Figure 3 as the curves illustrating the accumulation of metal cations in a stripping solution, $Q_s = f(t)$. These curves correspond with PPOPPs of different overall molecular mass (Table I) and different POP components. The respective numerical data in Table II show that the fluxes observed under the same experimental conditions range from 2 to 40×10^{-11} equiv $\text{cm}^{-2}\text{s}^{-1}$ (i.e., these fluxes are quite satisfactory from a practical standpoint). Typically, for diffusion-limited processes, the effective permeability coefficients (as calculated from these data) vary from 4×10^{-4} to 2×10^{-5} cm s^{-1} . The analogous data corresponding with PPG-400–PPG-2000 were recently reported.⁴⁶ In this case, the fluxes are not as differentiated as in the case of PPOPP and reach the values of one or two orders of magnitude lower (i.e., $3\text{--}4 \times 10^{-12}$ equiv $\text{cm}^{-2}\text{s}^{-1}$). Clearly, the efficient pertraction of cations by the macroionophores is effectively allowed by the presence and density of their ionic groups along the PPOPP chain. However, the normalized fluxes, expressed in equiv $\text{cm}^{-2}\text{s}^{-1}$ per mol of acidic groups, are slightly differentiated, the effect of which indicates that the fluxes are also influenced by the molecular mass of the POP units. To compare the efficiency of all compounds, the facilitation factors, as defined by eq. (4), were calculated and are presented in Table II. These values are very high in the case of PPOPP-400 and always much higher than the FF values observed for PPG-mediated transports. This result

proves that the cotransport of ion pairs, attributed to the possible cotransport mechanism generated by POP units themselves, can be considered here as negligible.

Pervaporation of water from the FLM

Previously¹³ we indicated the role of water uptake into the liquid membrane phase, the process of which was suggested to be responsible for enhancing the process of permeation with simultaneous lowering of the membrane system selectivity. We also suggested solving this problem by continuous dehydration of the organic liquid membrane by a pervaporation method. The respective method and membrane equipment were recently described and evaluated as applicable in the process of membrane extraction and liquid mem-

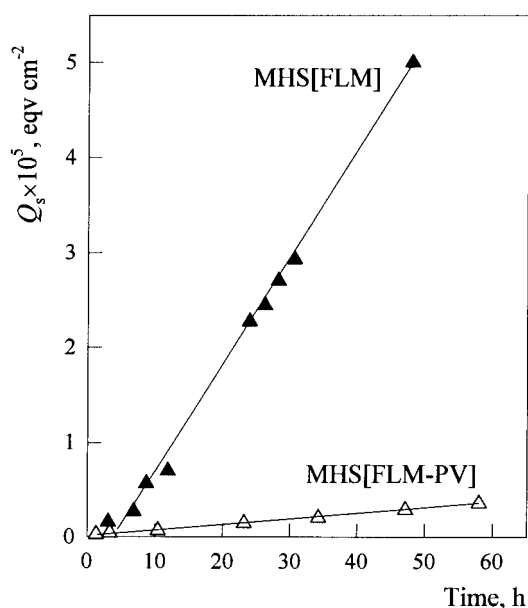


Figure 4 Comparison of pertraction process with PPOPP-2000 in (▲) MHS[FLM] and (△) MHS[FLM-PV] systems.

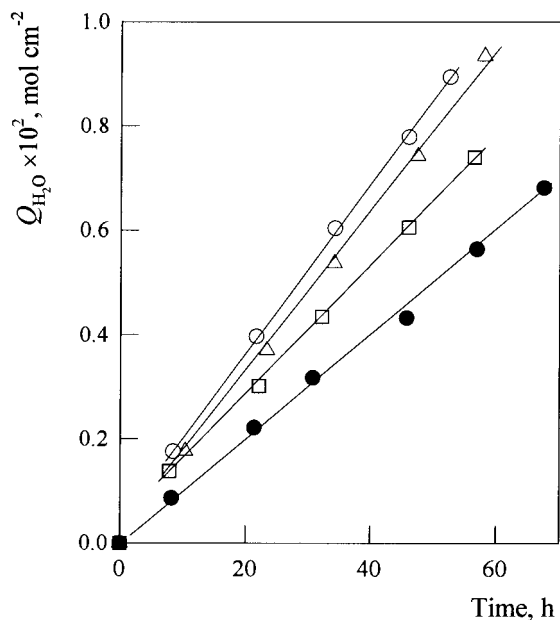


Figure 5 Pervaporation of water from FLM in the MHS[FLM-PV] system with (○) PPOPP-400, (□) PPOPP-1200, (△) PPOPP-2000, and with the (●) blank FLM.

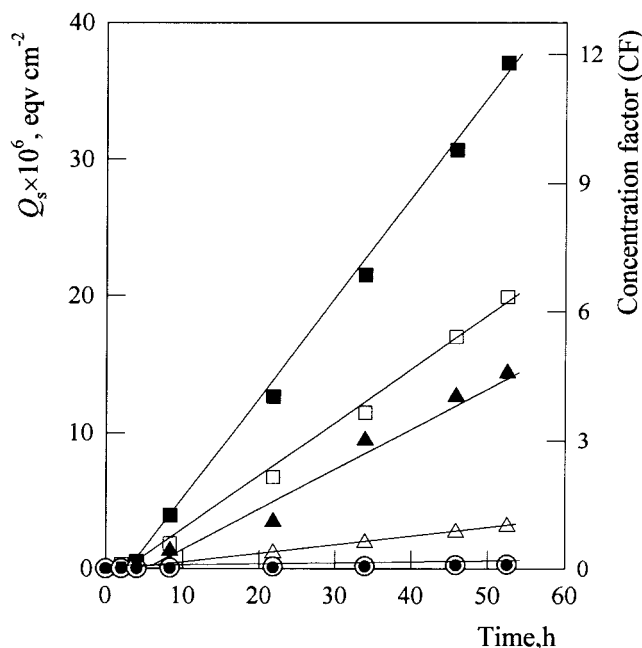


Figure 6 Transport and separation of metal cations in the MHS[FLM-PV] system with PPOPP-400 macroionophore: (■) Zn, (□) Cu, (▲) Ca, (△) Mg, (●) K, and (○) Na.

brane pertraction in the hybrid membrane systems.³⁵ When comparing the operation of respective pertractors (i.e., with and without pervaporation), the first important observation is that the MHS[FLM-PV] fluxes are about one order of magnitude lower than those observed in the MHS[FLM] system. For example, according to the plots in Figure 4, the fluxes enabled by PPOPP-2000 are 3.3×10^{-10} and 1.7×10^{-11} equiv $\text{cm}^{-2} \text{s}^{-1}$ for the MHS[FLM] and MHS[FLM-PV] systems, respectively. To present a quantitative description of the pervaporation process, the overall water pervaporation rates were calculated as the slopes of respective $Q_{\text{H}_2\text{O}} = f(t)$ plots drawn in Figure 5. The results listed in Table III vary from 8.0×10^{-8} to 10.4×10^{-8} mol H_2O per 1 cm^2 of the pervaporation membrane. The presence of hydrophilic ionic moieties in the PPOPPs probably increases

the amount of water transported into a liquid membrane phase. Consequently, this phenomenon increases the flux of water removed from the FLM by pervaporation. From the data in Table III, the contribution of water pervaporation associated with the

TABLE III
Characteristic of Pervaporation Processes in the MHS[FLM-PV] System with Different Macroionophores in FLM

Macroionophore	Pervaporation water flux, $J_{\text{H}_2\text{O}} \pm s^a$ (mol $\text{cm}^{-2} \text{s}^{-1}$)	Contribution of macroionophore, PV _{macroionophore} (%)
PPOPP-400	$10.4 \pm 0.2 \times 10^{-8}$	41.0
PPOPP-1200	$8.0 \pm 0.2 \times 10^{-8}$	23.2
PPOPP-2000	$9.8 \pm 0.1 \times 10^{-8}$	37.7
Blank system	$6.1 \pm 0.1 \times 10^{-8}$	

^a s, standard deviation.

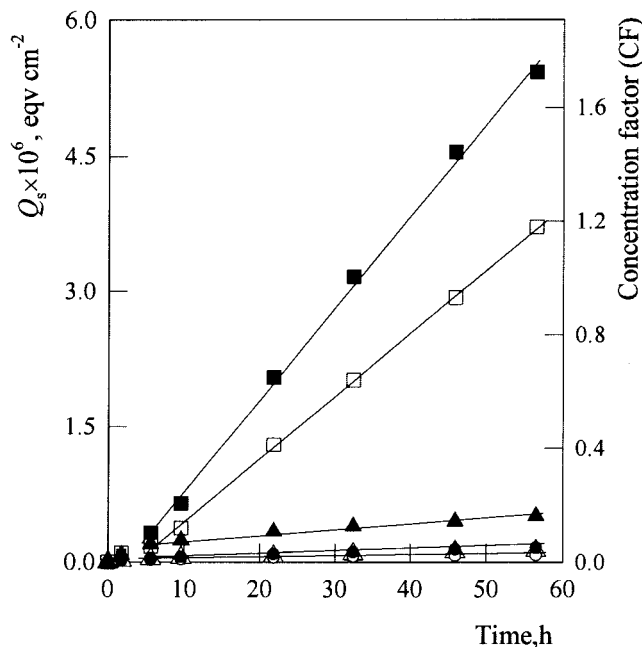


Figure 7 Transport and separation of metal cations in the MHS[FLM-PV] system with PPOPP-1200 macroionophore: (■) Zn, (□) Cu, (▲) Ca, (△) Mg, (●) K, and (○) Na.

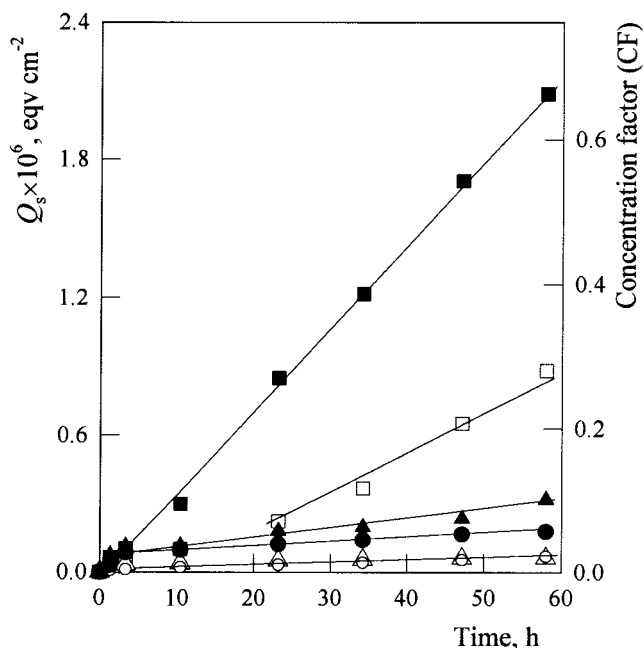


Figure 8 Transport and separation of metal cations in the MHS[FLM-PV] system with PPOPP-2000 macroionophore: (■) Zn, (□) Cu, (▲) Ca, (△) Mg, (●) K, and (○) Na.

presence of the PPOPPs macroionophores can be evaluated as

$$PV_{\text{ionophore}} (\%) = \frac{J_{\text{H}_2\text{O,ionophore}} - J_{\text{H}_2\text{O,blank}}}{J_{\text{H}_2\text{O,ionophore}}} \times 100 \quad (5)$$

This quantity reaches values from 23 to 42%, depending on the POP units in the PPOPP, with a tendency to diminish with an increase in its molecular mass.

System selectivity and separation phenomena

Having demonstrated significant transport efficiency of studied macroionophores, we focused our interest on the separation properties of the membrane systems as conditioned both by the system construction (MHS[FLM-PV] and MHS[FLM]) and the macroionophore properties. To show the separation ability of PPOPPs when used in the MHS[FLM-PV] pertractor, the cumulative transport curves for particular cations and macroionophores are presented in Figures 6–8. The

slopes of respective linear parts of presented curves demonstrate significant differentiation in the rates of pertraction, which leads to the effective separation of the cations. Moreover, in the case of PPOPP-400 and PPOPP-1200, the uphill transport of preferred Zn^{2+} and Cu^{2+} cations was observed during the experiments. This means that the concentrations of the preferentially transported cations in the stripping solution become higher than their initial concentrations in the feed, which is illustrated in Figures 6–8 by right axes scaled in the concentration factor (CF, defined as the ratio $[M]_{s,t}/[M]_{f,t=0}$) units. The value $\text{CF} > 1$ means that the cations are transferred from a dilute feed into a more concentrated stripping solution. Such an effect supplies the immediate evidence of the countertransport M^{2+}/H^+ as mediated by the carrier and forced by a high concentration of protons in the stripping solution.

To characterize the steady-state selectivity (related to quasi-stationary fluxes of cations), the fraction of specific cation flux in the overall flux and respective selectivity coefficients $\beta_{\text{Cu}}^{\text{Zn}}$, $\beta_{\text{Mg}}^{\text{Ca}}$, $\beta_{\text{Na}}^{\text{K}}$ were calculated from the data presented in Figures 6–8 and collected in Table IV. The results substantiate the conclusion that the system transports the cations in a way typical for the systems containing organic phosphates, which leads to typical inequalities $J_{\text{Zn}} > J_{\text{Cu}}$ and $J_{\text{Ca}} > J_{\text{Mg}}$. In the case of sodium and potassium cations, the fluxes are related as $J_{\text{K}} > J_{\text{Na}}$, which can be ascribed both to the properties of phosphoric acid groups and POP units acting as acyclic analogues of crown ethers. The results presented in Table IV indicate the selectivity orders to be almost independent on POP units: that is, in the case of PPOPP-400 and PPOPP-1200 the order of selectivity is $\text{Zn} > \text{Cu} > \text{Ca} \gg \text{Mg}, \text{K}, \text{Na}$. In the case of PPOPP-2000, this order changes to $\text{Zn} > \text{Cu} \gg \text{Ca}, \text{Mg} > \text{K}, \text{Na}$. The ability of the studied macroionophores to separate Zn^{2+} cations from mixtures with other cations seems to be a typical property of many organic carriers with phosphoric acid groups [e.g., di(2-ethylhexyl) phosphoric acid (D2EHPA)⁴¹]. Other properties such as preferential transport of K^+ cations can be attributed to the properties of POP units because the ability to transport K^+ increases with an increase in the mass of POP units forming the macroionophore. However, a very important feature of the PPOPP macroionophores, when compared to

TABLE IV
Selectivity of the MHS[FLM-PV] System in Pertraction of Cations

Macroionophore	Fractional flux (%)						Selectivity coefficient, $\beta_{M_i}^{M_j}$		
	Zn	Cu	Ca	Mg	K	Na	Zn/Cu	Ca/Mg	K/Na
PPOPP-400	48.2	26.6	20.4	4.0	0.4	0.4	1.8	5.1	1
PPOPP-1200	56.1	38.6	2.6	1	1.2	0.5	1.4	2.6	2.4
PPOPP-2000	58.7	30.3	6.2	0.6	2.7	1.5	1.9	10.3	1.8

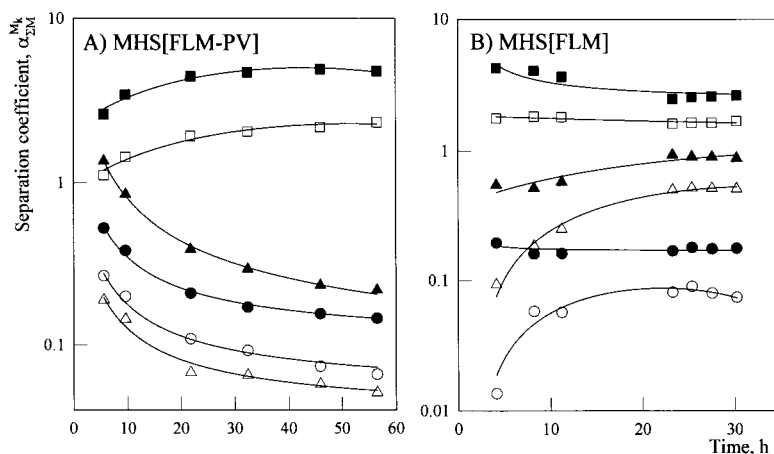


Figure 9 Separation curves for the (A) MHS[FLM-PV] and (B) MHS[FLM] systems with PPOPP-1200 macroionophore: (■) Zn, (□) Cu, (▲) Ca, (△) Mg, (●) K, and (○) Na.

D2EHPA being a classic Zn^{2+} carrier and extractant, is a significant discrimination of the flux of Ca^{2+} cations. In the case of PPOPPs, the relation $J_{Zn} \gg J_{Ca}$ was always observed, whereas, in the case of D2EHPA, these fluxes are comparable and the effect of separation is rather weak.^{35,47}

Another problem to discuss is the dependency of the separation ability of the system operating with and without the pervaporation process. For illustrative purposes in Figure 9(a), the separation coefficients for particular cations pertracted in the MHS[FLM-PV] system are drawn versus time of transport and compared to the results of the MHS[FLM] experiment [Fig. 9(b)]. The data concern the systems with PPOPP-1200 as a representative one, and indicate that the pervaporation of water from the liquid membrane causes a relative increase of the separation coefficients for the preferred Zn^{2+} cation. To compare all the macroionophores, the separation coefficients of the two preferred

cations (i.e., Zn^{2+} together with Cu^{2+}) over other cations (Ca^{2+} , Mg^{2+} , K^+ , and Na^+) are presented in Figure 10(a) and (b). It is evident from the plots of the supporting role of water pervaporation from the FLM during Zn^{2+} and Cu^{2+} separation from the mixture when using PPOPP-2000 and PPOPP-1200. In the case of a macroionophore such as PPOPP-400, the effect of pervaporation is lower, which can be ascribed to rather high hydrophilicity of this compound.

Bifunctionality of PPOPPs

The ability of soluble PPOPPs polymers to mediate transport and selectively separate cations is comparable to the properties of numerous ionizable macrocyclic polyethers of the lariat type,^{43–45} the ionizable groups of which cooperate with crown ether macrocycles. The bifunctional character of PPOPP macroionophores can be postulated to be attributable to the

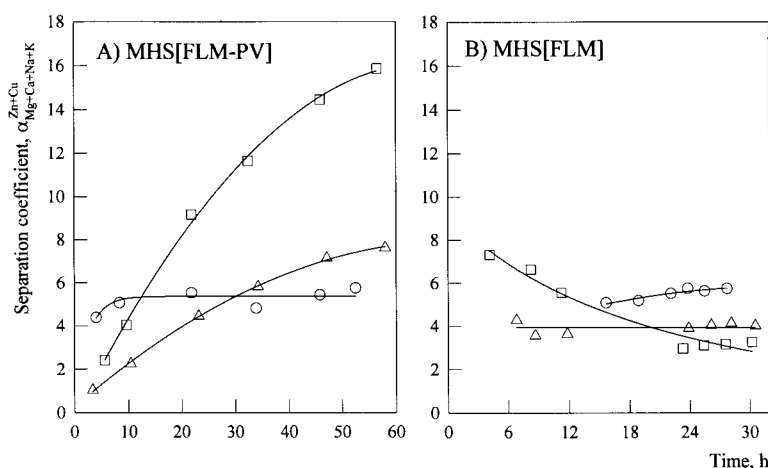


Figure 10 Separation of Zn^{2+} and Cu^{2+} cations over Ca^{2+} , Mg^{2+} , K^+ , and Na^+ in the (A) MHS[FLM-PV] and (B) MHS[FLM] systems with (○) PPOPP-400, (□) PPOPP-1200, and (△) PPOPP-2000 macroionophores.

TABLE V
Pertraction Selectivity in the MHS[FLM-PV] Systems with Different Feed pH

Feed pH	Macroionophore	Fractional flux (%)						Selectivity coefficient, $\beta_{M_i}^{M_k}$		
		Zn	Cu	Ca	Mg	K	Na	Zn/Cu	Ca/Mg	K/Na
3.5	PPG-2000	40.8	4.2	8.8	1.6	35.3	9.3	9.7	5.5	3.8
	POPBP-2000	62.2	31.2	2.8	2.0	1.5	0.3	2.0	1.4	5
	PPOPP-2000	58.7	30.3	6.2	0.6	2.7	1.5	1.9	10.3	1.8
0.6	PPG-2000	33.1	21.8	8	5.4	25.8	5.9	1.5	1.5	4.4
	POPBP-2000	34.6	39.5	n.d. ^a	n.d.	17.8	8.1	0.9	—	2.2
	PPOPP-2000	35.9	38.3	3.0	3.9	15.8	3.1	0.9	0.8	5.1

^a n.d., no detection.

properties of pseudocyclic structures of the POP chains, and cation-exchange properties of the overall liquid membrane as caused by the presence of ionizable groups. The contribution of the counter- and co-transport can thus be regulated by adjusting the pH of a feed solution (pH_f) and changing the degree of dissociation of the PPOPPs. To verify this hypothesis, the PPG, POPBP, and PPOPP macroionophores with POP-2000 units were used in the MHS[FLM-PV] pertractor with the feed pH adjusted to 3.5 or 0.6 by adding a respective amount of the nitric acid. Note that because of the specific cation-exchange sorption and the sorption of a free electrolyte into the aqueous internal phase of the cation-exchange membrane, the concentration of protons at the CEM/FLM interface is lower than that in the bulk feed solution.

The results of the experiments are presented in Table V as the fractional fluxes and selectivity coefficients. From these data, it can be concluded that, independently of the macroionophore composition, the fractional flux of Zn^{2+} always diminishes with a decrease in the feed pH. This behavior is especially visible in the case of ionizable POPBP and PPOPP macroionophores and can be interpreted as a feature of phosphoric acid derivatives. On the other hand, a significant increase of Cu^{2+} transport was observed in the case of PPG and, consequently, in the case of POPBP and PPOPP. However, the most important results concern the fractional flux of K^+ , which is always very high in the case of PPG, and which in the case of POPBP and PPOPP increases significantly after the feed acidification. It means that the properties of POPBP and PPOPP become similar to that of PPG because of a low dissociation degree of ionizable groups. It indicates, by analogy to poly(oxyethylene) chains, that poly(oxyethylene) chains form pseudocyclic structures similar to those of 18-crown-6 macrocyclic ether. However, each conclusion on this subject can appear very speculative, given that the knowledge concerning the POP-complexing properties is very limited. According to Yanagida,⁴⁸ PPG is a worse extractant of cations than PEG, and thus it can be expected that the role of POP units is not so clear as in the case of PEG derivatives studied before.^{13,32} Nev-

ertheless, the simple experiments discussed above demonstrate that the specific properties of POP chains are also observable in the case of pertraction processes described in this article.

CONCLUSIONS

The results of this study support the concept of "supramacromolecular" chemistry in liquid membrane systems. The application of macromolecules as selective and mobile ionophores in a liquid membrane system leads to results that can be observed in the case of ionizable lariat-type macrocyclic compounds. In both cases, the mechanism of transport involves two coupled mechanisms, that is, the access mechanism by exploiting the cation-exchange properties of the ionic moieties and the recognition mechanism conditioned by the macrocyclic or pseudocyclic structures produced by polyether chains. In some cases, as in the case of Zn^{2+} or K^+ transport and separation, these properties are in opposition, which leads to the competition between Zn^{2+} and K^+ cations. On the other hand, the PPOPP ionophores, opposite to the low molecular weight D2EHPA carrier, do not exhibit selectivity toward Ca^{2+} cations, the result of which is very advantageous from a practical standpoint. Moreover, the use of macroionophores as liquid membrane carriers gives evident profits because of convenient recycling of the macroionophore by simple filtration procedures. Also, the compounds studied are non-toxic, thus providing an opportunity to use them in environment-friendly pertraction technologies or food treatment. The problem is also related to the construction of the liquid membrane pertraction system. The MHS[FLM-PV] system is an example of the way in which different polymer membranes and soluble polymer components can be exploited as mutually responsible for proper performances of a multimembrane hybrid system. The addition of the pervaporation process to the pertraction results in significant changes of the system properties. Such a solution enables the effective use of amphiphilic compounds and has all the advantages known for membrane extraction technology (nondispersive extraction through

polymer membrane).³⁵ On the other hand, the pervaporation results reveal some imperfection of experimental results and conclusions concerning polyether polymers or crown ethers when used in classic bulk liquid membranes. The results of our investigations also show that some transport effects and low separations can be produced by water transfer or uptake into a liquid membrane phase, and cannot be ascribed to the carrier properties only.

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