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# Study on the Transport Kinetics of $\text{Hg}^{2+}$ Through Calix-Oligomer Bulk Liquid Membrane

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*In this article, a calix-oligomer derivative is used (1) as a carrier to transport  $\text{Hg}^{2+}$  ions from an aqueous solution into an aqueous receiving solution. The kinetic parameters were analyzed in the formation of two consecutive, irreversible first order reactions. The influence of temperature and solvent and stirring rate on the kinetic parameters ( $k_1$ ,  $k_2$ ,  $R_m^{\max}$ ,  $t_{\max}$ ,  $J_d^{\max}$ ,  $J_a^{\max}$ ) have also been investigated. The membrane entrance rate,  $k_1$ , and the membrane exit rate,  $k_2$ , constants were increased with temperature and stirring rate. The membrane entrance and exit rate constants depend on the solvent type and are found to be in the order  $\text{CH}_2\text{Cl}_2 > \text{CHCl}_3 > \text{CCl}_4$ . For the maximum membrane exit flux,  $J_a^{\max}$ , the activation energy was found from the slope of the linear Arrhenius relationship to be 7.06 kcal/mol, which indicates that the process is controlled by species diffusion.*

**Keywords** liquid membrane, transport kinetics, temperature effects, diffusional rate-determining step, calixarenes

## Introduction

Liquid membranes play an attractive role in separation science (1). Their efficiency and economic advantages designate them as the optimal solution of some important problems in science and technology, such as precious metal recovery, and toxic product (metals, organic molecules) elimination from wastewaters, etc. Therefore, scientific research in this field continues to be very active despite some important solution-awaiting technological problems, which at present are large scale applications of liquid membranes in the chemical industry.

Along with the crown ethers, cryptands, and cyclodextrins, the calixarenes are a major class of supramolecular hosts. Even though the calixarenes have many structural similarities with cyclodextrins, they are highly flexible molecules compared with cyclodextrins. The calixarene recognize cationic and anionic species, as well as neutral molecules. These receptors have the possibility to form interesting complexes both with metal cations and biological compounds by exhibiting extractibility and selectivity.

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There have been many studies published dedicated to calixarenes, particularly in the molecular inclusion of biological substrates, such as amines and amino acids, by these receptors (2–6). Various applications of calixarenes refer to purification, chromatography, catalysis, enzyme mimics, ion selective electrodes, phase transfer, transport across membranes, ion channels and self-assembling monolayers (7–12).

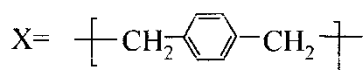
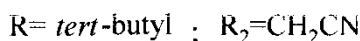
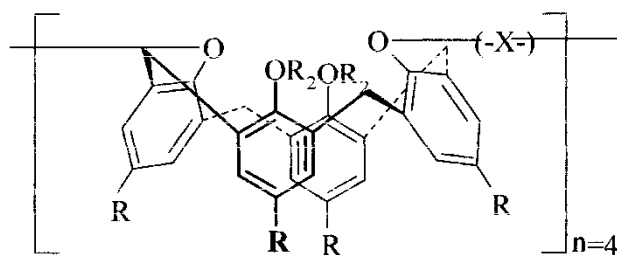
It is well known that the examination of mercury and its compound is of special interest because their widespread agricultural and industrial use throughout the world and also for their hazardous effects on human health (13). Hence, the development of new methods for the selective removal of  $\text{Hg}^{2+}$  ions for environmental remediation is a very important objective. However, despite the great potential of membrane transport for selective removal, there are only a few reports on membrane transport studies in liquid membranes (14–17). In recent years, we have been involved in the synthesis of calixarenes for the selective removal of toxic metal especially  $\text{Hg}^{2+}$  ions from the aqueous phase. For this reason, a variety of calix[4]arene derivatives was prepared for the problem of selective extraction of  $\text{Hg}^{2+}$  ions from waste effluents (18–20).

In the present study on the co-transport of  $\text{Hg}^{2+}$  ion through liquid membranes calix-oligomer (**1**) was used as the carrier ligand (as presented in Figure 1). The carrier was synthesized according to the literature method (21) and used to examine various parameters that are responsible for the transport of  $\text{Hg}$  (II) ions from donor solutions to an acceptor one. The kinetics of  $\text{Hg}^{2+}$  ion transport were analyzed at different temperatures in the range of 293–308 K and at different stirring rates in various solvents, and are discussed in the form of two irreversible first order reactions.

## Experimental

### Materials

The chemical reagents used in these experiments were mercury (II) nitrate, dichloromethane, chloroform,  $\text{CCl}_4$  and picric acid obtained from Merck Co. (Darmstadt,



(1)

Figure 1. The structure of ligand used as carrier.

Germany). Mercury (II) picrate solution was prepared by the addition of a  $1 \times 10^{-2}$  M mercury (II) nitrate to a  $2.5 \times 10^{-5}$  M aqueous picric acid solution and shaken at  $25^\circ\text{C}$  for 1 h. The aqueous solutions were prepared using demineralized water.

### ***Kinetic Procedure***

Co-transport experiments were conducted using a thermostated (Grand mark, model W14, Grants Instruments, Cambridge, England) apparatus. Transport experiments were carried out in a U-type cell. An organic solution (20 ml) containing the ionophore was placed in the bottom of the cell and two portions of aqueous donor and acceptor solutions (10 ml) were carefully added on top of them. Both surface areas were  $2.5 \text{ cm}^2$ . The organic phase was stirred at variable speeds magnetically. (Chiltern mark, model HS 31).

The initial phases consisted of the donor phase, which was an aqueous mercury (II) picrate ( $2.5 \times 10^{-5}$  M) solution, while the membrane phase was made up by dissolving carrier (1) ( $C_{\text{carrier}} = 10^{-3}$  M) in the organic phase. The acceptor phase consisted of twice-distilled water. Samples were taken from both water phases (acceptor and donor phases) at various intervals of time and the picrate ion concentration was analyzed by a spectrophotometric method (22). The spectrophotometric measurements were performed by means of an UV-VIS Spectrometer Shimadzu 160A. Each experimental result reported is the arithmetic mean of two independent measurements.

### **Results and Discussion**

In earlier reports (16, 17, 23) the nitrile and ketone derivatives of calix[4]arenes have been found to transport  $\text{Hg}^{2+}$  ions selectively from an aqueous phase. In this work, we have investigated transport of  $\text{Hg}^{2+}$  ion by carrier (1) in the bulk liquid membrane and the kinetic behavior of the transport process as a function temperature, stirring rate and solvent.

The liquid membrane technique contains two processes in a single stage: extraction of metal ion from the aqueous donor solution to the organic phase containing the carrier molecules (membrane) and a re-extraction of this metal ion from the membrane to the aqueous acceptor phase. The overall transport process consists of mixture diffusion steps and complexations/decomplexation reactions at two independent and possible different interfaces.

All the measurements were carried out under the exact same experimental conditions. A simple theoretical approach was used to obtain the consecutive kinetic equations for a transport system, which was discussed in details elsewhere (16, 17, 23–26).

In the experiments, the variation of picrate ion concentration with time was directly measured in both donor ( $C_d$ ) and acceptor phases ( $C_a$ ). The corresponding change of picrate ion concentration in the membrane phase was determined from the material balance between the phases. For practical reasons, the dimensionless reduced concentrations were used:

$$R_d = \frac{C_d}{C_{d0}} \quad R_m = \frac{C_m}{C_{d0}} \quad R_a = \frac{C_a}{C_{d0}} \quad (1)$$

where  $C_{d0}$  is the initial  $\text{Hg}^{2+}$  concentration in the donor phase,  $C_d$ ,  $C_m$  and  $C_a$  represents the  $\text{Hg}^{2+}$  concentration in donor, membrane. and acceptor phases, respectively. The

material balance, with respect to the reduced concentrations, can be expressed as  $R_d + R_m + R_a = 1$ . From this expression, the kinetic behavior of the consecutive irreversible first order reactions can be described as follows:



where  $k_1$  and  $k_2$  are the apparent membrane entrance and exit rate constants, respectively. The kinetic scheme for consecutive reaction systems can be described by considering the reduced concentrations as follows:

$$\frac{dR_d}{dt} = -k_1 R_d \equiv J_d \quad (3)$$

$$\frac{dR_m}{dt} = k_1 R_d - k_2 R_m \quad (4)$$

$$\frac{dR_a}{dt} = k_2 R_m = J_a \quad (5)$$

where  $J$  represents the flux. Integrating of Equations (3)–(5), assuming as  $k_1 \neq k_2$ , leads to the differential equations given as follows;

$$R_d = \exp(-k_1 t) \quad (6)$$

$$R_m = \frac{k_1}{k_2 - k_1} [\exp(-k_1 t) - \exp(-k_2 t)] \quad (7)$$

$$R_a = 1 - \frac{k_1}{k_2 - k_1} [k_2 \exp(-k_1 t) - k_1 \exp(-k_2 t)] \quad (8)$$

The maximum values of  $R_m$  and  $t_{\max}$  when  $dR_m/dt = 0$ , can be evaluated as;

$$R_m^{\max} = \left( \frac{k_1}{k_2} \right)^{-k_2/(k_1 - k_2)} \quad (9)$$

$$t_{\max} = \left( \frac{1}{k_1 - k_2} \right) \ln \frac{k_1}{k_2} \quad (10)$$

whereby considering the first-order time differentiation of Equations (6)–(8) leads to the following forms:

$$\left. \frac{dR_d}{dt} \right|_{\max} = -k_1 \left( \frac{k_1}{k_2} \right)^{-k_1/(k_1 - k_2)} \equiv J_d^{\max} \quad (11)$$

$$\left. \frac{dR_a}{dt} \right|_{\max} = k_2 \left( \frac{k_1}{k_2} \right)^{-k_2/(k_1 - k_2)} \equiv J_a^{\max} \quad (12)$$

$$\left. \frac{dR_m}{dt} \right|_{\max} = 0 \quad (13)$$

$$-\left. \frac{dR_d}{dt} \right|_{\max} = \left. \frac{dR_a}{dt} \right|_{\max} \quad (14)$$

It should be noted that the system is assumed to be in steady state at  $t = t_{\max}$ , since the concentration of  $Hg^{2+}$  ions in the membrane does not vary with time (Equation (13)). Consequently, the entrance and exit fluxes are equal having opposite signs.

**Table 1**

The kinetic parameters of  $\text{Hg}^{2+}$  transport using carrier (**1**) at different temperatures (stirring rate is 200 rpm; solvent is  $\text{CHCl}_3$ )

Temperature (K)	$k_1 \times 10^2$ ( $\text{min}^{-1}$ )	$k_2 \times 10^2$ ( $\text{min}^{-1}$ )	$R_m^{\text{max}}$	$t_{\text{max}}$ (min)	$J_d^{\text{max}} \times 10^3$ ( $\text{min}^{-1}$ )	$J_a^{\text{max}} \times 10^3$ ( $\text{min}^{-1}$ )
293	0.69	1.76	0.21	87.75	-3.76	3.76
298	0.88	1.85	0.24	76.78	-4.47	4.47
303	0.97	2.15	0.26	67.44	-5.53	5.53
308	1.41	2.37	0.28	54.11	-6.58	6.58

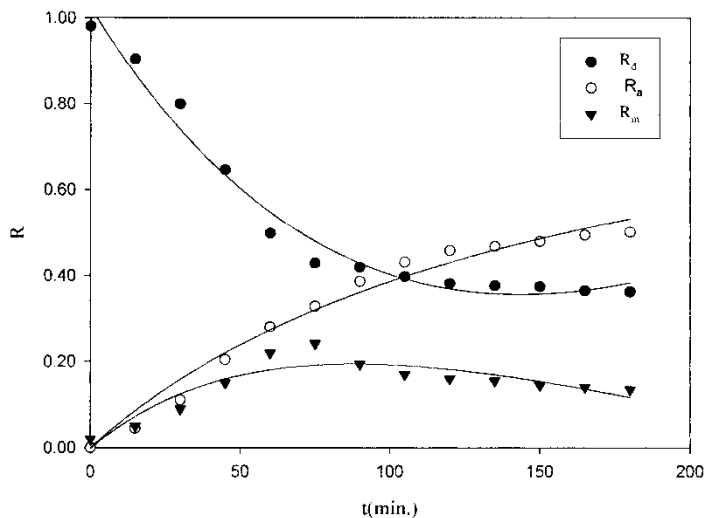
Here, the transport mechanism a co-transport (ion-pair mediated diffusion) process, in which co-transport of  $\text{Hg}^{2+}$  ion with the carrier (**1**) was studied over a temperature range of 293–298 K and at different stirring rates in the range of 200–400 rpm. The kinetic parameters of  $k_1$  and  $k_2$  from the obtained by fitting Equations 6 and 8 to this data. The calculated  $k_1$ ,  $k_2$ ,  $R_m^{\text{max}}$ ,  $t_{\text{max}}$ ,  $J_d^{\text{max}}$  and  $J_a^{\text{max}}$  values at different temperatures and different stirring rates for  $\text{CHCl}_3$  solvent are presented in Tables 1 and 2, respectively. As an example, the variation of the reduced concentration of  $\text{Hg}^{2+}$  ion through the liquid membrane in  $\text{CHCl}_3$  solvent at 200 rpm and 25°C is presented in Figure 2. It is seen that  $R_d$  decreases exponentially with time, accompanied by a simultaneous increase of  $R_a$ , whereas  $R_m$  presents at maximum at intermediate times. The maximum  $R_m$  values were found to lie between the 0.07 and 0.30 ranges. This shows that the membrane phase was also effective on the transport. It is also seen that the  $t_{\text{max}}$  values was decreased upon increasing of temperature and the stirring rates.

The variation of  $\text{Hg}^{2+}$  concentration in the acceptor phase with time is given in Figure 3 for different values of T. The numeric analysis of  $\text{Hg}^{2+}$  transport was solved to compare with the experimental results ( $R_a$  values) by using a non-linear curve-fitting as shown by the dashed lines in Figure 3; there is fairly good agreement between the theoretical curves and the experimental points. It is clearly seen that the highest transport efficiency was reached at 308 K and 400 rpm stirring rate, with the transport efficiency decreasing as these parameters decreased. As temperature and stirring rate increased,  $R_m^{\text{max}}$  increases somewhat, while  $t_{\text{max}}$  decreases, thus the  $\text{Hg}^{2+}$  ions are rapidly complexed with the ligand carrier. The membrane entrance ( $k_1$ ) and exit ( $k_2$ ) rate constants increase with increasing temperature, as well as with the stirring rate. It is

**Table 2**

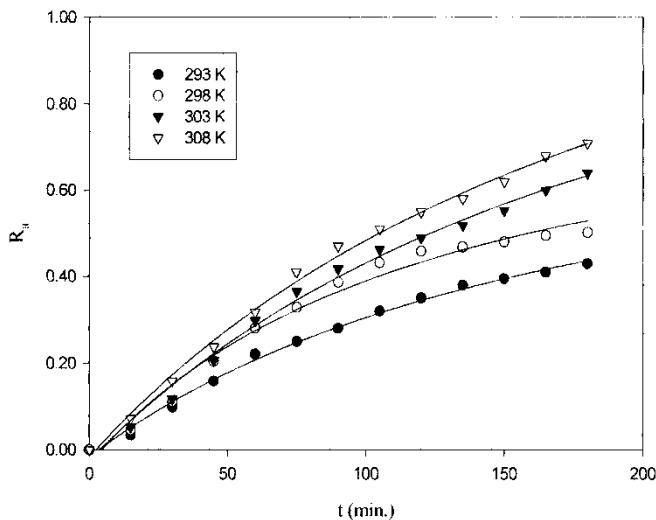
The kinetic parameters of  $\text{Hg}^{2+}$  transport using carrier (**1**) at different stirring rates (T = 298 K; solvent is  $\text{CHCl}_3$ )

Stirring rate (rpm)	$k_1 \times 10^2$ ( $\text{min}^{-1}$ )	$k_2 \times 10^2$ ( $\text{min}^{-1}$ )	$R_m^{\text{max}}$	$t_{\text{max}}$ (min)	$J_d^{\text{max}} \times 10^3$ ( $\text{min}^{-1}$ )	$J_a^{\text{max}} \times 10^3$ ( $\text{min}^{-1}$ )
200	0.88	1.85	0.24	76.78	-4.47	4.47
300	3.11	4.84	0.29	25.55	-14.00	14.00
400	3.72	5.44	0.30	22.10	-16.00	16.00

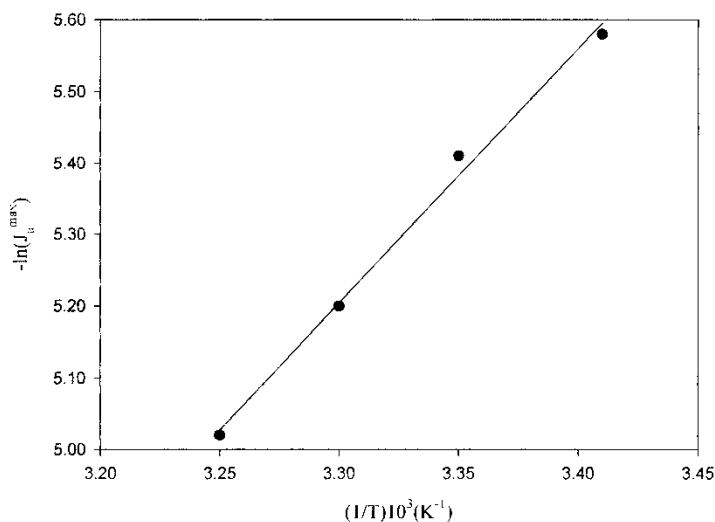


**Figure 2.** The changes of reduced concentrations of  $\text{Hg}^{2+}$  ion with time in co-transport through liquid membrane ( $T = 298 \text{ K}$ , solvent is  $\text{CHCl}_3$ ).

expected that the temperature and stirring effects are mainly exerted on the maximum complexation and decomplexation between  $\text{Hg}^{2+}$  picrate and ligand carrier at the aqueous-organic interfaces. On the other hand, the maximum membrane entrance exit fluxes take place in the reaction zones of ionic interfaces.



**Figure 3.** The changes of reduced concentrations of  $\text{Hg}^{2+}$  in the acceptor phase with time during co-transport through liquid membrane using a calix-oligomer carrier at different temperatures at a stirring rate of 200 rpm. (The symbols represent the experimental points, the lines are obtained from the curve-fitting program.)



**Figure 4.** Arrhenius plot of  $\text{Hg}^{2+}$  ion transport at  $J_a^{\max}$ .

The activation energy was calculated from a plot of the maximum membrane exit flux ( $J_a^{\max}$ ) vs.  $(1/T)$  at 200 rpm, as presented in Figure 4.

$$\ln(J) = \ln(A) - \frac{E_a}{R} \left( \frac{1}{T} \right) \quad (15)$$

The activation energy value for carrier (**1**) in the liquid membrane was found to be 7.06 kcal/mol. As known, activation energy values are quite low for diffusion-controlled processes, whose rate constants are strongly affected by temperature. The  $E_a$  values of diffusion-controlled processes are lower than those of chemically controlled processes. It was pointed out that the activation energies of diffusion-controlled processes are lower than 10 kcal/mol<sup>27</sup>. The calculated activation energy for carrier (**1**) shows that the transport of  $\text{Hg}^{2+}$  ion is diffusion-controlled processes.

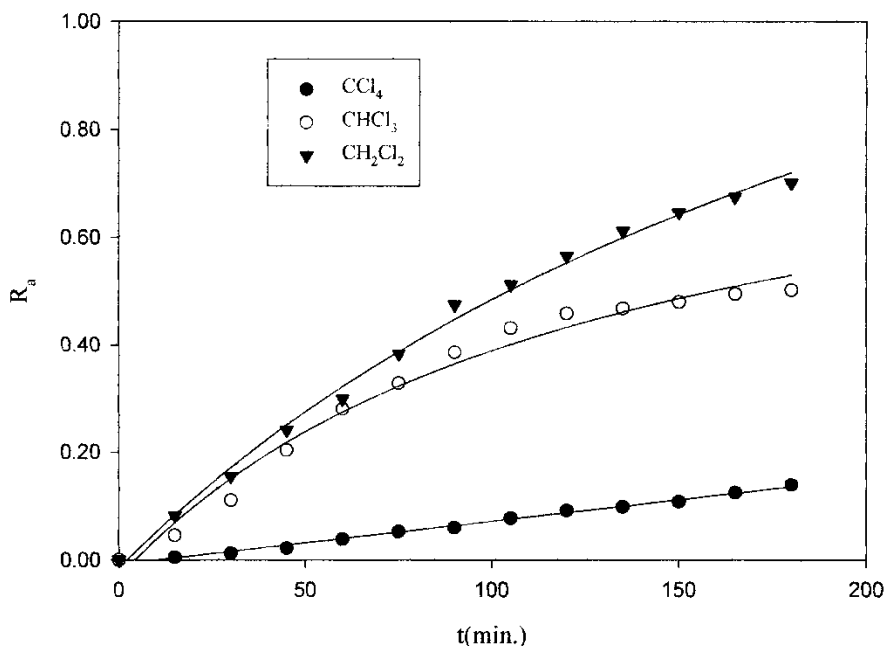
The present work was initiated with the aim of using a physicochemical approach to  $\text{Hg}^{2+}$  ion transport through a liquid membrane containing carrier (**1**). It was decided to also conduct experiments under the same conditions to study how different solvents affect the transport, as the nature of the solvent system passing through the liquid membranes may

**Table 3**

The kinetic parameters for  $\text{Hg}^{2+}$  transport using carrier (**1**) when different solvents are used ( $T = 298 \text{ K}$ ; stirring rate 200 rpm)

Solvent	$k_1 \times 10^2$ ( $\text{min}^{-1}$ )	$k_2 \times 10^2$ ( $\text{min}^{-1}$ )	$R_m^{\max}$	$t_{\max}$ (min)	$J_d^{\max} \times 10^3$ ( $\text{min}^{-1}$ )	$J_a^{\max} \times 10^3$ ( $\text{min}^{-1}$ )
$\text{CH}_2\text{Cl}_2$	1.21	2.30	0.30	58.98	-6.88	6.88
$\text{CHCl}_3$	0.88	1.85	0.24	76.78	-4.47	4.47
$\text{CCl}_4$	0.14	1.58	0.07	170.33	-1.08	1.08





**Figure 5.** The changes of reduced concentrations of  $\text{Hg}^{2+}$  in the acceptor phase with time during co-transport through liquid membrane using of calix-oligomer carrier in different solvents at a stirring rate of 200 rpm. (The symbols represent the experimental points; the lines are obtained from the curve-fitting program.)

also have a great influence on the efficiency of ion transport. The results obtained with  $\text{CH}_2\text{Cl}_2$  and  $\text{CCl}_4$  are presented in Table 3, along with analogous results for  $\text{CHCl}_3$ . As can be seen, the membrane entrance and exit rate constants are found to vary in the order  $\text{CH}_2\text{Cl}_2 > \text{CHCl}_3 > \text{CCl}_4$ .

The variation of  $R_a$  values for the different solvent systems is illustrated in Figure 5; showing that the  $R_a$  values are strongly affected by the choice of membrane solvent system. The transport efficiency was observed to be the highest with  $\text{CH}_2\text{Cl}_2$ . This

**Table 4**  
Physicochemical characteristics of solvents used

Solvent	$\epsilon_0$	$n_D$	$\mu$	$\eta$	$V_m$
$\text{CH}_2\text{Cl}_2$	9.08	1.424	1.959	0.437	64.2
$\text{CHCl}_3$	4.81	1.446	1.354	0.58	96.5
$\text{CCl}_4$	2.24	1.466	0	0.969	96.5

$\epsilon_0$ : dielectric constant (20°C).

$n_D$ : refractive index (20°C).

$\mu$ : dipole moment (D).

$\eta$ : viscosity (cP).

$V_m$ : molar volume ( $\text{M}^{-1}$ ).

result is in agreement with those in Ref. (28), in which the efficiency of dichloromethane, based on the  $R_a$  values, was higher than of  $\text{CHCl}_3$  and  $\text{CCl}_4$ . The physicochemical properties of the solvents are given in Table 4. These observations suggest that viscosity plays a major role in ion transport, as well as the polarity. Thus, we have shown that the nature of the membrane solvent is one of the main factors in establishing transport efficiency.

## References

1. Noble, R.D. and Way, J.D. (1987) Liquid membrane technology. In *Liquid Membranes: Theory and Applications*. Nobel, R.D. and Way, J.D., eds; Am. Chem. Soc. Symp. Ser. No. 347, American Chemical Society: Washington, DC1.
2. Gutsche, C.D. (1989) *Calixarenes in Monographs in Supramolecular Chemistry*. Stoddart, J.F. and Cambridge, J.F., ed.; The Royal Society of Chemistry: UK.
3. Ikeda, A. and Shinkai, S. (1997) Novel cavity design using calix[n]arene skeletons: toward molecular recognition and metal binding. *Chem. Rev.*, 97: 1713–1734.
4. Vicens, J. and Bohmer, V. (1991) *Calixarenes: A Versatile Class of Macrocyclic Compounds*. and Davied, J.E.D., eds.; Kluwer Academic Publishers: Dordrecht.
5. Danil de Namor, F., Cleverley, R.M., and Zapata-Ormachea, M.L. (1998) Thermodynamics of calixarene chemistry. *Chem. Rev.*, 98: 2495–2525.
6. Buschmann, H.J., Cleve, E., Jansen, K., Wego, A., and Schollmeyer, E. (2001) The Determination of complex stabilities between different cyclodextrins and dibenzo-18-crown-6, cucurbit[6]uril, decamethylcucurbit[S]uril, Cucurbit-[5]uriluril, p-tert-butylcalix[4]arene and p-tert-butylcalix[6]arene in aqueous solutions using a spectrophotometric method. *Mat. Sci. & Eng. C.*, 14: 35–39.
7. Arnaud-Neu, F. and Schwing-Weill, M.-J. (1997) Calixarenes, new selective molecular receptors. *Synthetic Metals*, 90: 157–164.
8. Fraternali, E. and Wipff, G. (1997) Binding of  $\text{NMe}_4^+$  and  $\text{NH}_4^+$  ammonium Ions by a bridged calix[6]arene in chloroform. A molecular dynamics investigation. *An. Quim. Int. Ed.*, 93: 376–384.
9. Chrisstoffels, L.A.J., Struijk, W., and Jong, F.; de and Reinhoudt, D.N. (1996) Carrier mediated transport through supported liquid membranes; determination of transport parameters from a single transport experiment. *J. Chem. Soc., Perkin Trans.*, 2: 1617–1622.
10. Antipin, I., Stoikov, I.I., Pinkhassik, E.M., Fitseva, N.A., Stibor, I., and Konovalov, A.I. (1997) Calix[4]arene based  $\alpha$ -aminophosphonates: novel carriers for Zwitterionic amino acids transport. *Tetrahedron Lett.*, 33: 5865–5868.
11. Chang, S.-K., Hwang, H.-S., Son, H., Youk, J., and Kang, Y.S. (1991) Selective transport of amino acid esters through a chloroform liquid membrane by a calix[6]arene-based ester carrier. *J. Chem. Soc. Chem. Commun.*, 217–218.
12. Chung, T.D., Kang, S.K., Kim, J., Kim, H.-S., and Kim, H. (1997) Interaction between various alkylammonium ions and quinone-derivatized calix[4]arenes in aprotic media. *J. Electroanal. Chem.*, 438: 71–78.
13. Katzung, B.G. (1987) *Basic and Clinical Pharmacology*, 3rd Ed.; Appleton and Lange: Norwalk, CT, 734–735.
14. Safavi, A. and Rastegarzadeh, S. (1995) Selective and efficient uphill transport of Cu(II) through liquid membrane. *Talanta*, 42 (12): 2039–2042.
15. Parham, A. and Shamsipur, M. (1994) Highly selective and efficient uphill transport of mercury as  $\text{Hg}(\text{NO}_2)_4^{2-}$  ion using  $\text{Ba}^{2+}$ -18-crown-5 as carrier. *J. Membr. Sci.*, 86 (1–2): 29–35.
16. Alpoguz, H.K., Memon, S., Ersoz, M., and Yilmaz, M. (2002) Transport of  $\text{Hg}^{2+}$  through bulk liquid membrane using a bis-calix[4]arene nitrile derivative as carrier: kinetic analysis. *New J. Chem.*, 26 (4): 477–480.

17. Alpoguz, H.K., Memon, S., Ersoz, M., and Yilmaz, M. (2002) Transport of metals through a liquid membrane containing calix[4]arene derivatives as carrier. *Sep. Sci. Technol.*, 37 (9): 2201–2213.
18. Memon, S. and Yilmaz, M. (2000) Liquid-liquid extraction of alkali and transition metal cations by two bis-calix[4]arenes. *Sep. Sci. Technol.*, 35 (3): 457–467.
19. Memon, S., Uysal, G., and Yilmaz, M. (2000) Selective complexation of  $\text{Hg}^{2+}$  by bis-calix[4]-arene nitriles. *Sep. Sci. Technol.*, 35 (8): 1247–1256.
20. Uysal, G., Memon, S., and Yilmaz, M. (2001) Synthesis and binding properties of polymeric calix[4]arene nitriles. *React. Funct. Poly.*, 47 (3): 165–174.
21. Memon, S., Yilmaz, A., Max Roundhill, D., and Yilmaz, M. (2004) Synthesis of polymeric calix[4]arene dinitrile and diamino-derivatives: exploration of their extraction properties towards dichromate anion. *J. Macromol. Sci. Pure Appl. Chem.*, A41 (4): 433–447.
22. Deligöz, H. and Yilmaz, M. (1995) Liquid-liquid extraction of transition metal cation by calixarenes-based cyclic ligands. *Solvent Extr. Ion Exch.*, 13 (1): 19–26.
23. Alpoguz, H.K., Memon, S., Ersoz, M., and Yilmaz, M. (2004) Transport kinetics of  $\text{Hg}^{2+}$  through bulk liquid membrane using calyx[4]arene ketone derivative as carrier. *Sep. Sci. Technol.*, 39 (4): 799–810.
24. Szpakowska, M. and Naggy, O.B. (1993) Non-steady state vs. steady state kinetic analysis of coupled ion transport through binary liquid membranes. *J. Membr. Sci.*, 76 (1): 27–38.
25. Szpakowska, M. (1994) Kinetics of coupled transport of Cu (II) ions through liquid membranes composed of technical solvents and paraffin mixtures. *J. Membr. Sci.*, 92 (3): 267–273.
26. Szpakowska, M. (1996) Coupled transport of copper through different types of liquid membranes containing Acorga P-50 as carrier. *J. Membr. Sci.*, 109 (1): 77–86.
27. Szpakowska, M. and Naggy, O.B. (1990) Copper (II) Ion transport mono and binary liquid membranes. *Bull. Soc. Chim. Belg.*, 99 (4): 243–253.
28. Lazarova, Z. and Boyadzhiev, L. (1993) Kinetic aspects of copper (II) transport across liquid membrane containing LIX-860 as a carrier. *J. Membr. Sci.*, 78 (3): 239–245.