

Coupled Membrane Processes and their Biomimetic Fundamentals*

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The paper deals with liquid membrane transport and separation phenomena that are related to their natural counterparts. Designing of some complex multimembrane hybrid systems and their practical embodiment are presented. Metal cation fluxes and separation characteristics for a simple multimembrane hybrid system (MHS) and its variants such as Donnan dialysis-MHS (DD-MHS) and pervaporation-MHS (PV-MHS) integrated processes are presented and discussed. Experimental studies have been carried out with the use of commercial cation-exchange membranes, a liquid membrane (kerosene with D2EHPA) and the pervaporation membrane (Pervap 1000). The membrane systems were tested and recognized to exhibit selective and stable permeation rates of Zn^{2+} from multicomponent aqueous solutions containing zinc, calcium, magnesium, sodium, and potassium nitrates.

Membrane mimetic chemistry (MMC) deals with the reconstitution of some functions and phenomena characteristic of biomembranes as components of living organisms [1]. Initially, the main task of MMC was oriented to the structure, mechanism of forming, and final properties of various mono-, bi-, and multilayers composed of natural and synthetic lipids. Nowadays, the research field of MMC is considerably extended and involves numerous membrane systems the functions or composition of which are inspired by their natural patterns. In general, the studies are directed towards the application of macromolecular compounds, *e.g.* polylipids or other functionalized polymers, which allow construction of stable biomimetic membrane systems of practical interest [2]. On the basic level, the transport phenomena of biomembranes [3], composed mainly of a lipid bilayer, are dependent on some specialized transport molecules known as channel or carrier ionophores. In the case of more complex systems like bacterial species the cytoplasmic membrane is associated with a polymeric cell wall forming together a very specific transport system (cell envelope) in which the hydrophilic polymer membrane collaborates with a quasi-liquid hydrophobic membrane [4].

The simplest way to reconstitute some transport functions of cytoplasmic membrane is the use of liquid membrane (LM) technique [5]. The sequence of the diffusion and reaction steps (pertraction), recognized as characteristic of any quasi-liquid biomembrane, can be further mimicked by using synthetic carriers enabling or facilitating the solubilization and diffusion of ionic

species in the LM phase. A quite different process occurs in the bacteria cell wall, the main component of which can be regarded as a hydrophilic ion exchanging polymer membrane with attached phosphodiester and carboxylic acid groups. Consequently, the mechanism of the uptake and transport of cations in the cell wall can be mimicked by a synthetic ion-exchange membrane (IEM) [6]. Two synthetic membranes of different nature, *i.e.* a liquid membrane (LM) combined in a series with a cation-exchange membrane (CEM), lead to the system of the architecture parallel to the bacteria cell envelope. Transport processes in biomembranes are also mediated by channel ionophores. However, up-to-now any practical pertractor based on channel membranes has been constructed despite the promising results of fundamental studies in this field [7, 8].

Generally, the formulation and application of network thermodynamics [3, 9] was a fundamental step in the development and understanding of coupled biomembrane transport processes and their energetics. This approach, when applied for describing the reaction-diffusion transport processes in cellular membrane systems, clearly emphasizes their compartmentalization and hierarchy of related processes. Thus, it was concluded that the final result of processes occurring in natural systems can be highly influenced by their topology and the sequence of events. According to the scheme in Fig. 1, the system inspired by the structure and functions of bacterial cell envelope takes the form of multimembrane hybrid systems composed of two ion-exchange membranes separated by

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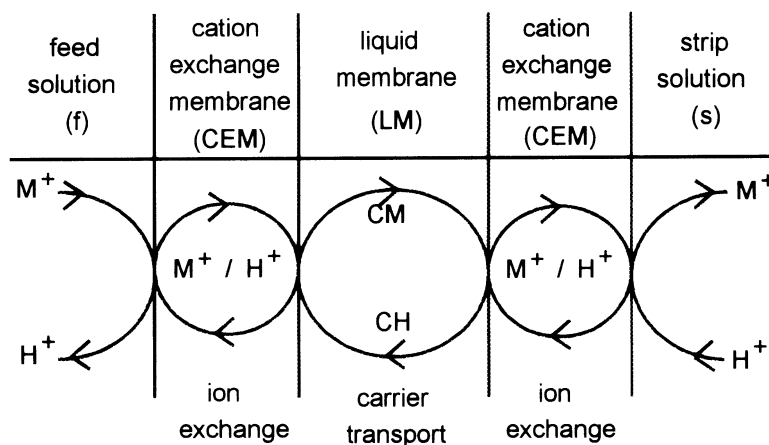


Fig. 1. Scheme of the species transport in a multimembrane hybrid system (MHS).

a liquid membrane. Such systems were designed and constructed in order to recover metal cations from aqueous solutions [4, 6, 10–13] and carboxylic acids from fermentation broth [14]. In this paper the MHS is treated as the main component of more complex systems resulting from the coupling of the MHS to the Donnan dialysis (DD-MHS) or pervaporation process (PV-MHS). The general task of the experimental studies presented in this paper was to verify the concept of biomimetic pertractors in a long-time operation and to evaluate their ability to transport Zn^{2+} cations in relation to potential practical applications.

EXPERIMENTAL

Materials and Reagents

Polystyrene sulfonic acid-based membranes Neosepta CM-1 (Tokuyama Corp., Japan) were applied as ion-exchange polymer separators between organic and aqueous phases, in the case of the MHS and the DD-MHS. The standard equivalent ion-exchange capacity of the membrane expressed per mass of dry Na^+ form is 2–2.5 mol kg^{-1} , its thickness 0.13–0.16 mm, and water relative mass fraction based on the mass of dry form 0.35–0.4 [15]. In the case of the PV-MHS, the FKS membrane (FuMa Tech, St. Ingbert, Germany) made of sulfonated poly(ether ketone) has been used. The pervaporation unit was equipped with the hydrophilic Pervap-1000 membrane (Sulzer Chemtech GmbH, Germany) which is made of a composite material with skin layer composed of poly(vinyl alcohol). The membrane (thickness 0.140 mm) allows water transport with the rate as high as approximately 280 g $H_2O m^{-2} h^{-1}$. After the experiment, the membranes were regenerated by soaking in sulfuric acid solution (1 mol dm^{-3}) and by further washing in distilled water to remove absorbed free acid. The liquid membrane was prepared by using bis(2-ethylhexyl)phosphoric acid (D2EHPA, Sigma Chem. Co., USA, 95 %). This reagent was dissolved in kerosene (Maker, Poland,

boiling point 124–174°C, viscosity 0.69 mPa s, and density 0.783 g cm^{-3}) to the concentration of 0.1 mol dm^{-3} . Sulfuric acid with the concentration of 1 mol dm^{-3} was used as a stripping solution. The same reagent (0.1 mol dm^{-3}) was used as the mediating solution for the experiments with DD-MHS. The feed solution for the MHS and the DD-MHS contained zinc, calcium, magnesium, sodium, and potassium nitrates, each of concentration 0.002 mol dm^{-3} . For the PV-MHS experiments the feed solution was of similar composition but a concentration of 0.01 mol dm^{-3} was used. Samples of the 0.5 cm^3 volume were taken from the feed and stripping solution, and analyzed off-line using a Varian atomic absorption spectrophotometer. All experiments were carried out at room temperature ($(22 \pm 2)^\circ C$).

Transport Cell and Operating Conditions

Simple Multimembrane Hybrid System, MHS

Transport experiments were carried out using a transport cell made of plexiglass and the experimental set-up schematically depicted in Fig. 2. The overall working area of CEM's contacted to a liquid membrane was 30 cm^2 . The flowing liquid membrane (FLM) of the 125 cm^3 volume circulated continuously between two chambers separated from organic and aqueous phases by two CEM's. The feed solution of volume 1 dm^3 was supplied from an external reservoir at the flow-rate 20 $cm^3 min^{-1}$. The solution of sulfuric acid in the strip compartment (150 cm^3) was agitated with a magnetic bar at 500 min^{-1} .

Integrated Donnan Dialysis and Pertraction in the MHS, DD-MHS

The experiments were performed in the extended MHS pertractor schematically presented in Fig. 3. The mediating solution, containing initially only sulfuric acid (50 cm^3 , $c = 0.1$ mol dm^{-3}), has been used as

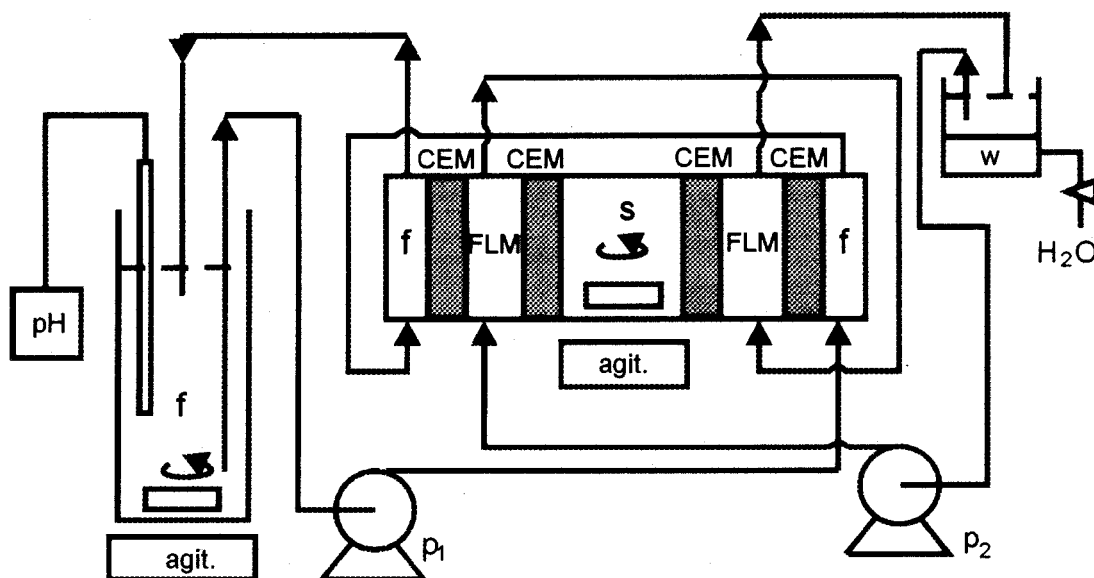


Fig. 2. Scheme of the MHS unit. CEM – cation-exchange membrane, FLM – flowing liquid membrane, f – feed solution, s – stripping solution, w – water settler, pH – pH-meter, agit. – agitator, p – pump.

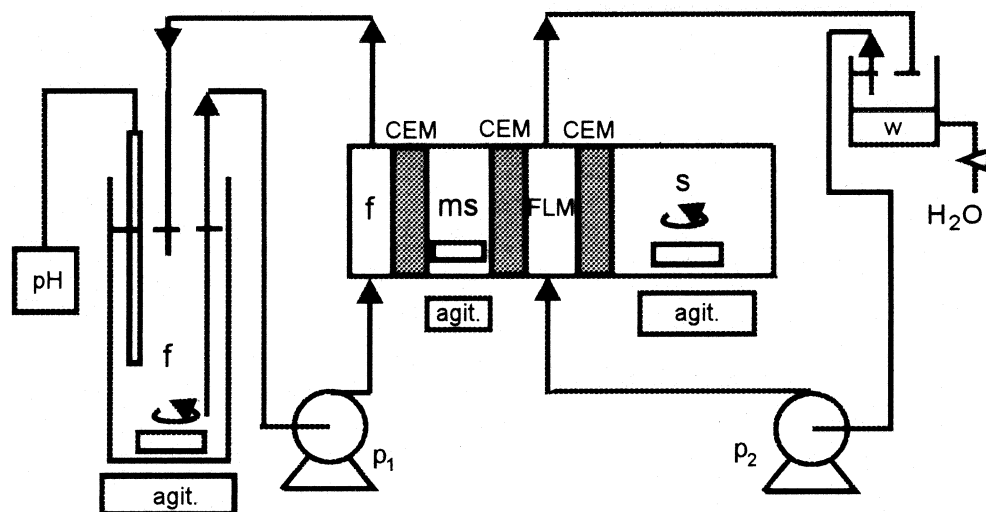


Fig. 3. Scheme of the DD-MHS. ms – mediating solution, other labels as in Fig. 2.

the stripping solution for the Donnan dialysis and as the feed solution for the MHS process. Other operating conditions were the same as in the case of the simple MHS.

Coupled Pervaporation and Pertraction with MHS, PV-MHS

The membrane system (Fig. 4) was composed of the MHS device with two CEM's of 200 cm² working area. The external solution, *i.e.* the feed of the volume 10 dm³ and the stripping solution of the volume 100 cm³ were run (20 cm³ min⁻¹) throughout the PVC tubing and respective chambers. The liquid membrane of the volume 300 cm³ was pumped

through a pervaporation unit of 23 cm² working area. The pervaporation membrane was placed horizontally on a stainless steel porous support. The pervaporation unit was connected with a vacuum system operating at 1300–1900 Pa pressure. Water transported into the vacuum side was then removed by freezing in a receiver cooled by solid carbon dioxide. The amount of water removed from the FLM was determined by subsequent weighting of receivers with water.

Calculations

The transport rates of ionic species were determined as the equivalent quasi-stationary fluxes defined by the following equations

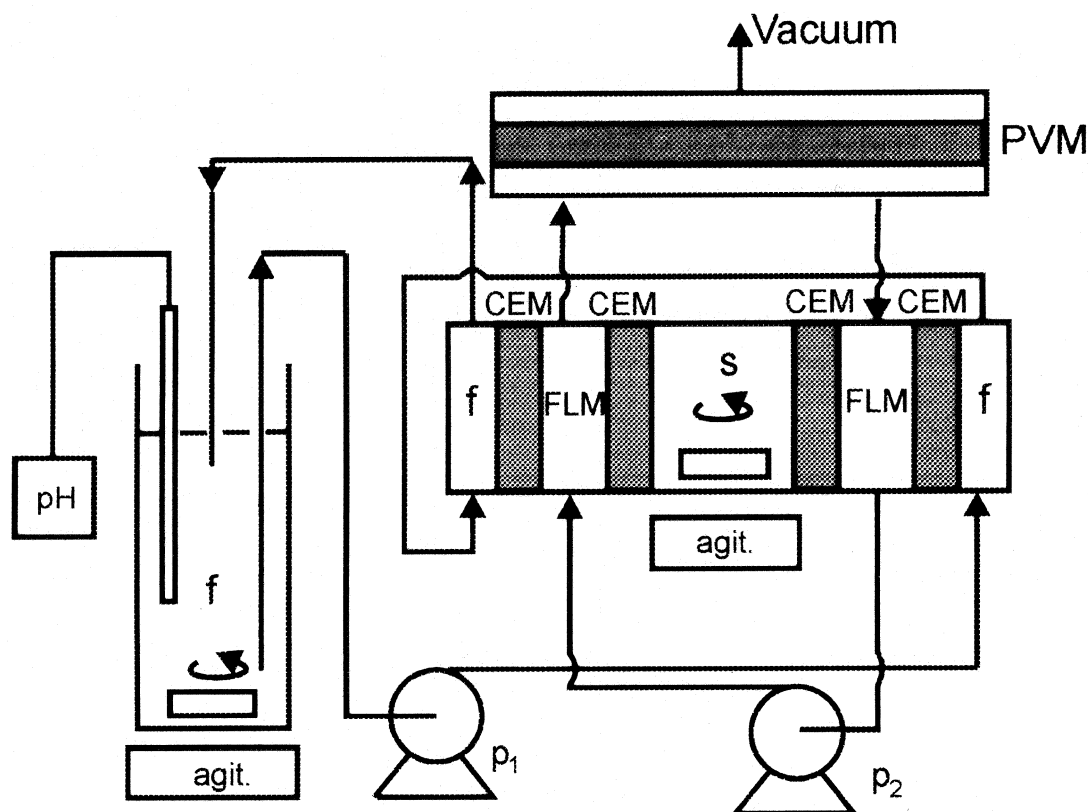


Fig. 4. Scheme of the PV-MHS. PVM – pervaporation membrane, other symbols as in Fig. 2.

$$J_M = \Delta Q_s / \Delta t \quad \text{mol cm}^{-2} \text{ s}^{-1} \quad (1)$$

$$\Delta Q_s = \Delta[M]_{s,t} V_s / 1000 A_s \quad \text{mol cm}^{-2} \quad (2)$$

Q_s denotes the amount of metal species in equivalents transported to the receiver after the time t , through 1 cm^2 of the stripping CEM area (A_s , cm^2), V_s (cm^3) is the volume of the stripping solution, $[M]_{s,t}$ (mol dm^{-3}) is the concentration of metal species at time t . To evaluate the separation ability of the membrane systems towards k -cations the separation coefficients (α) were calculated according to the following equation

$$\alpha_k^M = \frac{[M]_{k,s} \sum_{j \neq k} [M]_{j,f}}{[M]_{k,f} \sum_{j \neq k} [M]_{j,f}} \quad (3)$$

where $[M]$ denotes the concentration (mol dm^{-3}) in the stripping (s) or feed (f) solution.

RESULTS AND DISCUSSION

Simple Multimembrane Hybrid System, MHS

In this system, ion-exchange membrane processes are coupled to the liquid membrane transport through interfacial ion-exchange reaction between an ionic carrier and ionogenic groups attached to the polymer.

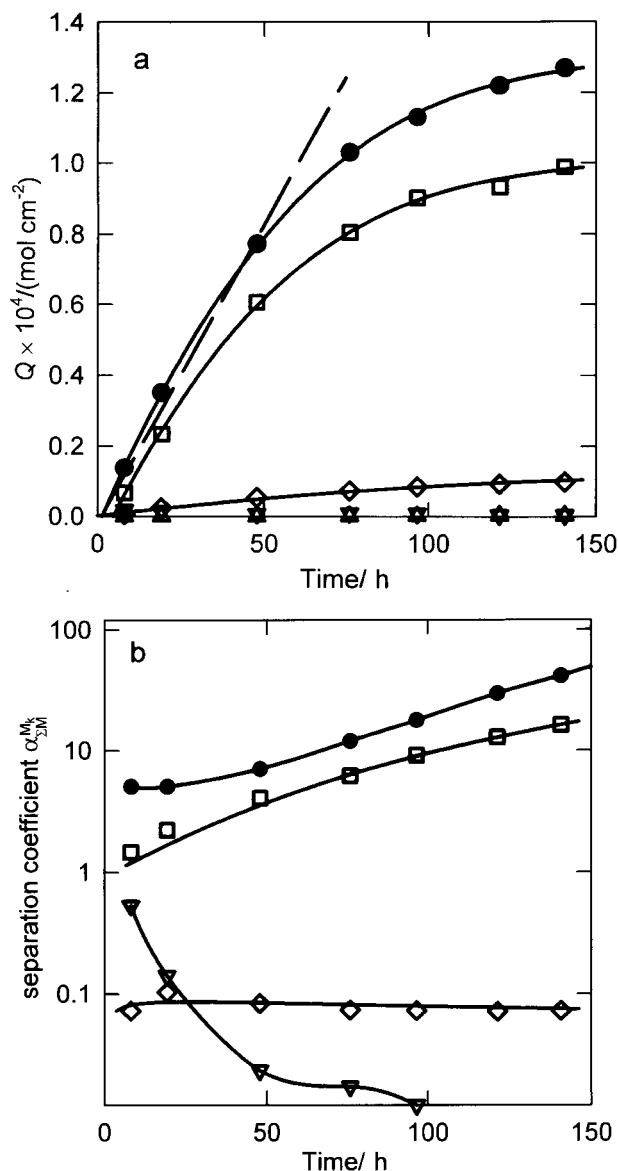
The system functioning is thus dependent on the properties of the IEM and LM. Some representative results concerning the fluxes and separation characteristics of the MHS are presented in Figs. 5a and b, and Table 1. The results show that the transport process is dominated by the pertraction of Zn^{2+} and Ca^{2+} . The system was operated continuously for 150 h (or more) without loss of its integrity. Water was observed to penetrate into a liquid membrane phase at very long times (100–600 h).

Integrated Donnan Dialysis and Pertraction in the MHS, DD-MHS

The properties of the MHS are satisfactory when the device works under the optimum conditions providing low osmotic fluxes of water and maintaining the interfacial pH required for keeping the effectiveness of the carrier in a liquid membrane. However, in some cases, there is a need to contact the device with alkaline solutions containing cations which promote the surface activity of the carrier, for example, sodium salts of D2EHPA. As it was proved before [16], such a system contacted with slightly alkaline industrial wastewater loses its selectivity analogously to a simple liquid membrane system because of the formation of micelles and emulsification of the liquid membrane phase. This can be solved partly by using the additional mediating solution, which provides optimum

Table 1. Comparison of Fluxes and Transport Rate Constants for Multimembrane Hybrid Systems

Characteristics	MHS	DD-MHS	PV-MHS
Overall flux, $J/(\text{mol cm}^{-2} \text{s}^{-1})$	8.4×10^{-10}	2.8×10^{-10}	2.0×10^{-9}
Overall rate constant, $k_i/(\text{cm s}^{-1})$	5.3×10^{-5}	1.8×10^{-5}	2.0×10^{-5}
Rate constant for i -cation:			
Zn	1.1×10^{-4}	5.3×10^{-5}	4.8×10^{-5}
Cu			9.1×10^{-6}
Ca	9.0×10^{-5}	1.5×10^{-5}	4.0×10^{-5}
Mg	8.5×10^{-6}	4.5×10^{-7}	5.9×10^{-7}
K	1.0×10^{-7}	2.2×10^{-7}	3.1×10^{-8}
Na	$< 1 \times 10^{-7}$	1.2×10^{-7}	6.1×10^{-8}
Initial and final pH of the feed	5.1; 1.9	5.1; 1.8	3.1; 2.0
Overall cation equivalent concentration in the feed/ (mol dm^{-3})	0.016	0.016	0.1

**Fig. 5.** Transport of cations in the MHS pertractor. ● Zn, □ Ca, ◇ Mg, △ K, ▽ Na. a) Cumulative transport curves, b) separation coefficients.

conditions for the MHS pertraction. The results corresponding with the DD-MHS pertraction data are

presented in Fig. 6. As it was expected, the selectivity towards Zn^{2+} as compared to Ca^{2+} , is higher than the one observed for the simpler MHS. The increased selectivity is, however, associated with lowering the Zn^{2+} flux, which after adding an additional CEM, drops from $4.4 \times 10^{-10} \text{ mol cm}^{-2} \text{ s}^{-1}$ to $2.1 \times 10^{-10} \text{ mol cm}^{-2} \text{ s}^{-1}$. The presented results and those published elsewhere [16] show an exceptional stability of the system under changing feed properties. Thus, the pertractors of this construction can be regarded as promising devices for continuous and prolonged operation processes in the electroplating industry for treating various rinse solutions. Another possible application of the DD-MHS pertractor is the preconcentration of Zn^{2+} or other metal cations (after changing the carrier in the MHS unit) for environment monitoring of natural water resources.

Coupled Pervaporation and Pertraction in the MHS, PV-MHS

The problem of liquid membrane hydration appears as a result of osmotic transport of water, and can be considered as an intrinsic property of both the ion-exchange membrane transport and liquid membranes. In natural systems, there are coupled processes that regulate the osmotic pressure and water balance in the cell. It is possible to reconstitute some of them but from the technological point of view this approach would be impractical. Therefore, we now consider the coupling of the basic membrane system (formed by the MHS) with an additional membrane system for the pervaporation [17] of water from an organic phase of the liquid membrane. Representative results concerning the pertraction of metal species and pervaporative removing of water from the liquid membrane are presented in Fig. 7. The results show that the permeation of metals is associated with the transport of water, which can be removed from the FLM at the rate of $9 \times 10^{-8} \text{ mol cm}^{-2} \text{ s}^{-1}$.

Comparison of Fluxes and Transport Rates

Transport systems presented in this paper can be

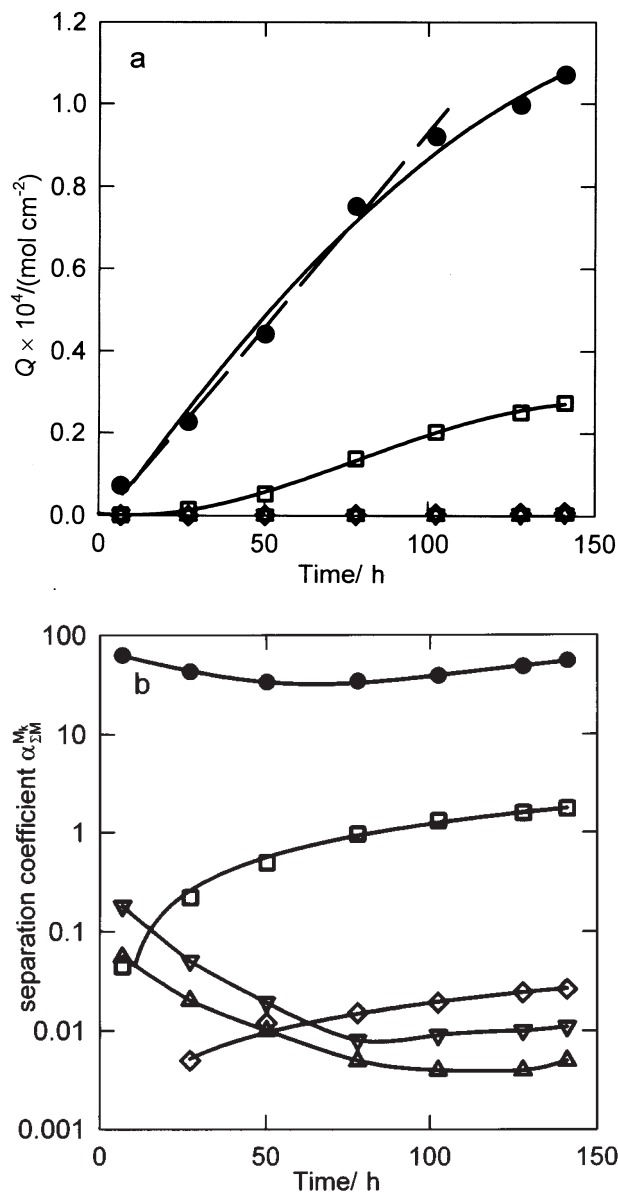


Fig. 6. Transport of cations in the DD-MHS pertractor. ● Zn, □ Ca, ◇ Mg, △ K, ▽ Na. a) Cumulative transport curves, b) separation coefficients.

roughly compared by the values of overall fluxes and apparent rate constants k (cm s^{-1}). The approximate rate constants (overall mass transfer coefficients, effective permeability coefficients) can be calculated by dividing the corresponding quasi-stationary fluxes (J) by initial feed concentrations $[M]_{f,0}$.

$$k = 1000 J/[M]_{f,0} \quad (4)$$

The results of calculations are collected in Table 1. One can conclude from these data that the overall rate constant values are of the order $10^{-5} \text{ cm s}^{-1}$, which are the values typical for many membrane processes being limited by diffusion phenomena. The compar-

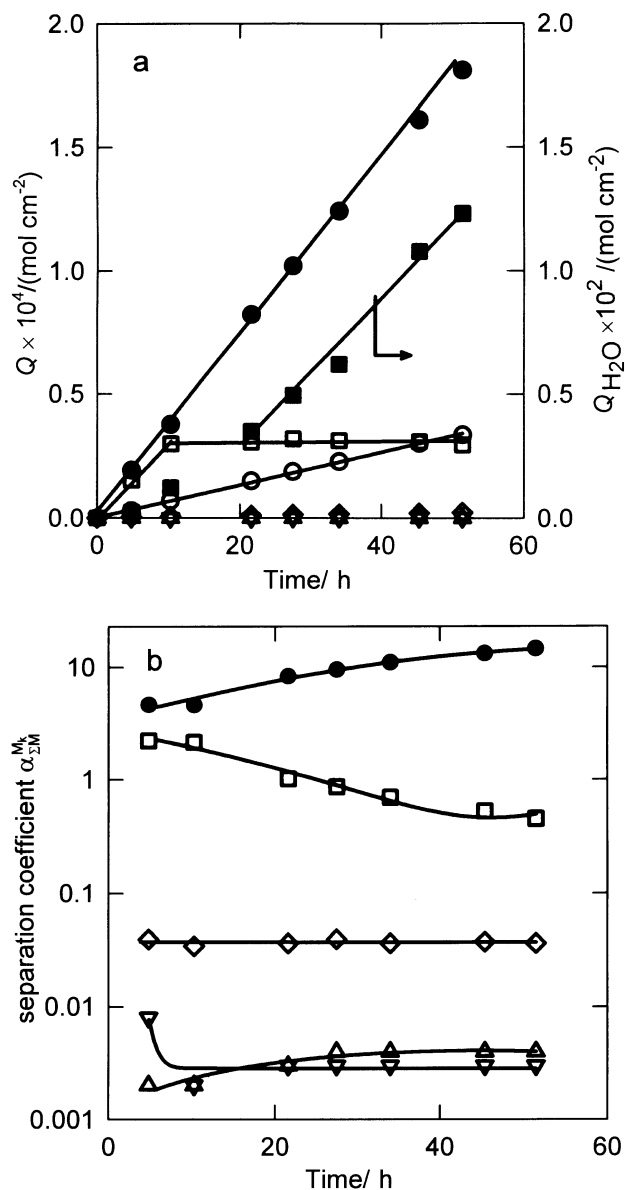


Fig. 7. Transport of cations and pervaporation of water in the PV-MHS pertractor. ● Zn, ○ Cu, □ Ca, ◇ Mg, △ K, ▽ Na, ■ H₂O. a) Cumulative transport curves, b) separation coefficients.

ison of the results for the MHS and DD-MHS indicates that the integration of the Donnan dialysis unit with the MHS results in lowering of the Ca^{2+} flux and achieving a required state when k_{Zn} is larger than k_{Ca} . In the case of the PV-MHS, the overall rate constant k for target cations (Zn^{2+} , Cu^{2+}) is nearly the same as the rate constant for Zn^{2+} in the case of the simpler MHS. Differences appear in the case of univalent cations (K^+ , Na^+) the rate constants of which are by one order of magnitude lower than in the case of the MHS. This seems to prove the hypothesis that univalent cations are transported partly in the LM after extraction into aqueous aggregates formed in the organic LM phase.

CONCLUSION

The general principle of functioning of any natural membrane system as the assembly of different membranes and coupled reaction and diffusion phenomena were the inspiration for constructing hybrid membrane pertractors of practical interest. The first of the discussed systems, the multimembrane hybrid system (MHS), resulted from the analysis of the structure and composition of the bacteria cell envelope. The second system, the DD-MHS, based on the general principle of compartmentalization (characteristic of eukaryotic organisms), enabled a continuous pre-concentration of metal species (DD process) before the proper selective transport and separation (MHS). The third system, PV-MHS, resulted from a coupling of the biomimetic MHS pertractor to the pervaporation process that protected the system from the accumulation of water in the liquid membrane compartment. This approach allowed to apply the MHS under conditions of high osmotic fluxes of water from aqueous external solutions to liquid membrane compartment.

The final aim of the above studies is to combine both systems in one efficient and compact membrane device, which would be applicable in prolonged processes, and under drastically changing conditions, as required by some procedures of environmental monitoring and industrial technology. Following that idea, a compact "superintegrated hybrid system" involving all systems presented herein is under testing in our laboratory.

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