

Extraction and separation of metal cations in solution by supported liquid membrane using lasalocid A as carrier*

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Abstract: Flat-sheet-supported liquid membranes incorporating lasalocid A (a natural ionophore), were previously shown to be permeable to metal cations (Cd^{2+} and Zn^{2+}) against a proton gradient (ΔpH), which is the driving force of the process [1]. This transport process has been extended to other metal species such as Pb^{2+} , Na^+ , and Ag^+ and also to the case where two metal species compete for transport. A higher transport flux for Pb^{2+} as compared to Cd^{2+} and Zn^{2+} is observed and partly explained by a higher rate of interfacial complexation owing to the smaller hydration shell of this species. This effect is confirmed by the data obtained with Ag^+ . However, the size of the metal cation in relation to its hydration shell does not appear as the major parameter to take into account for an estimate of the trans-membrane transport efficiency, as the Na^+ ions escape to this behavior, which has been considered until now as a general trend for metal cation ionophores.

INTRODUCTION

The requirement to limit industrial waste in the natural environment is responsible for the increase in the number of research programs devoted to the improvement of technical processes for the separation and recuperation of valuable and/or toxic species.

The cleaning of waste water by the removal of soluble metal species, particularly transition- and heavy-metal cations, is one of the major objectives of the research in this field. The separation processes based on membrane technologies represent a sophisticated route for that purpose, where reasonable volumes of wastewater have to be treated, since they are reported to strongly limit the number of elementary steps involved in the usual separation and recuperation processes [1]. However, the membrane processes generally present some inconveniences, such as a higher cost, long-term instability, and often an insufficient selectivity for the separation of species of a similar chemical nature.

The improvement of the selectivity of the trans-membrane transport has been the subject of many attempts. Classical routes concern the synthesis of porous inorganic or hybrid membranes of well-defined pore size [2] or the modification of the surface properties of commercial available membranes so as to introduce specific interactions or electrostatic repulsive or attractive effects, as it is the case for membranes used for electrodialysis processes [3].

More specific approaches based on the involvement of molecular recognition processes and accelerated by the breakthroughs in supramolecular chemistry, have provided very sophisticated chemical structures, such as highly specific molecular or ionic complexing agents [4], however, more time is needed to fully characterize such systems incorporated in artificial membranes and to develop large

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scale industrial applications. Most of these attempts are biologically inspired in the sense that they mimic well-known biological processes such as the facilitated ion transport. An alternative to such synthetic biomimetic systems is the use of species extracted from biomembranes, cells, or natural tissues for species recognition, and to use these compounds for the building of separation membranes.

Supported liquid membranes (SLMs) are composed of an organic solution of a carrier, this solution being immobilized in a porous material (in general, a polymer). The cation transport is ensured by a cyclic mechanism (similar to the carrier mechanism of biomembranes) involving complexation at the source side of the membrane and release at the receiving side. The driving force is a proton concentration difference (ΔpH) between the two aqueous phases. Flat-sheet-supported liquid membranes (FSSLMs) are generally preferred to when the porous polymer is a planar sheet.

In a previous work, Aouad *et al.* have shown that by means of a ΔpH driving force [5], the natural ionophore lasalocid A dissolved in *o*-nitrophenyl-octyl-ether (NPOE) and incorporated in an FSSLM can almost completely separate Zn^{2+} from Cd^{2+} cations dissolved in the feed phase of a double aqueous phase system, these metal ions being different from the *in vivo* metal target of this ionophore.

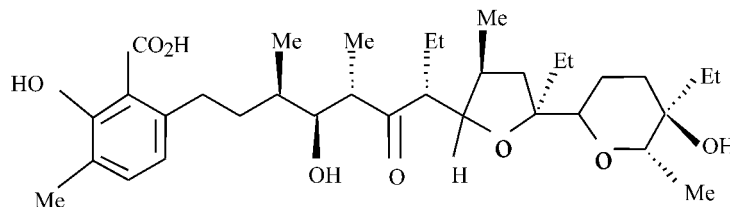
In a previous work, the role of the interfacial potentials was investigated, and we have shown the importance of the kinetics of the association–dissociation reactions at the membrane interfaces and the modelization of the metal cation transport [6].

In this paper, we present comparative transport data for Pb, Cd, Ag, and Na metal cations by lasalocid A across FSSLM, under experimental conditions similar to those previously reported. These results show that Pb(II) is more efficiently transported by this type of supported liquid membrane in comparison to Cd(II), with a selectivity coefficient of about 20. This behavior suggests that such biomimetic FSSLMs could be promising candidates for specific membrane separation processes in industry.

EXPERIMENTAL

The cell used for the membrane experiments consisted of two cubic compartments, the supported liquid membrane being sandwiched between them, at the level of circular holes drilled in each adjacent septum. For flux measurements, the volume was either 1.7 or 50 mL, and the hole radius 0.29 or 1 cm, respectively, depending on the chosen duration of the flux measurement (from initial conditions to complete depletion of the feed phase).

The membrane support Accurel[®] PP was a generous gift of Akzo Nobel Faser AG (Germany). The physical characteristics of these polypropylene membranes are: porosity in the range of 75%, mean pore diameter 0.2 μm , and thickness 150 μm . The organic solvent inside the membrane was *o*-nitrophenyl-octyl-ether (NPOE from Sigma), which gives particularly stable membranes of lifetime exceeding several weeks. The carrier used, lasalocid A from Aldrich, is an antibiotic that belongs to the family of polycyclic carboxyl polyether. It is a good complexing agent for heavy and transition metals. Its minimum concentration before saturation of the flux of transported cation was determined in the range of $5 \cdot 10^{-3} \text{ M}^{\text{i}}$.



The influence of the metal species was studied and for flux comparison, the metal cation (10^{-3} M) was fed into the source compartment in its chloride or nitrate salt form. For cadmium, lead, and zinc, both the chloride and nitrate salts were used. However, since silver chloride is relatively insoluble, only

the nitrate salt was used. The aqueous solutions were prepared with deionized water (MilliQ Plus Column Millipore system), the water resistivity being in the range of $18 \text{ M}\Omega \text{ cm}^{-1}$. For the flux measurements, the change in metal concentration in the receiving phase was measured by sampling 1 mL of stirred solution every 12 h. The samples were diluted so as to coincide with the measuring range of the atomic absorption spectrophotometer (Varian Spectrum A. A. 20).

The source solution was buffered, and its pH adjusted to $\text{pH} = 8$ using a mixture of 10^{-2} M triethanol amine (TEA) and *N*-tris(hydroxy methyl) methyl glycine (tricine). The pH value of the receiving phase was adjusted to $\text{pH} = 3$ by the addition of HCl or HNO_3 .

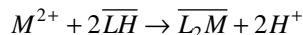
The cation flux J across the SLM is expressed as mole number of transported cations from the source phase toward the receiving phase per unit of time (s^{-1}) and of area (m^{-2}).

Association constant determination

The association constant was determined in biphasic equilibrium experiment. The exchange of metal cation was achieved by contact of two phases of 1 mL of aqueous phase put in contact with 0.5 mL of organic solvent containing the carrier. The two phases were shaken for a period of 48 h. After this time, no significant change in the cation concentration in the aqueous phase was observed, and the metal exchange was considered at equilibrium. For divalent species, the initial cation concentration was 1 or $1.3 \cdot 10^{-3} \text{ M}$. In the case of silver, the initial cation concentration was 1 or $3.5 \cdot 10^{-3} \text{ M}$.

The metal cation concentrations before and after association with a carrier were determined by atomic absorption, and the concentration of the complexed and acid form of the lasalocid in the NPOE was obtained by calculation. From the mole number of complexed cations, the concentration of associated metal-carrier species was expressed, and the concentration of acid form of lasalocid was also determined. In all experiments, the pH of the buffered source phase was fixed to 8.

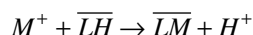
In the case of divalent cations, we considered the reaction of association as follows:



As we worked in dilute solution, the association constant K_a was computed using the expression:

$$K_a = \frac{[\overline{L_2M}] \times [H^+]^2}{[\overline{LH}]^2 \times [M^{2+}]}$$

where the brackets stand for the concentration of the corresponding species. For monovalent metal species, the following reaction was considered:



and the expression of the association constant is written as :

$$K_a = \frac{[\overline{LM}] \times [H^+]}{[\overline{LH}] \times [M^+]}$$

RESULTS AND DISCUSSION

We report in Table 1, the measured experimental association constant of Ag^+ , Na^+ , Pb^{2+} , Cd^{2+} , and Zn^{2+} with lasalocid A obtained in biphasic equilibrium experiments along with the metal cation and hydrated cation radii [7].

A progression is observed that shows that the association constant varies as the inverse of the radius when the hydrated metal cation is considered. Thus, the smaller the size of the metal cation the higher the constant of complexation, which in turn corresponds to a higher value of the electric densi-

Table 1

| Cation | Association constant | r : hydrated cation radius (nm) | cation radius (nm) [8] |
|------------------|-----------------------|---------------------------------|------------------------|
| Ag ⁺ | 4.9 10 ⁻⁴ | 0.212 | 0.126 |
| Na ⁺ | <10 ⁻¹³ | 0.218 | 0.097 |
| Pb ²⁺ | 1.6 10 ⁻⁹ | 0.261 | 0.120 |
| Cd ²⁺ | 5.4 10 ⁻¹⁰ | 0.275 | 0.097 |
| Zn ²⁺ | 3.8 10 ⁻¹¹ | 0.295 | 0.074 |

ty of charge of the ion. This result stresses the importance of the hydration of the ion in the association mechanism. However, this tendency is not followed for Na⁺ cations, which are characterized by a lower association constant than other cations such as cadmium, for instance, which has a bigger radius and a similar density of charge (see Fig. 1). Moreover, these experimental studies differ from that of transport measurements through FSSLM, which concern a three-phase system where sequential complexation, transport through the membrane, and decomplexation occur. Thus, we also measured the flux of transport for different metal cations in the same physicochemical conditions than those determined for cadmium transport, i.e., pH_S = 8 and pH_R = 2. The choice of HCl or HNO₃ for the acidification of the receiving phase did not change the results.

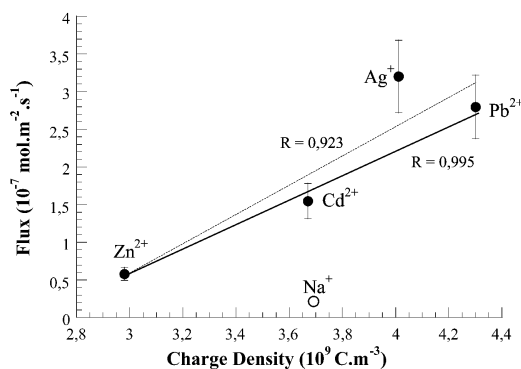


Fig. 1 Cation flux versus density of charge of the metal cation; linear fit for all cations (dotted line) except sodium and linear fit for divalent cations (solid line). The error bars represent standard deviations of the flux values.

The density of charge of the cation is calculated as the ratio of the electric charge and volume of the hydrated metal ion:

$$d = \frac{3 \times Q}{4\pi \times r^3}$$

where Q and r represent the charge of the cation expressed in coulombs and the radius of the hydrated cation in metres respectively.

If the measured fluxes across the membrane are plotted vs. the charge density of the ions in the case of the divalent cations, a linear relationship is observed for divalent cations (see Fig. 1, solid straight line). A slight discrepancy with this linear relationship is observed in the case of the transport of the monovalent Ag⁺ cation (see Fig. 1, dashed straight line), although the tendency to observe an

increased value of the metal cation flux when the density of charge of the ion is higher is still valid. However, the Na^+ ions escape to this behavior, and another linear variation with a different slope could be found for these monovalent cations (see Fig. 1, dashed line). The different type of stoichiometry of the Ag or Na-lasalocid complex (1-1) presumably plays a role in the stability of the association, and as a result, in the kinetics of the interfacial association-dissociation steps and obviously on the overall transfer membrane process, explaining the discrepancy observed in Fig. 1 as compared to divalent cations.

As a result of this correlation, the density of charge of the cation could be taken as an indicator of the selectivity of the membrane transport. However, this correlation has to be taken into account for a given series of metal species as monovalent and divalent cations behave differently.

In order to check the validity of this concept we have measured the transmembrane cation fluxes in experiments where two different metal cations complexed by lasalocid are competitively transported. We worked in the same experimental conditions as for single metal transport experiments, but the two metal cations have been introduced in the feed phase at the same concentration.

Competitive transport experiments

Competition between Cd^{2+} and Na^+

Figure 2 shows the variation of the concentration of Cd^{2+} and Na^+ in the receiving phase vs. time. The linear parts of the plots correspond to the establishment of a constant transport flux of metal cations across the membrane, allowing the determination of the respective fluxes of Cd and Na.

Two metal cations are extracted in the same time from the source solution.

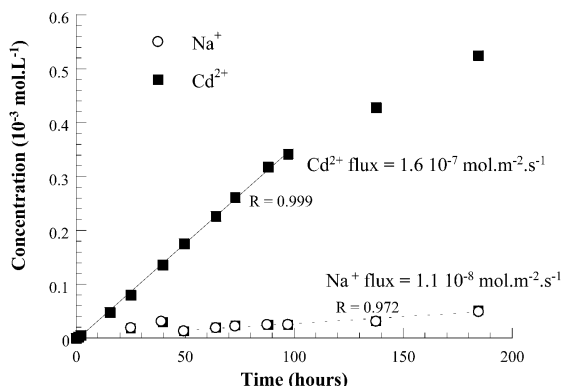


Fig. 2 Transported metal cation concentration vs. time. Competition between Cd^{2+} and Na^+ (source phase pH = 8, receiving phase pH = 3, metal cation initial concentrations 10^{-3} M, lasalocid A concentration $5 \cdot 10^{-3}$ M).

Competition between Cd^{2+} and Zn^{2+}

Figure 3 shows the variation of the concentration of Cd^{2+} and Zn^{2+} in the receiving phase vs. time. The Cd^{2+} transported concentration levels off after about 150 h owing to the depletion of the feed phase.

The cadmium flux ($2.1 \cdot 10^{-7} \text{ mol.m}^{-2} \cdot \text{s}^{-1}$) is higher than that of zinc ($5.2 \cdot 10^{-8} \text{ mol.m}^{-2} \cdot \text{s}^{-1}$). These slopes correspond to a ratio of selectivity of about 4. However in relation to the remark made for the threshold, even if this ratio does not correspond to a very high selectivity of transport of one cation as compared to the other, the separation between Cd and Zn is achieved almost completely by the membrane process after 150 h in the feed phase where only zinc cations are remaining after that time.

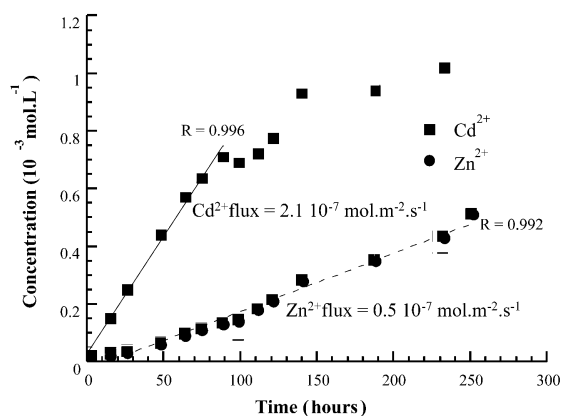


Fig. 3 Transported metal cation concentration vs. time. Competition between Cd^{2+} and Zn^{2+} (source phase pH = 8, receiving phase pH = 3, metal cation initial concentrations 10^{-3} M, lasalocid A concentration $5 \cdot 10^{-3}$ M).

It can be noticed that the respective values of each metal flux (in cases a and b) are not strongly affected by the competition for transport as compared to their values in separate transport experiments (see Fig. 1).

Competition between Cd^{2+} and Pb^{2+}

Figure 4 shows the variation of the concentration of Cd^{2+} and Pb^{2+} in the receiving phase versus time. A stronger selectivity ratio is observed as compared to that for Cd^{2+} and Zn^{2+} . The transport of lead is achieved almost completely as if this metal cation was alone in the receiving phase during the first 150 h, while the transport of Cd appears to be only just beginning when the transport of lead has almost reached its completion.

As in the previous case, the flux values calculated in competitive experiments are not significantly different from those measured in individual transport experiments.

In this case, conversely to the case of competitive transport between Cd^{2+} and Zn^{2+} , the best efficiency of separation between Pb^{2+} and Cd^{2+} is achieved in the receiving phase during the first 100 h of membrane working. This is due to the observed much higher selectivity of transport of the lead cations in competitive transport experiments as compared to the cadmium ones, which is to some extent unexpected on the basis of the results of individual transport experiments.

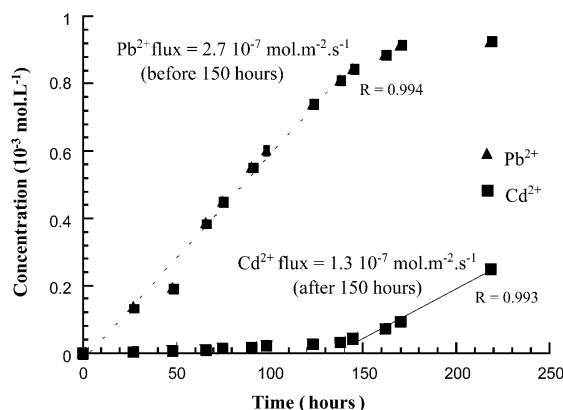


Fig. 4 Transported metal cation concentration vs. time. Competition between Pb^{2+} and Cd^{2+} (source phase pH = 8, receiving phase pH = 3, metal cation initial concentrations 10^{-3} M, lasalocid A concentration $5 \cdot 10^{-3}$ M).

Competition between Ag^+ and Pb^{2+}

Figure 5 shows the variation of the concentration of Ag^+ and Pb^{2+} in the receiving phase vs. time. The flux of Pb^{2+} is higher than that of Ag^+ . The selectivity ratio is of the order of 2.5 in favor of Pb^{2+} . This behavior is also unexpected if we compare this data with that listed in Fig. 1 where the flux of the monovalent Ag^+ cation was higher than that of Pb^{2+} .

The influence of the density of charge appears effective because the lead cation, which has a higher density of electrical charge, is extracted prior to silver; therefore, the flux of silver is higher than that of lead. However, this competition strongly decreases the transport flux of each respective metal cation.

The sum of the cation fluxes in competitive transport experiments was observed lower or equal to the maximum flux: $2.8 \cdot 10^{-7} \text{ mol} \cdot \text{m}^{-2} \cdot \text{s}^{-1}$ determined for lead in separate experiments. This result suggests that this value practically corresponds to the maximum rate that can be obtained for cation transport fluxes in the conditions of our FSSLM system processing.

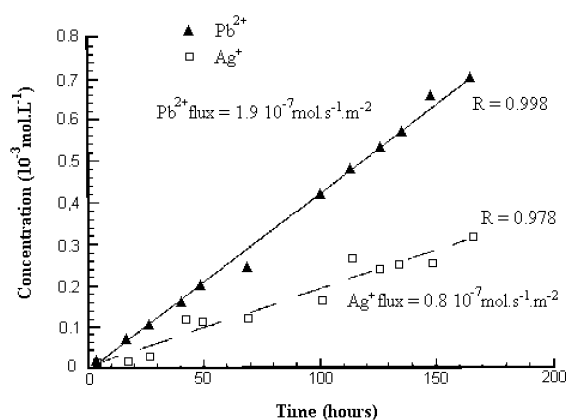


Fig. 5 Transported metal cation concentration vs. time. Competition between Pb^{2+} and Ag^+ (source phase pH = 8, receiving phase pH = 3, metal cation initial concentrations 10^{-3} M , lasalocid A concentration $5 \cdot 10^{-3} \text{ M}$).

CONCLUSIONS

The lasalocid ionophore was shown to be an efficient carrier for toxic water-soluble metal cations such as Pb^{2+} , Zn^{2+} , and Cd^{2+} across artificial FSSLM, these membranes representing potential systems for separation. The equilibrium association experiments that lead to the knowledge of the sequence of the affinities between the metal cation and the carrier in the liquid organic membrane phase showed that the charge density of the cation, which is mainly governed by the hydration number of the ion, is the determining parameter. In the case of monovalent Na^+ and Ag^+ metal cations, the behavior is similar to that of divalent cations. Ag^+ is more transported than Na^+ , which has a lower density of charge. However, Na^+ ions are poorly complexed by lasalocid A (see Table 1), although their charge density is similar to that of Cd^{2+} , which is more complexed. This observation stresses on the mechanism and stability of the association. Even though the driving force of the association between the metal cation and the lasalocid A is the density of charge, the stability of the complex depends on other factors influencing the adaptation of the ion to the cavity of the complexing agent. Depending on the hydration of the ion and, thus, of its size, the stability of the complex differs, and correlatively the association constant values, which were shown to differ by several orders of magnitude. In the case of divalent cations, the 1-2 stoichiometry of the association makes these species less sensitive to adaptation factors mentioned above. Finally, the transport mechanism in competitive bi-metallic experiments appears more complex than that for sin-

gle metal cations, and, in that case, the potential efficiency of such a type of carrier dissolved in FSSLM for metal separation cannot be postulated from such simple thermodynamical considerations.

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