Separation Science and Technology
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713708471

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To cite this Article Canet, L. , Ilpide, M. and Seta, P.(2002) 'Efficient facilitated transport of lead, cadmium, zinc, and silver across a flat-sheet-supported liquid membrane mediated by lasalocid A', Separation Science and Technology, 37: 8, 1851 — 1860

To link to this Article: DOI: 10.1081/SS-120003047
URL: http://dx.doi.org/10.1081/SS-120003047

SEPARATION SCIENCE AND TECHNOLOGY, 37(8), 1851–1860 (2002)

EFFICIENT FACILITATED TRANSPORT OF LEAD, CADMIUM, ZINC, AND SILVER ACROSS A FLAT-SHEET-SUPPORTED LIQUID MEMBRANE MEDIATED BY LASALOCID A

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ABSTRACT

Flat-sheet-supported liquid membranes incorporating lasalocid A (a natural ionophore) were shown in previous works to achieve the transport of divalent transition metal cations such as Cd^{2+} and Zn^{2+} against a proton gradient, which is the driving force behind the process. This transport process has been extended to other metal species such as Pb^{2+} and Ag^{+} and also to the case where the two metal species compete for transport. A higher transport flux for Pb^{2+} as compared to Cd^{2+} and Zn^{2+} is observed, which is partly explained by a higher rate of interfacial complexation due to a smaller hydration shell of this species. This effect is confirmed by the data obtained with Ag(I).

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INTRODUCTION

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

Improvement of the selectivity of the trans-membrane transport has been the subject of much discussion. Classical routes concern synthesis of porous inorganic or hybrid membranes of well-defined pore size (2) or modification of the surface properties so as to introduce specific interactions or electrostatic repulsive–attractive effects as in the case of membranes for electrodialysis (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-scale industrial applications. Most of these attempts are biologically inspired in the sense that they mimic well-known biological processes such as 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 building the separation membranes.

In a previous work, Canet et al. (6) have shown that by means of a proton gradient (ΔpH) driving force, the natural ionophore, lasalocid A dissolved in *o*-nitrophenyl-octyl-ether (NPOE) and incorporated in a flat-sheet-supported liquid membrane (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.

A previous work investigated the role of interfacial potentials, and the authors have shown the importance of the kinetics of the association–dissociation reactions at the membrane interfaces and a model of the metal cation transport (6).

In this paper, we present comparative transport data for Pb, Cd, and Ag metal cations by lasalocid A across FSSLM, under experimental conditions similar to those reported previously. 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 FSSLM 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 was sandwiched between the two compartment walls in which a circular hole was drilled. 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, Wuppertal (Germany). The physical characteristics of these polypropylene membranes are: porosity in the range of 75%, mean pore diameter $0.2\,\mu$m, and thickness $150\,\mu$m. The organic solvent inside the membrane was NPOE from Sigma-Aldrich, St Quentin Fallavier (France), which gives particularly stable membranes with lifetime longer than several weeks. The carrier used, lasalocid A from Sigma-Aldrich, St Quentin Fallavier (France), is an antibiotic that belongs to the family of polycyclic carboxyl polyethers. It is a good complexing agent for heavy and transition metals. Its minimum concentration before saturation of the flux of transported cation was determined to be in the range $5 \times 10^{-3}\,M$ (1).

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 Cd, Pb, and Zn, both 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) St Quentin Yvelines (France), the water resistivity being in the range of $18\,\mathrm{M\Omega\,cm^{-1}}$. For the flux measurements, the change in metal concentration in the receiving phase was measured by sampling 1 mL of stirred solution every 12 hr. The samples were diluted so as to coincide with the measuring range of the atomic absorption spectrophotometer (Varian Spectrum A. A. 20) Les Ulis (France).

The source solution was buffered and its pH adjusted to 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 pH = 3 by the addition of HCl or HNO_3. The cation flux J across the supported liquid membrane (SLM) is expressed as mole number of the transported cation from the source phase toward the receiving phase per unit of time (sec) and of area (m^2).

We determined the association constant (K_a) in biphasic equilibrium experiment. The exchange of metal cation was achieved by contact of two phases: 1 mL of aqueous phase with 0.5 mL of organic solvent containing the carrier. The two phases were shaken for a period of 48 hr. After this time, no significant change in the cation concentration in the aqueous phase was observed. For divalent species, the initial cation concentration was 1 or $1.3 \times 10^{-3}\,M$. In the case of Ag, the initial cation concentration was 1 or $3.5 \times 10^{-3}\,M$.

We measured the concentration before and after association with a carrier 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 the complexed cations, the concentration of the associated metal-carrier species was expressed and the concentration of the acid form of lasalocid was also determined. In all the experiments, pH of the buffered source phase was fixed to eight.

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

$$M^{2+} + 2\overline{LH} \rightarrow \overline{L_2M} + 2H^+$$

As we worked with dilute solution, K_a was computed using the expression:

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

For monovalent metal species, the following reaction was considered:

$$M^+ + \overline{LH} \rightarrow \overline{LM} + H^+$$

and the expression for the association constant, K_a, is written as:

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

RESULTS AND DISCUSSION

We report in Table 1, the measured experimental K_a of Ag^+, Pb^{2+}, Cd^{2+}, and Zn^{2+} with lasalocid obtained in biphasic equilibrium experiments along with the hydrated cation radius (7).

A progression is observed, which shows that the association constant varies as the inverse of the hydrated radius of the complexed metal cation. Thus, the

Table 1. Metal Cation–Lasalocid A Association Constants and Respective Cation Hydrated Radii

Cation	Association Constant	Hydrated Radius (*r*, nm)
Ag^{+}	4.9×10^{-4}	0.212
Pb^{2+}	1.6×10^{-9}	0.261
Cd^{2+}	5.4×10^{-10}	0.275
Zn^{2+}	3.8×10^{-11}	0.295

smaller the size of the metal cation, the higher the constant of complexation, which in turn corresponds to a higher value of the electric density of charge of the ion. However, 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 physico-chemical conditions than those determined for Cd transport, i.e., $pH_S = 8$ and $pH_R = 2$. The choice of HCl or HNO_3 for the acidification of the receiving phase did not change the results.

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

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

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

If the measured fluxes across the membrane are plotted against the charge density of the ions in the case of the divalent cations, a linear relationship is observed (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, dash 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. The different types of stoichiometry of the Ag–lasalocid complex (1:1) presumably plays a role in the kinetics of the interfacial association–dissociation steps and obviously in 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. In order to check the validity of this concept, we have measured the trans-membrane cation fluxes in experiments where two different metal cations complexed by lasalocid are transported competitively. We worked with the same experimental conditions

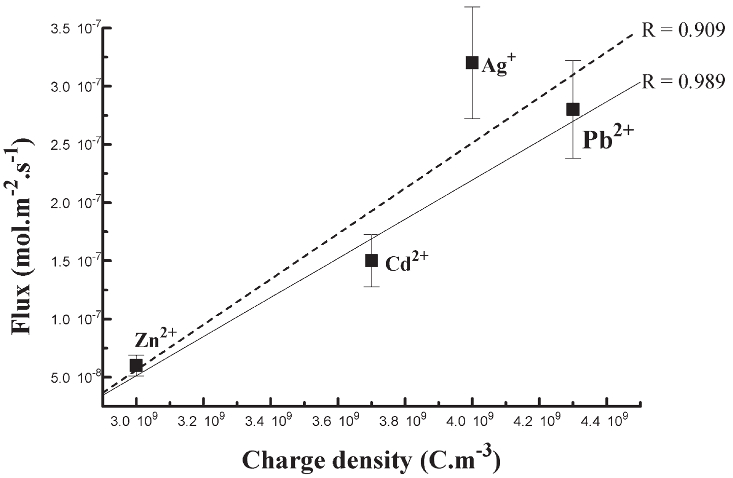

Figure 1. Cation flux vs. density of charge of the metal cation; linear fit for all cations (dash line) and linear fit for divalent cations (solid line). The error bars represent standard deviations of the flux values.

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 Zn^{2+}

Figure 2 shows variation of the concentration of Cd^{2+} and Zn^{2+} in the receiving phase with 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 Zn. The Cd^{2+} transported concentration levels off after about 150 hr due to the depletion of the feed phase.

The Cd flux (2.1×10^{-7} mol m^{-2} sec^{-1}) is higher than that of Zn (5.2×10^{-8} mol m^{-2} sec^{-1}). These slopes correspond to a ratio of selectivity of about four. 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 hr in the feed phase where only Zn cations remain after that time.

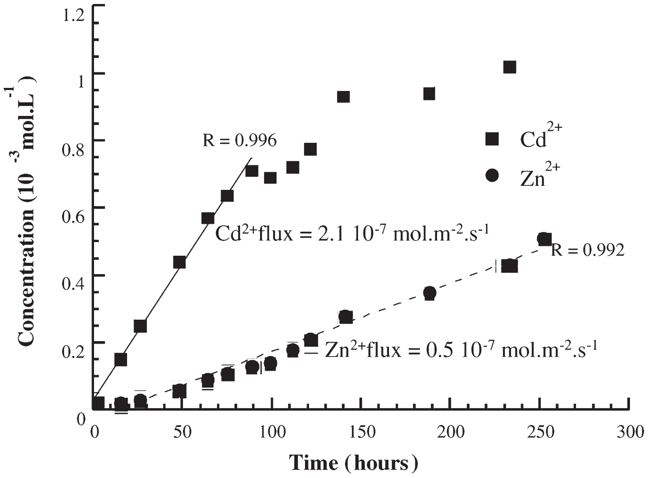

Figure 2. Transported metal cation concentration vs. time. Competition between Cd^{2+} and Zn^{2+} (source phase $pH = 8$, receiving phase $pH = 3$; metal cation initial concentrations $10^{-3}\,M$; lasalocid A concentration $5 \times 10^{-3}\,M$).

The respective values of the fluxes 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 3 shows the variation of the concentration of Cd^{2+} and Pb^{2+} in the receiving phase with time. A stronger selectivity ratio is observed as compared to that for Cd^{2+} and Zn^{2+}. The transport of Pb is achieved almost completely as if this metal cation was alone in the receiving phase during the first 150 hr whilst the transport of Cd appears to be only just beginning when the transport of Pb 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(II) and Zn(II), the best efficiency of separation between Pb (II) and Cd(II) is achieved in the receiving phase during the first 100 hr of membrane working. This is due to the much higher selectivity of transport of the Pb cations in competitive transport experiments observed as compared to the Cd ones, which is to some extent unexpected on the basis of the results of individual transport experiments.

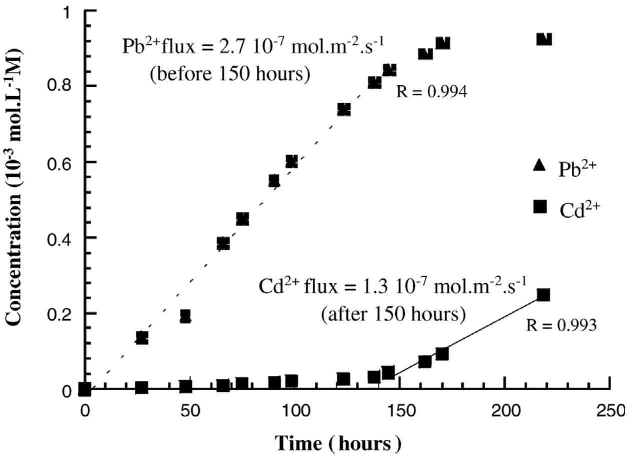

Figure 3. Transported metal cation concentration vs. time. Competition between Pb^{2+} and Cd^{2+} (source phase $pH = 8$, receiving phase $pH = 3$; metal cation initial concentrations $10^{-3}\,M$; lasalocid A concentration $5 \times 10^{-3}\,M$).

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

Figure 4 shows the variation of the concentration of Ag(I) and Pb(II) in the receiving phase with time. The flux of Pb(II) is higher than that of Ag(I). The selectivity ratio is of the order of 2.5 in favor of Pb(II). This behavior is also unexpected if we compare this data with that listed in Table 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 Pb cation, which has a higher density of electrical charge, is extracted prior to Ag, and therefore the flux of Ag is higher than that of Pb. However, this competition strongly decreases the transport flux of each respective metal cation.

We observed that the sum of the cation fluxes in competitive transport experiments is lower or equal to the maximum flux: $2.8 \times 10^{-7}\,\mathrm{mol\,m^{-2}\,sec^{-1}}$ determined for Pb in separate experiments. This result suggests that this value corresponds to the maximum rate that can be obtained for cation transport fluxes in the conditions of our FSSLM system processing.

In conclusion, 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, which 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

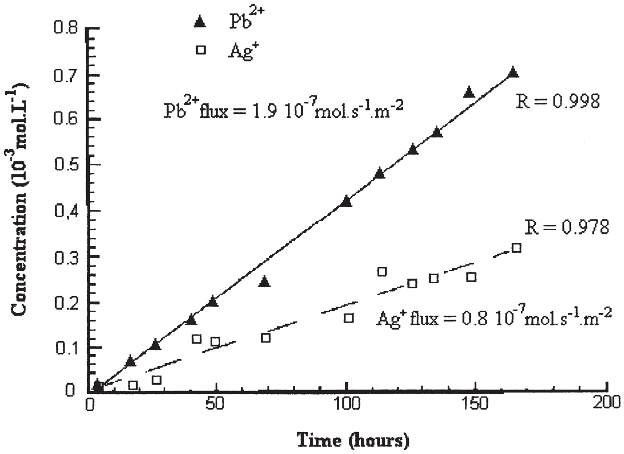

Figure 4. Transported metal cation concentration vs. time. Competition between Pb^{2+} and Ag^+ (source phase pH = 8, receiving phase pH = 3; metal cation initial concentrations 10^{-3} *M*; lasalocid A concentration 5×10^{-3} *M*).

governed by the hydration number of the ion, is the determining parameter. However, the transport mechanism in competitive bi-metallic experiments appears more complex than that for single-metal cations, and in that case, the potential efficiency of such type of carrier dissolved in FSSLM for metal separation cannot be postulated from such simple considerations.

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Received December 2000