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Separation Science and Technology

Publication details, including instructions for authors and subscription information:
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Transport of Hg^2 Ions across a Supported Liquid Membrane Containing Calix[4]arene Nitrile Derivatives as a Specific Ion Carrrier

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To cite this Article Alpoguz, H. Korkmaz , Memon, Shahabuddin , Ersoz, Mustafa and Yilmaz, Mustafa(2005) 'Transport of Hg^2 Ions across a Supported Liquid Membrane Containing Calix[4]arene Nitrile Derivatives as a Specific Ion Carrrier', Separation Science and Technology, 40: 11, 2365 — 2372

To link to this Article: DOI: 10.1080/01496390500202605

URL: http://dx.doi.org/10.1080/01496390500202605

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Separation Science and Technology, 40: 2365–2372, 2005
Copyright © Taylor & Francis, Inc.
ISSN 0149-6395 print/1520-5754 online
DOI: 10.1080/01496390500202605

Transport of Hg^{2+} Ions across a Supported Liquid Membrane Containing Calix[4]arene Nitrile Derivatives as a Specific Ion Carrrier

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Abstract: The transport behavior of Hg^{2+} from aqueous solution through a flat-sheet-supported liquid membrane (SLM) has been investigated by using of calix[4]arene derivatives (**1** and **2**) as carriers and Celgrad 2400 and 2500 as the solid support. The effect of solvent type and anions such as chloride and nitrate ions on the transport of Hg^{2+} was examined. Danesi mass transfer model was used to calculate the permeability coefficients for each parameter studied. The highest values of permeability were obtained with 2-nitrophenyl ethyl ether (NPOE) solvent and the influence was found to be in the order, NPOE > chloroform > xylene. The transport efficiency on the supported liquid membrane was dependent on the type of carrier, its characteristics, and the type of the solvent.

Keywords: Calixarene, metal transport, supported liquid membrane, transport models

Received September 20, 2004, Accepted April 18, 2005

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INTRODUCTION

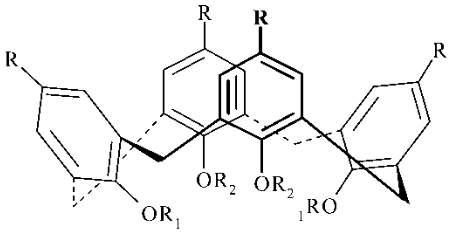
The most attractive techniques in different liquid membrane configurations (precipitation, solvent extraction, and liquid membrane) for industrial applications are supported liquid membranes (SLMs), which have been used for the concentration and separation of metal ions (1–5). The attractive features of SLMs are high selectivity, simultaneous separation, and preconcentration of elements, therefore, they are mostly used for a broad spectrum of elements by proper choice of the carrier. The potential advantages of SLMs over traditional separation techniques are lower capital and operating costs, low energy and extractant consumption, high concentration factors, and high fluxes compared with solid membranes. Due to these advantages SLMs may be very useful for the recovery of metal ions, which are present together in leaching solutions of poly-metallic ores (6). The design and synthesis of calixarenes, an important class of macrocyclic ion receptors, are very well documented in supramolecular chemistry (7, 8). The highly ordered structure of calixarenes offers not only boundless possibilities for chemical modifications but also makes them extremely useful in the study of molecular recognition in supramolecular processes. The present study deals with the use of calixarene-based carriers in SLMs systems. For these reasons we have chosen the calix[4]arene skeleton as a vehicle for modeling such phenomena in liquid membrane technique.

During the past two decades, the assay of mercury compounds has been of special interest because of their widespread agricultural and industrial use in the world and also their hazardous effects on human health. Hence, the development of new methods for selective removal of Hg^{2+} ions for environmental remediation is a very important objective. In earlier reports the nitrile derivatives of calix[4]arenes have been found to transport Hg^{2+} ions selectively from aqueous phase (9, 10). In this work the transport of Hg^{2+} by calix[4]arene derivatives (**1** and **2**) as carriers through supported liquid membrane have been investigated according to Danesi mass-transfer model and the anion effects, the type of solvent such as xylene, chloroform, 2-nitrophenyloctylether (NPOE) for **(1)** and **(2)** carriers was examined.

EXPERIMENTAL

Materials

The carriers 5,11,17,23-Tetra-tert-butyl-25, 27-dicyanomethoxy-26, 28-dihydroxycalix[4]arene **(1)** and 5,11,17,23-Tetra-tert-butyl-25,26,27,28-tetracyanomethoxycalix[4]arene **(2)** used (as presented in Fig. 1) in the study were synthesized according to literature methods (11). Mercury (II) nitrate, mercury (II) chloride, chloroform, and xylene were obtained from Merck Co., 2-nitrophenyl octyl ether from Fluka and used without further



1 R − tert-butyl; R_1= CH_2CN,R_2= H

2 R = tert-butyl; R_1, R_2 −CH_2CN

Figure 1. The ligands used as carriers.

purification. The polymeric films were obtained from Celgard 2400 (thickness: 0.04 μm × 12 μm, porosity 41%) and Celgard 2500 (thickness: 25 μm, porosity 45%) were obtained Celgard Inc. (The samples were kindly supplied by Oketek Co., I.stanbul.)

Transport Measurements

The transport experiments were carried out in a permeation cell consisting of two identical cylindrical compartments (half-cell volume: 40 mL) as previously described (12). The supported liquid membranes consist of a thin, microporous polypropylene film Celgard 2400 or Celgard 2500 immobilizing the solution of carriers in organic solvents. Aqueous mercury (II) nitrate and mercury (II) chloride solutions were used as the feed phase, and deionized water was used as the stripping phase. The measurements were performed at a constant temperature of 25°C at least two times. The transported Hg^{2+} in nitrate and chloride salt forms were determined by monitoring the conductivity of the stripping phase as a function of time (Philips PW 9527 conductivity meter). The standard deviation in the transport measurements is about 15%.

RESULTS AND DISCUSSION

The transport experiments were carried out with an apparatus designed by Stolwijk et al. (12) shown as in Fig. 2. The organic phase impregnated a microporous support of polypropylene placed between the aqueous phases. The mass of organic phase incorporated in a membrane was determined by weighing the membrane before and after impregnation.

We have induced a coupled co-transport of Hg^{2+} ion with nitrate and chloride anions, establishing a chemical gradient between the feed solution

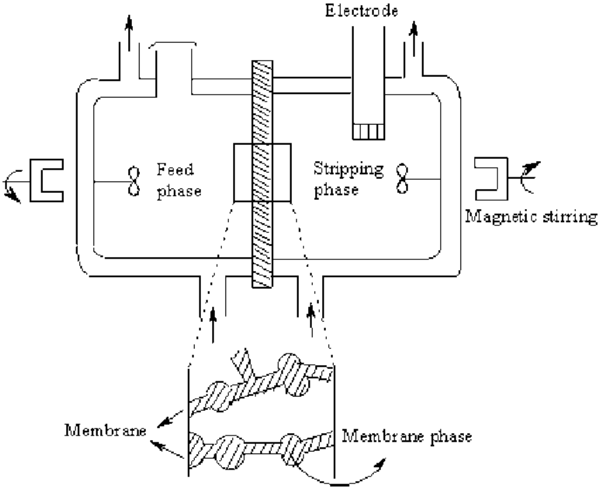


Figure 2. Supported liquid membrane apparatus.

and stripping one. According to the mass-transfer model described by Danesi (13), the permeability (P) is obtained using Eqs. (1) and (2). According to the mass-transfer model described by Danesi (13), the permeability (P) is obtained using Eqs. (1) and (2).

$$\text{Feed Solution: } \ln\left(\frac{C}{C_0}\right) = -\varepsilon \frac{S}{V_B} P_F t \tag{1}$$

$$\text{Strip Solution: } \ln\left(1 - \frac{C'}{C_0}\right) = -\varepsilon \frac{S}{V_A} P_S t \tag{2}$$

where

C/C': concentration of the Hg^{2+} in the feed/stripping solution at time t;

C_0: initial concentration of the Hg^{2+} in the feed solution;

ε: porosity of SLM (%);

S: membrane surface area (cm^2);

V: volume of feed or stripping solution (cm^3).

P_F and P_S were determined graphically from the slope of plots $\ln(C/C_0)$ and $\ln(1 - C'/C_0)$, respectively, vs. t. In ideal cases P_F is equal to P_S. In this study, supported liquid membrane transport works for Hg (II) have been carried out by using Celgard 2400 and Celgard 2500 model membranes and permeabilities have been determinated by using versalities metal salts

(Hg(NO$_3$)$_2$, HgCl$_2$) and different solvents (xylene, chloroform, and 2-nitrophenyl octyl ether).

Depending upon these results, plots of ln C$_1$/C$_0$ vs. time for the nitrate and chloride salts of the Hg^{2+} together with the relevant carrier **1** and **2** in NPOE solvent using Celgrad 2400 and 2500 solid support membranes are presented in Figs. 3 and 4. Both plots give a straight line with slopes which verify that the transport efficiency depends upon the type of solid support. The values of permeabilites (P) were given in Table 1. The percentage permeability of Celgard 2500 membrane (45%) is higher than that of Celgard 2400 (41%). Though the thickness of Celgrad 2400 is smaller than the Celgrad 2500, even then the results show that the values of permeabilities for Celgard 2500 model membrane are higher than that of permeabilities for Celgard 2400 model membrane. Thus, it can be assumed that the permeability depends upon the nature of the membrane.When compared with the chloride and nitrate forms, the transport of Hg^{2+} was found to be higher in the chloride form and the permeability values in chloride form was almost two times of that of nitrate form. These results can be ascribed to the low solubility of (NO$_3$)$^-$ in organic phase by the polarity of co-transport ion and also it could be explained by the fact that the radius of chloride anion (0.168 nm) is smaller more than that of nitrate anion (0.200 nm).

Permeability values of Hg^{2+} in case of carrier **1** are higher than that of using carrier **2**. It can be easily compared with the slopes of the curves, i.e., the slope of carrier **1** and **2** for Hg^{2+} in chloride form for Celgrad 2400 solid membrane gives 6.172×10^{-5} and 5.245×10^{-5}, respectively. It is

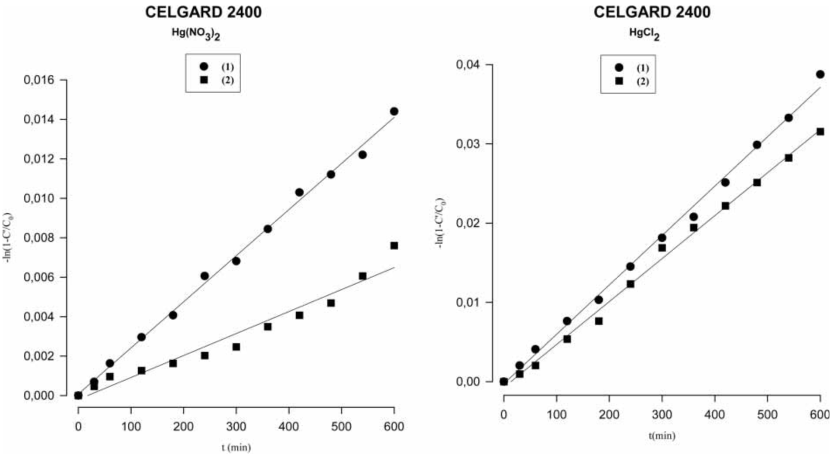


Figure 3. Hg^{2+} transport experiment with calix[4]arenes **1** and **2** for Celgard 2400 membrane. Feed solution: 0.01 M Hg-X (X = NO$_3^-$ ve X = Cl$^-$), organic membrane: **1** and **2** = 10^{-3} M in NPOE, stripping solution: Deionized water, V$_F$ = V$_S$ = 40 cm^3, S = 8.04 cm^2, ε: 0.41.

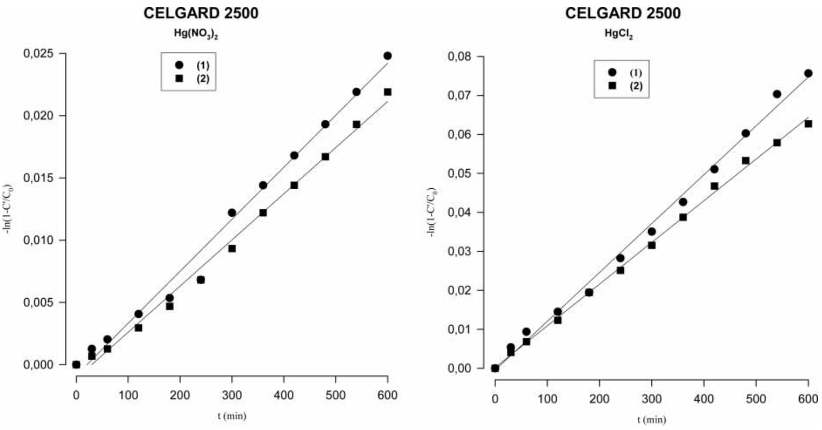


Figure 4. Hg^{2+} transport experiment with calix[4]arenes **1** and **2** for Celgard 2500 membrane. Feed solution: 0.01 M Hg-X ($X = NO_3^-$ ve $X = Cl^-$), organic membrane: **1** and **2** $= 10^{-3}$ M in NPOE, stripping solution: Deionized water, $V_F = V_S = 40\,cm^3$, $S = 8.04\,cm^2$, ε: 0.41.

thought that the permeability is low due to high molecular weight of carrier **2**, and the stripping reaction rate is low due to the stable complex between Hg^{2+} ion and R groups, which are the same for R_1 and R_2 positions. The transport of Hg^{2+} through supported liquid membranes by using calix[4]arene derivatives **1** and **2** as carriers was investigated. In case of the plot give a straight line with

Table 1. Permeabilities P for transport through supported liquid membranes by calixarenes 1 and 2 for Celgard 2400 and 2500 membrane

			$P \times 10^4$ ($cm \cdot min^{-1}$)	
Ligand	Ion pair	Solvent	Celgrad 2400	Celgrad 2500
(**1**)	$Hg(NO_3)_2$	Xylene	0.67	1.23
		Chloroform	0.68	1.44
		NPOE	2.84	4.42
(**1**)	$HgCl_2$	Xylene	1.14	1.7
		Chloroform	4.70	4.86
		NPOE	7.56	13.8
(**2**)	$Hg(NO_3)_2$	Xylene	0.58	0.86
		Chloroform	0.66	1.16
		NPOE	1.35	4.1
(**2**)	$HgCl_2$	Xylene	0.76	1.35
		Chloroform	1.43	1.65
		NPOE	6.58	11.8

a slope of 1.243×10^{-4} but in case of $Hg(NO_3)_2$ the slope decreased to 3.974×10^{-5} for Celgrad 2500 model membrane (Fig. 4). These results showed that the polarity of co-transport-ion resulted in a decrease of the permeability values by the low solubility of $(NO_3)^-$ in organic phase. From SLM experiments, the effect of various operating variables on Hg^{2+} permeability were investigated and permeability of Hg^{2+} in case of using carrier **1** is higher than that of using carrier **2**.

When different solvents were used for both of the carriers the values of permeabilities obtained were also different. It has been previously pointed out that the nature of solvent has a great influence on the transport efficiency through bulk liquid membranes (9, 10). The results obtained for permeablity with solvents are presented in Table 1. It is apparent from the results that the premeability values are remarkably different in different solvents and found to be in the order NPOE > chloroform > xylene. In case of xylene and chloroform the values of permeabilities are smaller than that of NPOE. Nitrophenyl alkyl ethers (NPHE-hexyl; NPOE-octyl) were used because they lead to a stable membrane due to their very low solubility in water (14–18).

In conclusion, these results showed that the polarity of co-transport-ion resulted in a decrease of the permeability values by the low solubility of (NO_3^-) in organic phase. From SLMs experiments, the effect of various operating variables on Hg^{2+} permeability were investigated and permeability of Hg^{2+} in case of using carrier **1** is higher than that of carrier **2**. The transport efficiency on the liquid membrane transport was dependent on the type of carrier and its characteristics, the type of solvent and the type of anion.

ACKNOWLEDGMENT

The authors are grateful for the financal support provided by Selcuk University Research Foundation (SUAF) under Project FBE 2001/026.

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