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Journal of Macromolecular Science, Part A
Publication details, including instructions for authors and subscription information:
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To cite this Article Alpoguz, H. Korkmaz , Kaya, Ahmet , Memon, Shahabuddin and Yilmaz, Mustafa(2007) 'Facilitated Supported Liquid Membrane Transport of Hg^{2} Using Calix[4]arene Derivatives', Journal of Macromolecular Science, Part A, 44: 1, 17 — 20

To link to this Article: DOI: 10.1080/10601320601044302

URL: http://dx.doi.org/10.1080/10601320601044302

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Journal of Macromolecular Science®, Part A: Pure and Applied Chemistry (2007) **44**, 17–20
Copyright © Taylor & Francis Group, LLC
ISSN: 1060-1325 print/1520-5738 online
DOI: 10.1080/10601320601044302

Facilitated Supported Liquid Membrane Transport of Hg^{2+} Using Calix[4]arene Derivatives

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Received April, 2006, Accepted May, 2006

The transport behavior of Hg^{2+} from aqueous solution through a flat-sheet supported liquid membrane has been investigated by the use of calix[4]arene derivatives (**1** and **2**) as carriers and Celgard 2400 and Celgard 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. A Danesi mass transfer model was used to calculate the permeability coefficients for each parameter studied. The highest values of permeability were obtained with 2-nitrophenyloctyl-ether (NPOE) solvent and the influence was found to be in the order of NPOE > chloroform > xylene. The transport efficiency on the liquid membrane transport was dependent on the type of solvent, anion, and carrier.

Keywords: supported liquid membrane; metal transport; transport models; calixarenes

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1 Introduction

Several technologies can be used to remove these toxic metals from liquid effluents, including precipitation, solvent extraction, ion exchange, etc. Among these, the liquid membrane technique has turned out to be important for its use in separation, concentration or even analytical application. Though this technology is still in the research or development stage, it retains a worthy position in the field of membrane separations due to its advantages over conventional separation operations.

The different types of liquid membranes are reviewed in the literature (1, 2). Supported liquid membranes and emulsion liquid membranes are the most commonly used. Supported liquid membranes usually consist of an organic solvent immobilized in the pores of a hydrophobic microfiltration membrane (3–7). This liquid membrane phase contains a carrier which binds one or a class of components in the feed phase transporting it (or they) in the stripping phase through the membrane. Solute permeation is due to the concentration gradient existing between the two sides of the membrane (8).

The main advantage of supported liquid membranes in comparison with traditional techniques is the high process selectivity achieved when an appropriate carrier molecule is employed (9–11).

Despite the increasing industrial use of mercury in the world and its hazardous effects to human health (12), information about the transport of this ion across liquid membrane is quite sparse (13–18). Hence, the development of new methods for selective removal of Hg^{2+} ions for environmental remediation is a very important objective.

In this paper, the transport of Hg^{2+} by calix[4]arene derivatives (**1** and **2**) as carriers through supported liquid membrane have been investigated according to the Danesi mass transfer model and the anion effects, the type of solvent such as xylene, 2-nitrophenyloctyl-ether (NPOE) for (**1**) and (**2**) carriers was examined.

2 Experimental

2.1 Materials

The carriers 2-2′-bis[5,11,17,23-tetra-*tert*-butyl-26,27,28-tris(cyanomethoxy)calix[4]arene] diethyl ether (**1**) and calix[4]arene dinitrile-oligomer (**2**) used (Figure 1) in the study were synthesized according to literature methods (19, 20). Mercury (II) nitrate, mercury (II) chloride, chloroform and xylene were obtained from Merck Co., 2-nitrophenyl octyl ether from Fluka and used without further purification. The polymeric films Celgard 2400 (thickness: 25 μm porosity 41%) and Celgard 2500 (thickness: 25 μm,

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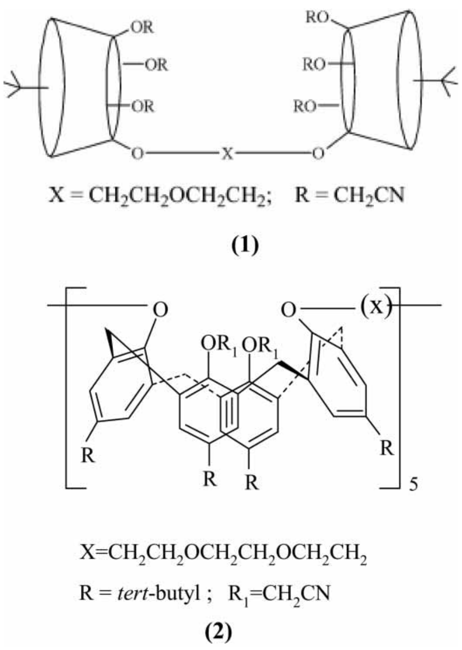

$X = CH_2CH_2OCH_2CH_2$; $R = CH_2CN$

(1)

$X = CH_2CH_2OCH_2CH_2OCH_2CH_2$

R = *tert*-butyl ; $R_1 = CH_2CN$

(2)

Fig. 1. The ligands used as carriers.

porosity 45%) were obtained Celgard Inc. (Samples were kindly supplied by Oketek Co., Istanbul).

2.2 *Transport Measurements*

The transport experiments were carried out in a permeation cell consisting of two identical cylindrical compartments (half-cell volume: 30 ml) (Figure 2), previously described (21). The supported liquid membranes consisted of a thin, microporous polypropylene film (Celgard 2400; thickness: 25 μm, porosity 41%; Celgard 2500; thickness: 25 μm, porosity 45%) 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 soaking time of the Celgard 2400 and Celgard 2500 membranes is 24 h and the stirring speed is chosen as 300 rpm in the all transport experiments. The measurements were performed at a constant temperature of 25°C at least twice. 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%.

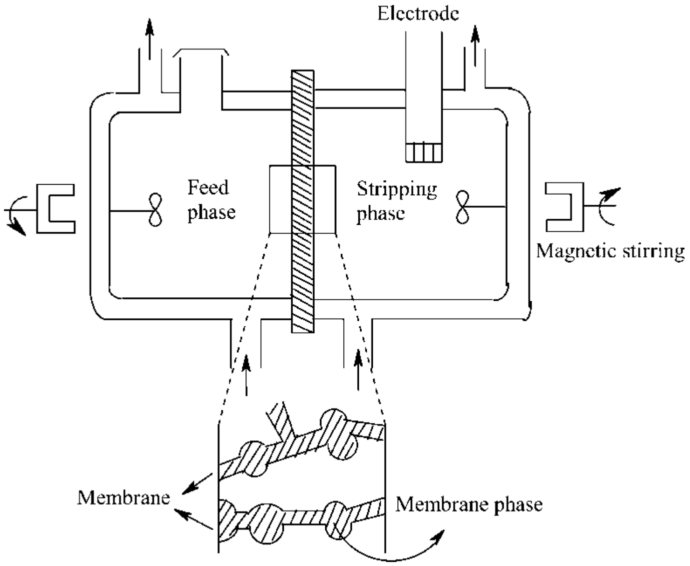

Fig. 2. Supported liquid membrane apparatus.

3 Results and Discussion

The transport experiments were carried out with an apparatus designed by Reinhoudt et al. (21) shown as in Figure 2. The

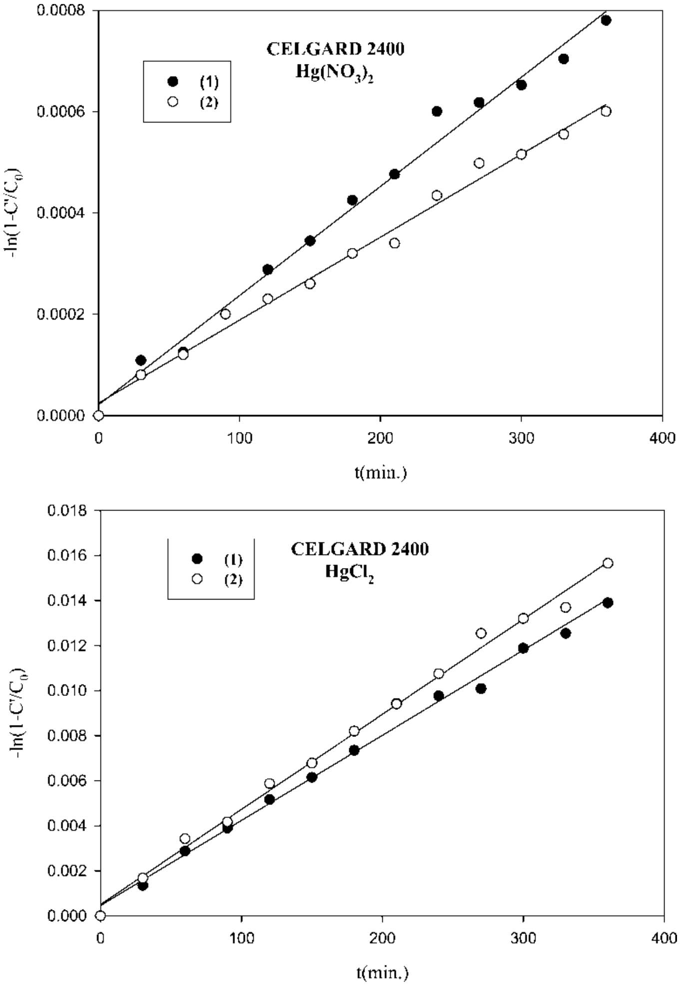

Fig. 3. Hg^{2+} transport experiment with calix[4]arenes **1** and **2** for Celgard 2400 membrane. Feed solution: 0.01 M Hg-X ($X = NO_3^-$ ve $X = Cl^-$), organic membrane: **1** and **2** $= 10^{-3}$ M in NPOE, stripping solution: Deionized water, $V_F = V_S = 30\ cm^3$, $S = 9.08\ cm^2$, ε: 0.41.

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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 and nitrate and chloride anions, establishing a chemical gradient between the feed and stripping solutions. According to the mass transfer model described by Danesi (22), the permeability (P) is obtained using Equations (1) and (2).

$$\text{Feed solution: } \ln\left(\frac{C}{C_0}\right) = -\varepsilon \frac{S}{V_B} P_{Ft} \qquad (1)$$

$$\text{Strip solution: } \ln\left(1\frac{C'}{C_0}\right) = -\varepsilon \frac{S}{V_A} P_{St} \qquad (2)$$

where C/C': concentration of the cation, respectively in the feed/stripping solution at time t; C_0: initial concentration of the cation in the feed solution; ε: porosity of supported liquid membrane (%); 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 determined by using versatile metal salts ($Hg(NO_3)_2$, $HgCl_2$) and different solvents (xylene, chloroform and 2-nitrophenyl octyl ether).

Depending upon these results, plots of $\ln(1 - C'/C_0)$ vs. time for the nitrate and chloride salts of the Hg^{2+}, together with the relevant carrier **1** and **2** in NPOE solvent using Celgard 2400 and Celgard 2500, solid support membranes are presented in Figures 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 permeabilities (P) are given in Table 1. The percentage permeability of Celgard 2500 membrane (45%) is higher than that of Celgard 2400 (41%). Though the thickness of Celgard 2400 is smaller than the Celgard 2500, 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. These results can be ascribed to the low solubility of (NO_3^-) in organic phase by the polarity of co-transport ion and it could also 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).

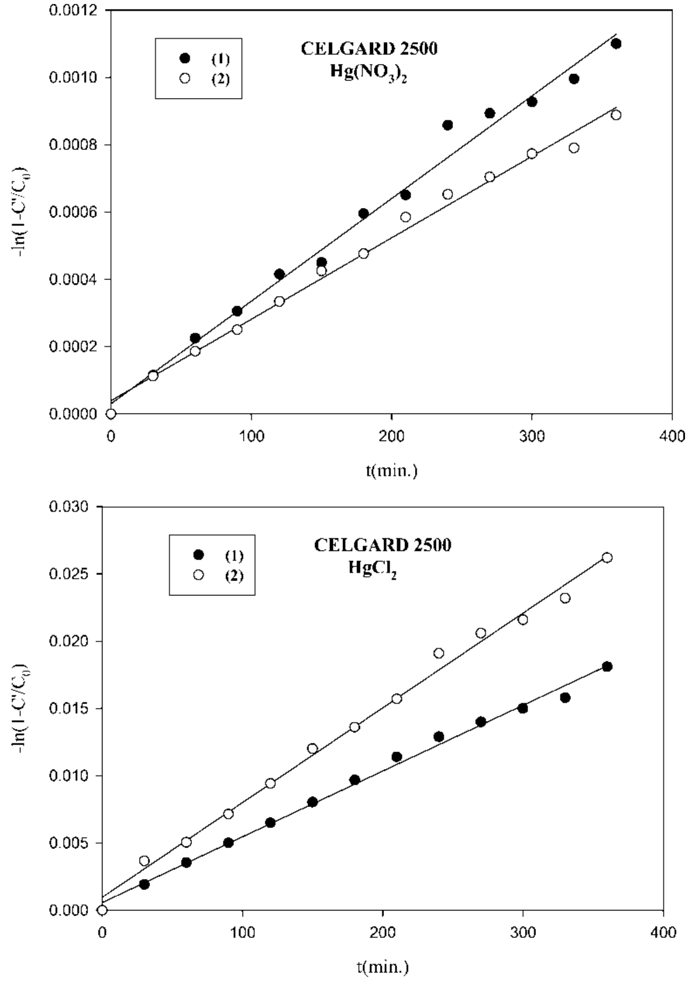

Fig. 4. Hg^{2+} transport experiment with calix[4]arenes **1** and **2** for Celgard 2500 membrane. Feed solution: 0.01 M Hg-X ($X = NO_3^-$ ve $X = Cl^-$), organic membrane: **1** and **2** $= 10^{-3}$ M in NPOE, stripping solution: Deionized water, $V_F = V_S = 30\ cm^3$, $S = 9.08\ cm^2$, ε: 0.45.

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

			$P \times 10^5$ (cm · min^{-1})	
Ligand	Ion pair	Solvent	Celgrad 2400	Celgrad 2500
1	$Hg(NO_3)_2$	Xylene	0.87	0.92
		Chloroform	1.08	1.31
		NPOE	1.74	2.24
1	$HgCl_2$	Xylene	8.88	16.18
		Chloroform	10.18	21.78
		NPOE	30.46	35.87
2	$Hg(NO_3)_2$	Xylene	0.51	0.53
		Chloroform	0.67	0.92
		NPOE	1.32	1.78
2	$HgCl_2$	Xylene	7.35	10.43
		Chloroform	9.62	12.99
		NPOE	34.00	51.77

When the 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 (16, 17, 23, 24). The results obtained for permeability with solvents are presented in Table 1. It is apparent from the results that the permeability values are remarkably different in different solvents and found to be in the order of NPOE > chloroform > xylene. In the 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 (25–28). Also, the polymeric support materials used are very important in the stability of the membrane. The requirement for a good polymeric support are high porosity, small pore size, good mechanical strength, chemical resistance, thinness, hydrophobicity, and low cost.

4 Conclusions

These results showed the polarity of co-transportion resulted in a decrease of the permeability values by the low solubility of (NO_3^-) in organic phase. From supported liquid membranes experiments, the effects of various operating variables on Hg^{2+} permeability were investigated. The transport efficiency on the liquid membrane transport was dependent on the type of solvent, the type of anion, the type of carrier.

5 References

1. Sastre, A.M., Kumar, A., Shukla, J.P. and Sing, R.K. (1998) *Sep. Purif. Meth.*, **27**, 213–298.
2. Ho, W.S.W. (2003) *Ann. NY Acad. Sci.*, **984**, 97–122.
3. Lin, S.H. and Juang, R.S. (2001) *J. Membr. Sci.*, **188**, 251–262.
4. Saikia, B., Dutta, N.N. and Dass, N.N. (2003) *J. Membr. Sci.*, **225**, 1–13.
5. Tayeb, R., Fontas, C., Dhahbi, M., Tingry, S. and Seta, P. (2005) **42**, 189–193.
6. Alguacil, F.J., Alonso, M. and Sastre, A.M. (2005) *J. Membr. Sci.*, **252**, 237–244.
7. Molinari, R., Poerio, T., Cassano, R., Picci, N. and Argurio, P. (2004) *Ind. Eng. Chem. Res.*, **43**, 623–628.
8. Yang, C.F. and Cussler, E.L. (2000) *J. Membr. Sci.*, **166**, 229–238.
9. Gholivand, M.B. and Khorsandipoor, S. (2000) *J. Membr. Sci.*, **180**, 115–120.
10. Shamsipur, M., Kazemi, S.Y., Azimi, G., Madaeni, S.S. and Lippolis, V. (2003) *J. Membr. Sci.*, **215**, 87–93.
11. Fontàs, C., Salvadò, V. and Hidalgo, M. (2003) *J. Membr. Sci.*, **223**, 39–48.
12. Katzung, B.G. Clinical pharmacology. In *Appleton and Lange*, 3rd ed.; Norwalk: C.T, 734–735, 1987.
13. Shamsipur, M., Mashhadizadeh, M.H. and Azimi, G. (2002) *Sep. Purif. Technol.*, **27**, 155–161.
14. Safavi, A. and Shams, E. (1998) *J. Membr. Sci.*, **144**, 37–43.
15. Pàez-Hernàndez, M.E., Aguilar-Arteaga, K., Valiente, M., Ramirez-Silva, M.T., Romero-Romo, M. and Palomar-Pardavè, M. (2004) *Anal. Bioanal. Chem.*, **380**, 690–697.
16. Alpoguz, H.K., Memon, S., Ersoz, M. and Yilmaz, M. (2002) *New J. Chem.*, **26**(**4**), 477–480.
17. Alpoguz, H.K., Kaya, A., Yilmaz, A. and Yilmaz, M. (2005) *J. Macromol. Sci. Part A: Pure Appl. Chem.*, **A42**, 577–586.
18. Alpoguz, H.K., Memon, S., Ersoz, M. and Yilmaz, M. (2005) *Sep. Sci. Technol.*, **40**, 2365–2372.
19. Memon, S., Uysal, G. and Yilmaz, M. (2000) *Sep. Sci. Technol.*, **35**, 1247–1256.
20. Memon, S. and Yilmaz, M. (2000) *React. Funct. Polym.*, **44**, 227–233.
21. Visser, H.C., Reinhoudt, D.N. and Dejong, F. (1994) *Chem. Soc. Rev.*, **23**, 75–81.
22. Danesi, P.R. (1984) *Sep. Sci. Technol.*, **19**, 857–894.
23. Alpoguz, H.K., Kaya, A., Yilmaz, A. and Yilmaz, M. (2005) *J. Macromol. Sci. Part A: Pure Appl. Chem.*, **A42**, 1159–1168.
24. Alpoguz, H.K., Memon, S., Ersoz, M. and Yilmaz, M. (2004) *Sep. Sci. Technol.*, **39**(**4**), 799–810.
25. Arnaud-Neu, F., Böhmer, V., Dozol, J.F., Grüttner, C., Kraft, R.A., Mauprivez, D.O., Rouquette, H., Schwing-Weill, M.J., Simon, N. and Vogt, W. (1996) *J. Chem. Soc. Perkin Trans. 2*, **2**(**6**), 1175–1182.
26. Casnati, A., Pochini, A., Ungaro, R., Ugozzoli, F., Arnaud-Neu, F., Fanni, S., Schwing, M.J., Egbering, R.J.M., Jong, F. and Reinhoudt, D.N. (1995) *J. Am. Chem. Soc.*, **117**, 2767–2777.
27. Dozol, J.F., Simon, N., Lamare, V., Rouquette, H., Eymard, S., Tournois, B., Marc DCC/DESD/SEP, D.D., Macias, R.M. and DIST/UDC (1999) *Sep. Sci. Technol.*, **34**(**6&7**), 877–909.
28. Kim, J.K., Kim, J.S., Shul, Y.G., Lee, K.W. and Oh, W.Z. (2001) *J. Membrane Sci.*, **187**, 3–11.

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