DOI: 10.1002/ejoc.200600249

# Quantitative Removal of Mercury(II) from Water Through Bulk Liquid Membranes by Lipophilic Polyamines

**Nicoletta Spreti,[a] Lucia Brinchi,[b] Raimondo Germani,[b] Maria Vincenza Mancini,[a] and Gianfranco Savelli*[b]**

**Keywords:** Bulk liquid membranes / Heavy metal ions / Lipophilic polyamines / Carrier-mediated transports / Carrier recycle

Transport of mercury(II) and copper(II) ions through bulk liquid membranes has been studied, the former because of its toxicity and wide distribution in the environment, the latter for comparative purposes. The abilities of two carriers, the known *N*,*N*′-bis[2-(hexadecylamino)ethyl]-*N*,*N*′-bis(hydroxyethyl)ethylenediamine (bis-HE16ED) and the new *N*,*N*′-bis(*p*-octyloxybenzyl)-3,6-dioxaoctane-1,8-diamine (bis-*p*ODODA), to complex and transport the selected metal ions are reported. Bis-HE16ED is a good carrier for $Cu^{2+}$ ions, but the high stability of the carrier/$Hg^{2+}$ ion complex in the membrane results in a lack of its transport. On the other hand, the new carrier displays a very high efficiency in $Hg^{2+}$ ion transport, effecting quantitative transfer of the metal ion into the receiving phase within 24 h, despite its chelating region being only slightly different from that in bis-HE16ED. The ability of bis-*p*ODODA to transport 100 % of $Hg^{2+}$ efficiently in consecutive cycles is also reported. This result provides a basis for future development of a decontamination process based on a carrier-mediated transport system.

(© Wiley-VCH Verlag GmbH & Co. KGaA, 69451 Weinheim, Germany, 2006)

## Introduction

Liquid membrane technology is an area of growing interest because of its potential and actual applications in industrial processes.[1–9] Extraction and separation methods are particularly attractive because of the environmental advantages deriving from their applications. Separation of heavy metal ion mixtures, for example, represents an ambitious target for their removal from industrial wastewater streams.

Bulk liquid membrane systems (BLMs), with the aqueous donor and acceptor phases separated by an immiscible membrane, are useful on a laboratory scale for preliminary investigations of the selective transport and removal of heavy metal ions.[10–14] These systems rely on the complexation capability of suitable carrier molecules solubilized in the membrane: selective interactions between the carrier and a metal ion of interest result in decontamination by means of the transport of the particular metal ion across the membrane.

The environmental importance of heavy metal ion decontamination is essentially due to their high persistence and toxicity; in particular, mercury(II), a very dangerous and diffuse contaminant, represents a major threat to human health.[15–19]

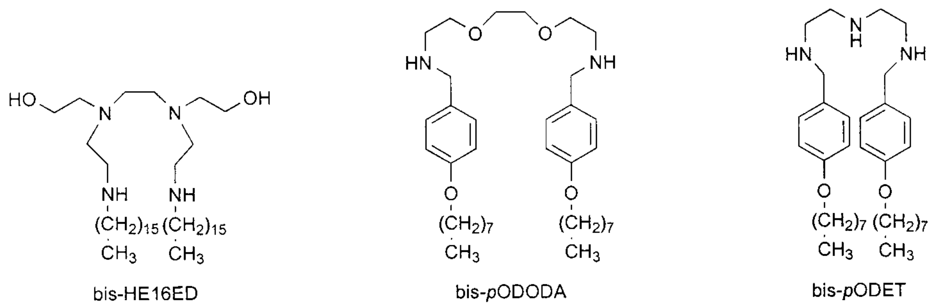
Mercury inputs into the environment come from both natural and anthropic sources; a number of human activities – such as oil and coal combustion, varnish and paper manufacture (where mercury is used as an antifungal agent), the plastics industry (as a catalyst in the synthesis of vinyl chloride and polyurethanes), chloro-soda works (as cathode for the electrolysis of sodium chloride), electrical device production (mercury vapour lamps, batteries, mercury switches) and manufacture of cup barometers and thermometers – give rise to mercury pollution.[20–21] Reducing the amount of $Hg^{2+}$ in the wastewater is therefore of great concern and it is a noteworthy subject of active research.

We have already reported our work on heavy metal ion transport through BLMs; a number of new carrier molecules have been synthesized in our laboratories and their high efficiency and selectivity have been demonstrated.[22–24]

This paper presents results obtained with a known carrier,[25] *N*,*N*′-bis[2-(hexadecylamino)ethyl]-*N*,*N*′-bis(hydroxyethyl)ethylenediamine (bis-HE16ED), and with the newly synthesized *N*,*N*′-bis(*p*-octyloxybenzyl)-3,6-dioxaoctane-1,8-diamine (bis-*p*ODODA). Moreover, results were also compared with others previously obtained in our laboratory with 2,2′-bis(*p*-octyloxybenzyl)diethylenetriamine (bis-*p*ODET).[24]

---

[a] Dipartimento di Chimica, Ingegneria Chimica e Materiali, Università di L'Aquila,
Via Vetoio Coppito, 67100 L'Aquila, Italy
E-mail: spreti@univaq.it
[b] CEMIN, Centro di Eccellenza Materiali Innovativi Nanostrutturati, Dipartimento di Chimica, Università di Perugia,
Via Elce di Sotto 8, 06123 Perugia, Italy
Fax: +39-075-5855538
E-mail: savelli@unipg.it



Scheme 1.

The chelating region of bis-HE16ED features two tertiary and two secondary aminic N atoms and two hydroxy groups. The chelating regions of bis-*p*ODET and of bis-*p*ODODA have different numbers and arrangements of the heteroatoms (N and O), whilst their chain systems each contain two phenyl rings facing one another. These aromatic rings can self-associate through π-stacking and are therefore preorganized to form a π complex with a central metal cation in a sandwich-like structure,[26] so these aromatic rings may therefore play important roles in the pincer-like structures of these two carriers. The chemical structures of all carriers are shown in Scheme 1.

The carriers' transport efficiencies in BLM systems were evaluated with regard to $Cu^{2+}$ and $Hg^{2+}$ ions, the former for comparative purposes and the latter because of the high toxicity and wide distribution referred to above. Optimization of experimental conditions was carried out and some hypotheses on the relationships between the structures of the carrier molecules and their transport efficiencies were proposed. Finally, the feasibility of recycling the carriers for the transport of $Hg^{2+}$ ions was examined.

## Results and Discussion

### Partition Measurements

Membrane uptake experiments were initially performed to investigate the abilities of both carriers to extract $Cu^{2+}$ and $Hg^{2+}$ ions from the source phase. Two organic solvents, dichloromethane and chloroform, were used as membranes, and results, along with spontaneous metal ion partitions,[24] are reported in Table 1. With $Cu^{2+}$ ions the carriers showed similar partition behaviour, and no significant differences between the two employed membranes were observed. In contrast, a more complex pattern of results was obtained with $Hg^{2+}$: bis-HE16ED seemed to have a much greater affinity than bis-*p*ODODA towards $Hg^{2+}$ ions in a dichloromethane membrane, with partition mol percentages of 41 and 27, respectively, whilst the extraction capabilities observed in chloroform were similar to one another (20 and 25%). Moreover, while bis-HE16ED extracted $Hg^{2+}$ into a dichloromethane phase to a greater extent than it did into chloroform, the opposite behaviour was reported for bis-*p*ODODA: indeed, despite the measured mol percentages of extraction being nearly the same, there also is significant partition of $Hg^{2+}$ into dichloromethane even in the absence of the carrier (11%) and the high level of extraction of $Hg^{2+}$ into chloroform performed by bis-*p*ODODA thus becomes evident.

Table 1. Mol percentages of $M^{2+}$ extracted from the source phase to the membrane.

| Carrier | $Cu^{2+}$ | | $Hg^{2+}$ | |
|---|---|---|---|---|
| | $CH_2Cl_2$ | $CHCl_3$ | $CH_2Cl_2$ | $CHCl_3$ |
| None [19] | < 1 | < 1 | 11 | < 1 |
| bis-HE16ED | 20 | 21 | 41 | 20 |
| bis-*p*ODODA | 20 | 14 | 27 | 25 |

However, as already shown in other reports,[22–24] such preliminary partitioning results are not necessarily correlated to metal ion transport efficiency of a carrier: transport processes are very complex systems, involving a number of equilibrium reactions, several interface phenomena and the interplay of various parameters.

### Transport Experiments

Menger reported the successful transport of $CuSO_4$ through a chloroform membrane with bis-HE16ED as carrier: 80% of metal ions were transferred into the receiving phase in only 10 hours.[25]

Data obtained with $CuSO_4$ and with $CuCl_2$ can be compared. In fact, in a previous work[22] we showed that the nature of the metal salt did not influence the efficiency of the transport processes: the accompanying anions of $Cu^{2+}$/carrier complexes probably come from the buffer systems and we always used metal chlorides.[22–24] Transport experiments with $CuCl_2$ and $HgCl_2$ were thus performed with both carrier molecules under the same experimental conditions as reported by Menger. The percentages of $M^{2+}$ in the source and in the receiving phases at different times are shown in Figure 1.

With regard to $Cu^{2+}$ results, transfer of ca. 80% of the $Cu^{2+}$ into the receiving phase was effected by bis-HE16ED in 48 h. The longer time required for the transport may be due to the slightly different device: even slight differences can imply different interface areas and thus influence the kinetics of the process. Bis-*p*ODODA was also able to

© 2006 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim

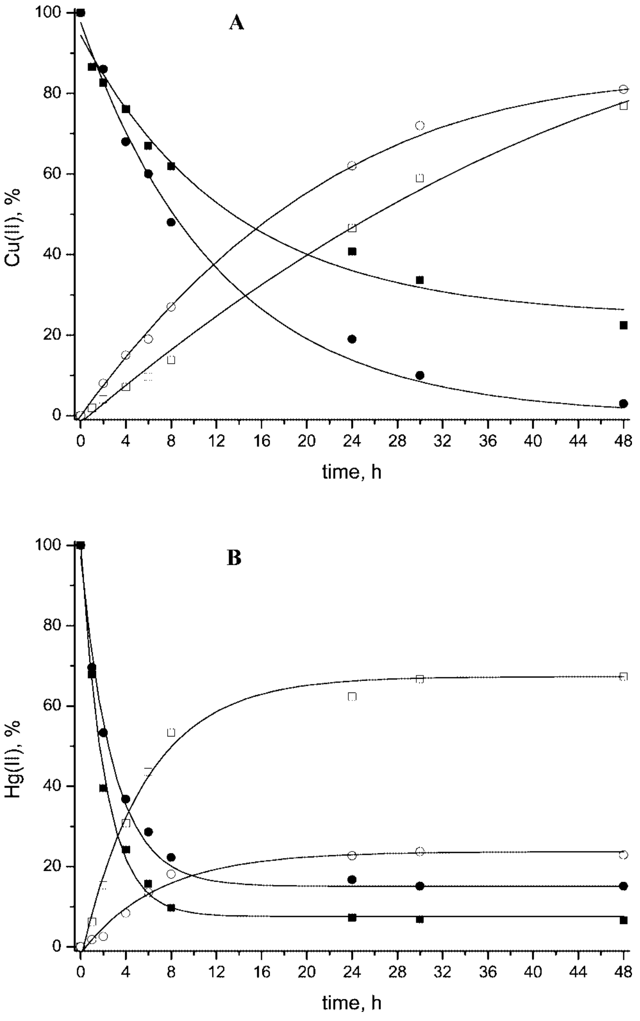


Figure 1. Mol percentages of $Cu^{2+}$ (A) and $Hg^{2+}$ (B) vs. time in the source phase (filled symbols) and the receiving phase (open symbols) with bis-HE16ED (●/○) and bis-*p*ODODA (■/□). [carrier] = $1\cdot10^{-3}$ M in chloroform; [$MCl_2$] = $5\cdot10^{-3}$ M in 0.15 M acetate buffer, pH 4.68; receiving phase: 0.1 M HCl; $T$ = 25 °C. Lines are drawn only to guide the eye.

transport ca. 80% of the $Cu^{2+}$ ions in 48 h, but with different trends from bis-HE16ED, as shown in part A of Figure 1. Bis-HE16ED, with just six coordination sites, probably has a greater affinity towards $Cu^{2+}$ ions than bis-*p*ODODA, which possesses a chelating region with only four coordination sites. Thus, at least in the first hours of transport, a sharper decrease in $Cu^{2+}$ ion concentration from the source phase was obtained with bis-HE16ED, because of its greater complex formation capability. These observations were also in agreement with partition measurements, with 21% of $Cu^{2+}$ ions being partitioned by bis-HE16ED vs. 14% by bis-*p*ODODA.

Figure 1 (part B) shows $Hg^{2+}$ transport results. The trends of the extraction curves were very similar for the two carriers: in the first 8 h of the transport very sharp decreases in the $Hg^{2+}$ levels in the source phase were observed, after which concentrations tended to reach limiting values and level off. With regard to the release of the metal ion into the receiving phase, plateaux were reached after 24 h in both cases, but bis-*p*ODODA was much more effective, transporting about three times more $Hg^{2+}$ than bis-HE16ED. Consequently, the mol percentages of $Hg^{2+}$ stored in the membrane as $Hg^{2+}$/carrier complexes proved to be far greater with bis-HE16ED than with bis-*p*ODODA: i.e., 62% and 26%, respectively. Furthermore, as already reported,[24] ca. 30% of $Hg^{2+}$ diffuses spontaneously into the receiving phase through chloroform in 48 h. In the case of bis-HE16ED, then, all the complexed $Hg^{2+}$ ions were simply partitioned into the membrane, and the transfer of these metal ions into the receiving phase was due only to the passive diffusion process. In these systems, the driving force behind the transport process is the pH gradient applied to the two aqueous phases. The release of metal ions is then essentially controlled by the rate of the chemical reaction between metal ion/carrier complex and hydrogen ions at the membrane/receiving phase interface, so variation of the pH of the stripping phase should give rise to a different pattern of the release process. In all experiments reported so far, a receiving phase at pH = 1 had been used; to promote faster and greater release of $Hg^{2+}$ ions, a trial with a more acidic value (pH = 0) was carried out, the results are shown in Figure 2.

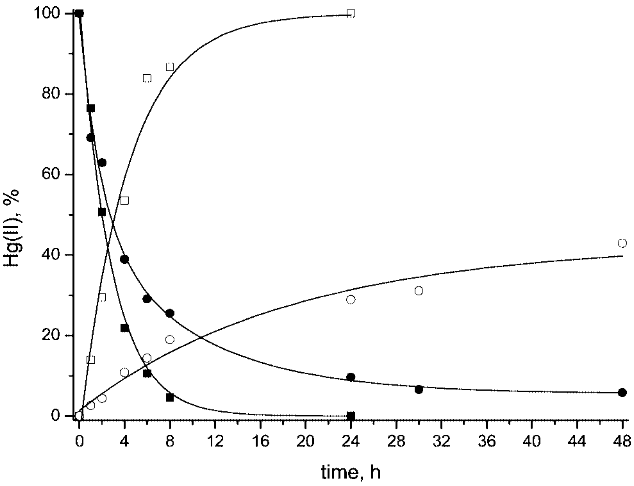


Figure 2. Mol percentages of $Hg^{2+}$ vs. time in the source phase (filled symbols) and the receiving phase (open symbols) with bis-HE16ED (●/○) and bis-*p*ODODA (■/□). [carrier] = $1\cdot10^{-3}$ M in chloroform; [$MCl_2$] = $5\cdot10^{-3}$ M in 0.15 M acetate buffer, pH 4.68; receiving phase: 1 M HCl; $T$ = 25 °C. Lines are drawn only to guide the eye.

A considerable improvement in $Hg^{2+}$ transport was obtained with bis-*p*ODODA, with 100% of the metal ion being transferred to the receiving phase in only 24 h. Of all our new synthesized carriers, this is the best for $Hg^{2+}$ transport. In contrast, the variation of the experimental conditions produced only a weak effect on the bis-HE16ED transport: the extraction percentages were nearly the same and only a moderate rise in $Hg^{2+}$ ion levels in the receiving phase was achieved (i.e., 43% vs. 23% with the receiving phase at pH = 1). After 48 h, however, ca. 50% of Hg$^{2+}$ ions were stored in the membrane. To explain the different behaviour observed with the more acidic stripping phase, the natures of the carriers have to be considered; in particular, the structures of the chelating regions may play relevant roles.

As regards mercury complexes, it is known that Hg$^{2+}$ ions show a strong preference for halogens (except for F), P, S, Se and certain N-type ligands; the coordination number can vary from 2 to 6, although there is a marked preference for linear two-coordination.[26] On the other hand, both carriers possess two O atoms but they differ in the number of N atoms in their structures. Bis-*p*ODODA, with only two N atoms in its chelating region, allowed quantitative transport of Hg$^{2+}$ simply through an increase in the concentration of hydrogen ions in the receiving phase: that is, through assistance of the exchange reaction between the hydrogen and the complexed metal ions at the membrane/receiving phase interface. Conversely, in the case of bis-HE16ED, with four N atoms in its chelating region, the new operation conditions probably did not produce adequate protonation of the complex, because of its high stability in the membrane phase, so slow release into the receiving phase and storage of the metal ion in the chloroform were observed. The heteroatoms involved in the complexation of Hg$^{2+}$ are therefore probably only the aminic N atoms, since two N atoms should be sufficient to form the Hg$^{2+}$/carrier complex.

We recently reported on the ability of 2,2′-bis(*p*-octyloxybenzyl)diethylenetriamine (bis-*p*ODET), a carrier prepared in our laboratory, to transport Hg$^{2+}$ ions.[24] Its structure is middle-way between bis-HE16ED and bis-*p*ODODA, also presenting a pincer-like structure, but containing a chelating region with three aminic N atoms. Results obtained with bis-*p*ODET were in agreement with the proposed hypothesis: indeed, like bis-*p*ODODA, it performed the quantitative transport of Hg$^{2+}$ ions, although both extraction and release proceeded more slowly, with ca. 100% of Hg$^{2+}$ having been transferred in 48 h.

We may therefore conclude that the much greater efficiency of Hg$^{2+}$ transport achieved with bis-*p*ODODA is essentially due to its versatility, which essentially amounts to the two main features of a carrier molecule: a high affinity towards the substrate and, at the same time, a high exchange speed to avoid saturation phenomena.

Partition measurements and transport results with the receiving phase at pH = 1 highlighted a much greater affinity of carrier bis-*p*ODODA towards Hg$^{2+}$ ions than towards Cu$^{2+}$. The extraction process was much more rapid, 90% of Hg$^{2+}$ being extracted in only 8 h. The release also proceeded to a greater extent in the first 24 h, after which Hg$^{2+}$ transfer into the receiving phase reached a plateau. The transport pattern of Cu$^{2+}$ ions was more regular and proved to be globally more efficient. Furthermore, no storage of Cu$^{2+}$ ions in the chloroform was observed. In contrast, ca. 25% of Hg$^{2+}$ remained in the membrane after 48 h, indicating a higher stability of the Hg$^{2+}$/carrier complex in comparison with Cu$^{2+}$.

A transport experiment with Cu$^{2+}$ ions and the more acidic stripping phase was then carried out and the results are reported in Table 2 (together with results at pH = 1 for comparative purposes).

Table 2. Mol percentages of Cu$^{2+}$ ions in the receiving (R) and source (S) phases with receiving phases at different pH values.

| | RP, pH = 1 | | RP, pH = 0 | |
|---|---|---|---|---|
| Time [h] | R | S | R | S |
| 4 | 7 | 76 | 18 | 65 |
| 8 | 14 | 62 | 33 | 53 |
| 24 | 47 | 41 | 71 | 27 |
| 48 | 77 | 22 | 85 | 12 |

As already described for Hg$^{2+}$, an improvement in the extraction and release trends was achieved, even though the

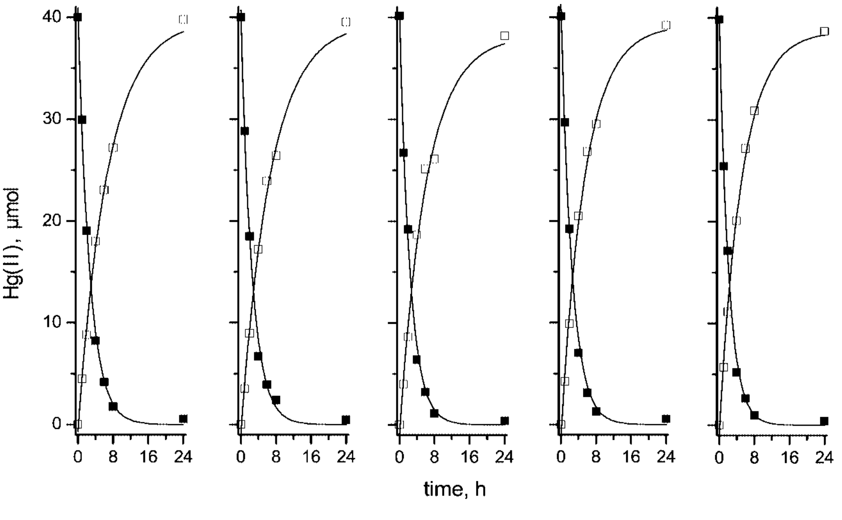


Figure 3. µMoles of Hg$^{2+}$ in the source phase (■) and the receiving phase (□) over five consecutive cycles. [bis-*p*ODODA] = $1\cdot10^{-3}$ M in chloroform; [HgCl$_2$] = $5\cdot10^{-3}$ M in 0.15 M acetate buffer, pH 4.68; receiving phase: 1 M HCl; $T$ = 25 °C. Lines are drawn only to guide the eye.

© 2006 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim

overall amounts of metal ions transported were nearly the same. However, in the first 24 h, a twofold increase in the release pattern was observed, again indicating that this carrier was able to improve its performance simply through assistance of the protonation of heteroatoms in the chelating region.

A set of transport experiments in a dichloromethane membrane was then carried out.

The results here showed the transport performances of the two carriers to be similar to or worse than those obtained in chloroform (data not shown), whilst no direct correlation with partition measurements could be found. A chloroform membrane thus has to be preferred in transport experiments with these two carrier molecules; their hydrophobic/hydrophilic balances probably match up better with the chemico-physical properties of this solvent. As already mentioned, the transport process is a very complex set of several equilibrium reactions, with mutual interactions of a number of parameters.

### Carrier Recycling

Reduction of $Hg^{2+}$ levels in wastewater streams is an essential step in many processes of decontamination from heavy metal ions. In view of future product engineering of a membrane-based decontamination system, a main requirement is the potential to reuse carriers for many consecutive cycles of work. A set of experiments in chloroform was thus carried out in order to verify the efficiency of bis-*p*ODODA in several $Hg^{2+}$ ion transport cycles. After the first transport process, both aqueous phases were removed and replaced with fresh solutions. Figure 3 gives µmoles/time profiles in the source and in the receiving phases for five consecutive cycles. The carrier retained its efficiency unchanged through all five cycles, transferring 100% of $Hg^{2+}$ into the receiving phase in only 24 h. As already reported, bis-*p*ODET was also able to transport ca. 90–95% of $Hg^{2+}$ ions for three consecutive cycles, but every transport process took a longer time, with minor practical advantages for applications.[24]

## Conclusions

Bulk liquid membranes were used to test the transport capabilities of a known carrier, bis-HE16ED, and of a newly synthesized one, bis-*p*ODODA. They both possess pincer-like structures and have only slightly different chelating regions, with the same heteroatoms as complexing agents.

$Cu^{2+}$ and $Hg^{2+}$ ions were chosen, the former for comparative purposes and the latter because of mercury's high toxicity and wide distribution.

Bis-HE16ED displayed good $Cu^{2+}$ transport efficiency and a very high affinity towards $Hg^{2+}$ ions; however, it was unable to transport $Hg^{2+}$ because a large proportion of the metal ion was stored in the membrane as the complex. The best performance was instead obtained with bis-*p*ODODA in a chloroform membrane: through appropriate variation of experimental conditions the carrier was able to transport 100% of $Hg^{2+}$ ions in only 24 h.

N atoms in the chelating regions of both carriers were hypothesized as coordination sites of choice in the complexation of $Hg^{2+}$ ions. Indeed, bis-HE16ED, with four N atoms, formed a too stable complex with $Hg^{2+}$, while bis-*p*ODODA, with two N atoms, displayed a great ion exchange speed and thus a very high transport efficiency.

Lastly, carrier recycling experiments were carried out and showed that bis-*p*ODODA can be used for several cycles of work maintaining 100% $Hg^{2+}$ transport in 24 h over all cycles. This result is particularly attractive in view of development of a membrane-based decontamination system.

## Experimental Section

**Membrane "Uptake":** A glass test tube, fitted with a screw cap, was filled with both the source phase (3 mL, $5\cdot10^{-3}$ M $MCl_2$) and the organic membrane (3 mL, $1\cdot10^{-3}$ M carrier). After a vigorous shake, the organic layer was slowly stirred (250 rpm) for 12–18 h. Quantitative determinations of the metal ions in the aqueous phase were then performed.

**Transport Experiments:** The glass transport cell used in these studies has already been reported in an earlier publication.[23] An organic solution (20 mL, $1\cdot10^{-3}$ M carrier) was used as a liquid membrane, separating two aqueous solutions: a source phase, containing the metal salt (8 mL, $5\cdot10^{-3}$ M $MCl_2$), and a receiving phase (8 mL, 0.1 M or 1 M HCl). The liquid membrane phase was slowly stirred (250 rpm) with a Teflon-coated magnetic bar. The metal ion concentrations in both aqueous phases were monitored as a function of time.

**Metal Ion Analysis:** The concentrations of the metal ions in both partition and transport experiments were measured by the sensitive spectrophotometric method described in an earlier publication.[23] A Hewlett–Packard 8452 A diode array spectrophotometer was used for the quantitative determinations. Each reported result is given as the arithmetic mean of three separate experiments; reproducibly was confirmed as ±5% or better.

**Materials:** Metal ion salts, 1,5-diphenylthiocarbazone, 4-hydroxybenzaldehyde, octyl bromide and 2,2′-(ethylenedioxy)bis(ethylamine) were analytical grade, purchased from Aldrich and used as received. Solvents, purchased from Carlo–Erba, were ACS-certified quality. $^1H$ NMR spectra were recorded on a Bruker instrument at 200 MHz; chemical shifts ($\delta$, ppm) are referenced to $(CH_3)_4Si$ as internal standard. Melting points were measured with a Büchi 510 melting point apparatus and are uncorrected. IR spectra were recorded with a Perkin–Elmer Paragon 500 FT-IR spectrophotometer. GLC was carried out on a HP 5890 (FID) instrument with a 30 m × 0.53 mm capillary column (HP-5, with a 1.5 µm film thickness) or a 15 m × 0.53 mm capillary column (HP-INNOVAX, with a 1 µm film thickness) with on-column injection. All column chromatography was carried out on silica gel from Riedel-de Haën (0.032–0.063 mm) with petroleum ether/$Et_2O$ (8:2) as eluent. TLC were carried out on silica gel (ALUGRAM® SIL G/$UV_{254}$) with petroleum ether/$Et_2O$ (8:2) as eluent.

### Synthesis of Carriers

***N*****,*****N*****′-Bis[2-(hexadecylamino)ethyl]-*****N*****,*****N*****′-bis(hydroxyethyl)ethylenediamine (bis-HE16ED):** This carrier was prepared by the reported procedure.[25] The IR and $^1$H NMR spectra confirmed the structure.

**N,N′-Bis(*p*-octyloxybenzyl)-3,6-dioxaoctane-1,8-diamine (bis-*p*ODODA)**

**i.** Freshly recrystallized (from water) and dried 4-hydroxybenzaldehyde (29.31 g, 0.24 mol), anhydrous potassium carbonate (40.05 g, 0.29 mol), and acetonitrile (400 mL) were placed in a 1-L round-bottomed flask fitted with a reflux condenser, nitrogen inlet, mechanical stirrer and pressure-equalizing dropping funnel. The reaction mixture was heated to reflux and stirred. Once reflux was reached, octyl bromide (44.42 g, 0.23 mol) was added dropwise over 1 h and the mixture was then heated at reflux for 12 h. After the mixture had cooled to room temperature, it was transferred to a separating funnel (2 L), treated with water (500 mL), and extracted with petroleum ether. The organic layer was washed twice with NaOH (10%) and finally with water until neutrality was reached. The organic solution, after drying with $Na_2SO_4$, was concentrated in a rotary evaporator to give *p*-octyloxybenzaldehyde as a pale yellow oil. The yield was 98% (52.82 g), and purity by GLC was 98%. No treatment of the oil followed. $^1$H NMR (200 MHz, $CDCl_3$, 25 °C): $\delta$ = 0.88 (t, 3 H, $CH_3$), 1.01–1.75 (m, 10 H, 5 $CH_2$), 1.80–1.95 (m, 2 H, $CH_2$), 4.06 (t, 2 H, $CH_2$–O), 7.00 (d, 2 H, Ar), 7.85 (d, 2 H, Ar), 9.01 (s, 1 H, COH) ppm. $C_{15}H_{22}O_2$ (234.34): calcd. C 76.88, H 9.46; found C 76.90, H 9.50.

**ii.** 2,2′-(Ethylenedioxy)bis(ethylamine) (8.60 g, 0.058 mol) was added to a solution of *p*-octyloxybenzaldehyde (28.36 g, 0.121 mol) in chloroform (200 mL) in a 500-mL round-bottomed flask fitted with a Dean–Stark separator. The mixture was heated to reflux while the water/chloroform azeotrope was distilled off. Once distillation had finished, a reflux condenser was substituted for the separator, and molecular sieves (10 g, 4 Å) were added. After the system had been heated at reflux for 12 h and cooled to room temperature, the molecular sieves were removed by filtration. The organic solution was concentrated in a rotary evaporator to give a light yellow, very viscous liquid, which was crystallized from petroleum ether and recrystallized from acetonitrile to give, after drying under vacuum, a crystalline solid. Yield 88% (29.65 g), m.p. 51–52 °C. $^1$H NMR (200 MHz, $CDCl_3$, 25 °C): $\delta$ = 0.86 (t, 6 H, 2 $CH_3$), 1.14–1.41 (m, 20 H, 10 $CH_2$), 1.60–1.81 (m, 4 H, 2 $CH_2$), 3.60 (s, 4 H, 2 =N–$CH_2$), 3.70 [s, 8 H, $CH_2$–O–$(CH_2)_2$–O–$CH_2$], 3.99 (t, 4 H, 2 $CH_2$–O–Ar), 6.86 (d, 4 H, Ar), 7.60 (d, 4 H, Ar), 8.16 (s, 2 H, 2 CH=N) ppm. $C_{36}H_{56}N_2O_4$ (580.95): calcd. C 74.44, H 9.72, N 4.82; found C 74.48, H 9.69, N 4.86.

**iii.** $NaBH_4$ (0.040 mol) was added in small aliquots to a stirred solution of the diimine (see ii. above) (0.015 mol, 8.71 g) in methanol (200 mL), in a round-bottomed flask fitted with a reflux condenser. The mixture was heated at reflux for 12 h, methanol was removed in a rotary evaporator, and the crude product was recovered and dissolved in diethyl ether. The organic layer was transferred to a separating funnel and was washed twice with NaOH (10%) and finally with water until neutrality was reached. After drying with $Na_2SO_4$, the solvent was removed in a rotary evaporator. The crude product was dissolved in petroleum ether and then cooled to –20 °C to give white crystalline bis-*p*ODODA, which was collected on a Büchner and washed with small amounts of cold petroleum ether (–20 °C). The solid was dried under vacuum at 15–20 °C. Yield 78% (6.84 g), m.p. 36–38 °C. $^1$H NMR (200 MHz, $CDCl_3$, 25 °C): $\delta$ = 0.85 (t, 6 H, 2 $CH_3$), 1.05–1.45 (m, 20 H, 10 $CH_2$), 1.60–1.75 (m, 6 H, 2 $CH_2$ + 2 NH), 2.73 (t, 4 H, 2 $CH_2$–N), 3.51 (m, 8 H, 2 $CH_2$–O + 2 $CH_2$–Ar), 3.66 [s, 4 H, O–$(CH_2)_2$–O], 3.89 (t, 4 H, 2 $CH_2$–O–Ar), 6.79 (d, 4 H, Ar), 7.19 (d, 4 H, Ar) ppm. $C_{36}H_{60}N_2O_4$ (584.98): calcd. C 73.92, H 10.34, N 4.78; found C 73.70, H 10.39, N 4.82.

## Acknowledgments

Support of this work by the Ministero dell'Istruzione, Università e Ricerca, Rome (COFIN 2003) is gratefully acknowledged.

---

[1] E. L. Cussler, *Diffusion*, Cambridge University Press, New York, **1997**.

[2] W. S. W. Ho, K. K. Sarkar (Eds.), *Membrane Handbook*, Van Nostrand Reinhold, New York, **1992**.

[3] R. M. Izatt, J. S. Bradshaw, J. D. Lamb, R. L. Brueing, "Emulsion and supported liquid membranes", in: *Liquid membranes: Chemical Applications* (Eds.: T. Araki, H. Tsukube), CRC Press, Boca Raton, **1990**, pp. 123–139.

[4] R. D. Noble, J. D. Way (Eds.), *Liquid Membranes: Theory and Applications*, American Chemical Society, Washington D.C., **1987**.

[5] M. E. Paez-Hernandez, M. T. Ramirez-Silva, C. A. Galan-Vidal, "Environmental applications of liquid membranes", in: *Applications of Analytical Chemistry in Environmental Research*" (Ed.: M. Palomar), Research Signpost, Trivandrum, India, **2005**, pp. 189–201.

[6] F. Hassaine-Sadi, L. Sadoun, *Desalination* **2005**, *185*, 335–340.

[7] R. Bucci, S. Canepari, E. Cardarelli, A. M. Girelli, A. Pietrodangelo, M. Valiente, *Sep. Sci. Technol.* **2004**, *39*, 3821–3838.

[8] J. D. Clark, B. Han, A. S. Bhown, S. R. Wickramasinghe, *Sep. Purif. Technol.* **2005**, *42*, 201–211.

[9] M. Grote, B. Haciosmanoglu, M. Bataineh, J. Nolte, *J. Environ. Sci. Health., Part A* **2004**, *39*, 1039–1053.

[10] M. Shamsipur, M. H. Mashhadizadeh, G. Azimi, *Sep. Purif. Technol.* **2002**, *27*, 155–161.

[11] J. S. Kim, M. H. Cho, J. H. Cho, J. H. Lee, R. A. Bartsch, Y. I. Lee, I. H. Kim, *Talanta* **2000**, *51*, 99–105.

[12] A. Safavi, E. Shams, *J. Membr. Sci.* **1998**, *144*, 37–43.

[13] H. Parham, M. Shamsipur, *J. Membr. Sci.* **1994**, *95*, 21–27.

[14] R. M. Izatt, *J. Inclusion Phenom. Macrocyclic Chem.* **1997**, *29*, 197–220.

[15] R. A. Goyer, "Toxic Effects of Metals" in: *Casarett and Doull's Toxicology: the Basic Science of Poisons* (Ed.: C. D. Klassen), McGraw-Hill, New York, **1996**, pp. 691–736.

[16] R. A. Goyer, M. G. Cherian (Eds.), *Toxicology of Metals: Biochemical Aspects*, Springer, Heidelberg, **1995**.

[17] H. G. Seiler, H. Sigel, A. Sigel (Eds.), *Handbook on Toxicity of Inorganic Compounds*, Marcel Dekker, New York, **1988**.

[18] L. Friberg, G. F. Nordberg, V. B. Vouk (Eds.), *Handbook on the Toxicology of Metals*, Elsevier, Amsterdam, **1986**, vol. 2.

[19] B. Sarkar (Ed.), *Biological Aspects of Metals and Metal-Related Diseases*, Raven Press, New York, **1983**.

[20] C. Baird, *Chimica ambientale*, Zanichelli, **1997**.

[21] S. E. Manahan, *Environmental Chemistry*, 6th ed., CRC Press Inc., Boca Raton, Florida, **1994**.

[22] L. Brinchi, P. Di Profio, R. Germani, G. Savelli, N. Spreti, *Eur. J. Org. Chem.* **2002**, 930–937.

[23] L. Brinchi, R. Germani, M. V. Mancini, G. Savelli, N. Spreti, *Eur. J. Org. Chem.* **2004**, 1330–1335.

[24] N. Spreti, L. Brinchi, R. Germani, M. V. Mancini, G. Savelli, *Eur. J. Org. Chem.* **2004**, 3865–3871.

[25] F. M. Menger, J. J. Lee, *J. Org. Chem.* **1993**, *58*, 1909–1916.

[26] F. A. Cotton, G. Wilkinson, C. A. Murillo, M. Bochmann, *Advanced Inorganic Chemistry*, John Wiley & Sons, New York, **1999**.

Received: March 21, 2006
Published Online: August 3, 2006

© 2006 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim