A New Carrier for Selective Removal of Heavy Metal Ions from Aqueous Solutions through Bulk Liquid Membranes

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The carrier-mediated transport of heavy metal ions through bulk liquid membranes has been examined: toxic Hg^{2+}, Cd^{2+} and Pb^{2+} ions were studied, along with Cu^{2+} ions for comparative purposes. The ability of a new carrier, 2,2′-bis(*p*-octyloxybenzyl)diethylenetriamine (bis-*p*ODET), to complex and transport all the selected metal ions is reported. Differing affinities of the carrier for the different metal ions and the different experimental conditions required for their release into the receiving phase allowed the selective separation of equimolar binary mixtures. For Hg^{2+}/Cd^{2+} and Hg^{2+}/Pb^{2+} mixtures, two different separation methods were performed, while the inefficacy of the separation of Cd^{2+}/Pb^{2+} and Hg^{2+}/Cu^{2+} mixtures was for two different reasons: (i) the carrier is able to extract the metal ions with similar levels of ability, and (ii) the carrier metal ion complexes require the same acidity of the receiving phase to release the metal ions. The capability of the carrier to transport Hg^{2+} efficiently in consecutive cycles is also reported: over 90% of the metal ions were transferred into the receiving phase for three consecutive processes.

Introduction

Environmental contamination by heavy metal ions reflects both natural sources and human industrial processes,[1−3] and their effects impact on several organ systems and biochemical activities.[4,5] The necessity to reduce the amount of heavy metal ions to acceptable levels in wastewater streams, and subsequent possible reuse of these metal ions, has resulted in increasing interest in the development of new methods for their selective removal from mixtures.

Liquid membrane technology, coupled with suitable selective carriers, provides a possible means by which to accomplish such separations.[6−9]

Bulk liquid membrane (BLM) systems are useful for screening carriers and they are widely used to study ion transport from aqueous compartments to others through organic membranes. Crown ethers and acyclic polyethers, with different donor atoms, as well as other complexing molecules, have been extensively employed to effect transport of some of the most toxic heavy metal ions, such as mercury(II),[10,11] lead(II)[12−15] and cadmium(II).[15,16] Moreover, the carrier must have a suitable lipophilic-hydrophilic balance so as both to be soluble in the membrane and at the same time to be able to reach aqueous/organic interfaces, and long-chained ligands have been successfully used to transport copper(II) ions across a chloroform membrane.[17]

We have recently reported the ability of 1,1,7,7-tetraethyl-4-(tetradecyl)diethylenetriamine (TE14DT) to act as a carrier for Cu^{2+}, Cd^{2+}, Hg^{2+} and Pb^{2+} ions.[18,19] While capable of extracting all the selected metal ions from the source phase into the membrane, TE14DT also displayed a remarkable efficacy to transport only Cu^{2+} and Cd^{2+}. In the case of Hg^{2+}, lack of transport was due to the high stability of the Hg^{2+}−carrier complex in the organic phase, and modifications of some external parameters (i.e., the pH of the receiving phase) did not allow the release of the metal ion.

This paper presents a new carrier: 2,2′-bis(*p*-octyloxybenzyl)diethylenetriamine (bis-*p*ODET). Its chelating region is very similar to that of TE14DT, since three N atoms act as complexing agents. On the other hand, it possesses two alkyl chains and aromatic moieties and has a pincer-type structure (Scheme 1).

Its transport capability was evaluated as a function of the nature of the membrane and of the pH of the receiving phase, and optimal experimental conditions for single-metal ion transport were found. Selectivity tests were also performed, and two different separation methods of binary mixtures are presented.

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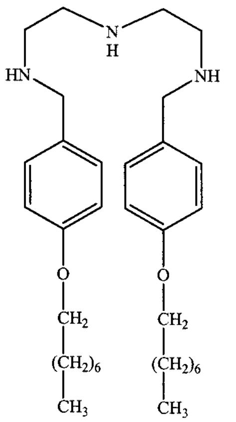

2,2'-bis(*p*-octyloxybenzyl)diethylenetriamine
(bis-*p*ODET)

Scheme 1

Results and Discussion

Partition Measurements

The ability of the carrier bis-*p*ODET to extract the metal ions from the source phase to the membrane was investigated with two different organic solvents, chloroform and dichloromethane, by the procedure reported in the Exp. Sect. Carrier extraction results, along with spontaneous metal ion partitions, are reported in Table 1.

Table 1. Mol percentages of M^{2+} extracted from the source phase to the organic phase (conditions: 25 °C; source phase: 3 mL of 5 × 10^{-3} M MCl_2 in 0.15 M acetate buffer pH = 4.68; membrane: 3 mL of 1 × 10^{-3} M carrier in the organic solvent)

Membrane	Cu^{2+}	Cd^{2+}	Pb^{2+}	Hg^{2+}
$CHCl_3$	< 1	< 1	< 1	< 1
CH_2Cl_2	< 1	< 1	< 1	11
bis-*p*ODET in $CHCl_3$	18	16	19	22
bis-*p*ODET in CH_2Cl_2	27	27	20	35

For the charge balance in the membrane, M^{2+} and M^{2+}−carrier complex partitioning in the organic phase should occur as ion pairs. In the case of Hg^{2+}, we have already shown that the main accompanying ion in the partition between source phase and membrane is Cl^-.[19]

In the absence of the carrier, only Hg^{2+} partitioned in the dichloromethane membrane, and its diffusion from the source phase to the receiving phase has already been reported.[19]

Furthermore, Table 1 shows that the carrier was able to extract all the metal ions and that only slight differences between the two organic phases were observed, except in the case of Hg^{2+}: the higher percentage in dichloromethane with respect to chloroform (35% vs. 22%) was probably due to its spontaneous partitioning (11%) in the former membrane.

For Hg^{2+}, partition experiments were also carried out with variation of [Hg^{2+}] in the source phase and constant values of carrier. The two sets of experiments, with [carrier] =1 × 10^{-3} M and 5 × 10^{-4} M, were both consistent with a ratio of 3:2 in the association of Hg^{2+} to the carrier.

Single Ion Transport

To choose the proper organic phase for selectivity studies, single ion transport experiments were performed. Table 2 reports the percentages of M^{2+} in the source phase and receiving phase at different times. A similar decrease in the amount of M^{2+} in the source phase was observed in the early hours of the transport processes, both in dichloromethane and in chloroform, and the ability of the carrier to extract all the metal ions seems very similar. Moreover, in dichloromethane no significant differences in metal ion extraction were found after 24 and 48 h, the percentages of metal ions in the source phase ranging from 20 to 34.

Transfer of M^{2+} in the chloroform membrane seemed to be quite different. In fact, after 48 h, ca. 10% of Cd^{2+} and Pb^{2+} remained in the source phase, while the percentages of Hg^{2+} and Cu^{2+} were 35 and 51, respectively, indicating a potential metal ion screening capability of bis-*p*ODET in the chloroform membrane.

Furthermore, only Cd^{2+} and Pb^{2+} ions were efficiently transferred into the receiving phase in both membranes (see Table 2), and the chloroform membrane showed better results and so was then chosen for the next experiments.

As reported in the Introduction, the structure of bis-*p*ODET is quite similar to that of TE14DT, with three N atoms representing the chelating region. Like TE14DT, this new carrier was able to transport Cd^{2+} ions, and its efficacy was practically the same.[19] However, different patterns were found for Cu^{2+} and Pb^{2+} ions, indicating that not only the nature of the chelating atoms but also many other factors can influence the carrier-mediated transport. In fact, TE14DT was an excellent carrier for Cu^{2+},[18] while the slow diffusion of Pb^{2+}−carrier complex through the membrane was probably the cause of the lack of transport, most of the Pb^{2+} remaining in the source phase.[19] On the other hand, in the presence of bis-*p*ODET, after 48 h, 58% Pb^{2+} had been transported, while Cu^{2+} was rapidly extracted into the chloroform, but its release into the receiving phase was negligible.

Similar behaviour (i.e., fast decrease of metal ion concentration in the source phase and slight release in the receiving one) was also observed for Hg^{2+} (11% after 48 h). Furthermore, Hg^{2+} diffused through the chloroform spontaneously in the absence of the carrier, and its percentage in the receiving phase after 48 h was ca. 30% (data not shown). This is probably due to formation of stable complexes between bis-*p*ODET and both Cu^{2+} and Hg^{2+} ions and, in order to improve their transport, variations of the experimental conditions seemed to be necessary.

Among the external factors involved in transport processes, the pH of the receiving phase could play a crucial role. Transport in these systems is indeed pH-driven: the metal ions in the source phase are exchanged by the carrier

Table 2. Mol percentages of M^{2+} in the receiving (R) and source (S) phases at 25 °C

Time [h]	bis-*p*ODET[a]																TE14DT[b]							
	$CHCl_3$								CH_2Cl_2								CH_2Cl_2							
	Cu^{2+}		Cd^{2+}		Pb^{2+}		Hg^{2+}		Cu^{2+}		Cd^{2+}		Pb^{2+}		Hg^{2+}		Cu^{2+}		Cd^{2+}		Pb^{2+}		Hg^{2+}	
	R	S	R	S	R	S	R	S	R	S	R	S	R	S	R	S	R	S	R	S	R	S	R	S
4	1	59	15	60	10	58	< 1	55	< 1	48	10	64	6	59	1	43	23	72	7	78	< 1	94	5	41
8	1	53	33	45	16	52	3	46	< 1	40	29	48	17	38	5	36	44	52	19	70	1	93	11	34
24	2	52	55	15	36	29	11	37	1	36	41	27	25	23	11	26	78	19	53	37	2	92	14	28
48	3	51	75	7	58	12	11	35	1	34	62	20	38	21	12	24	89	8	72	19	4	90	15	26

[a] Conditions: source phase: 8 mL of 5×10^{-3} M MCl_2 in 0.15 M acetate buffer pH = 4.68; membrane: 20 mL of 1×10^{-3} M carrier in the organic solvent; receiving phase: 8 mL of 3.2×10^{-3} M HCl (pH = 2.5). [b] Refs.[18,19] Conditions: source phase: 8 mL of 5×10^{-3} M MCl_2 in 0.15 M acetate buffer pH = 4.68; membrane: 20 mL of 1×10^{-3} M carrier in the organic solvent; receiving phase: 8 mL of 0.1 M HCl (pH = 1).

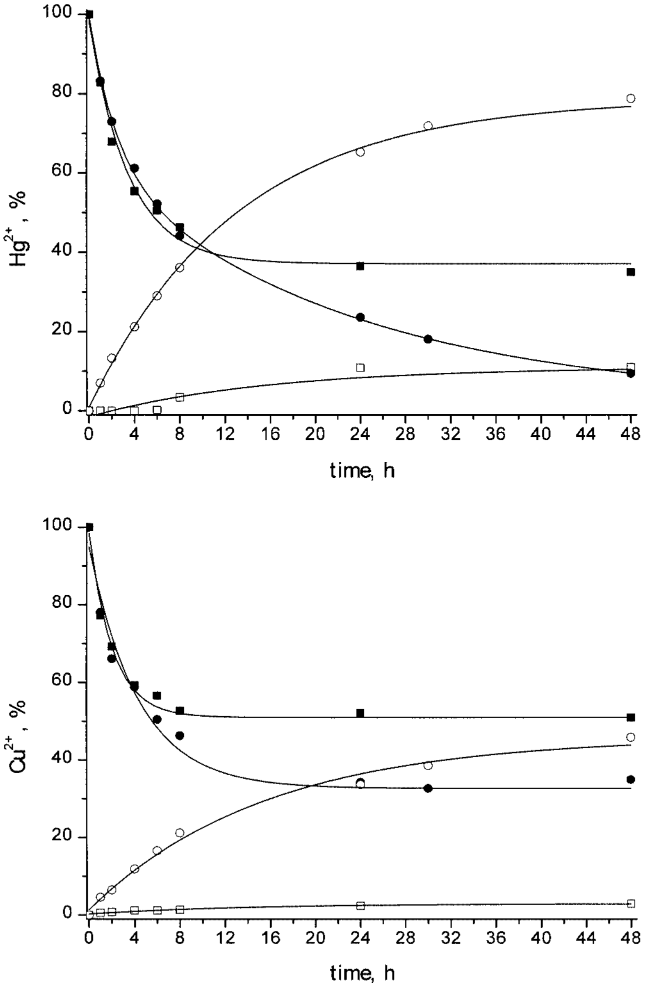

Figure 1. Mol percentages of Hg^{2+} (top) and Cu^{2+} (bottom) vs. time in the source phase (filled symbols) and receiving phase (open symbols) with 3.2×10^{-3} M HCl, pH = 2.5 (squares) and 0.5 M HCl, pH = 0.3 (circles) as receiving phase; [bis-*p*ODET] = 1×10^{-3} M in chloroform; [MCl_2] = 5×10^{-3} M in 0.15 M acetate buffer, pH = 4.68; *T* = 25 °C

for protons originating from the receiving one. A buffered aqueous solution was therefore used as source phase to minimize pH variation due to H^+ counter transport. The release of the metal ions into the stripping phase depended on the protonation of atoms in the chelating region, so when Hg^{2+} and Cu^{2+} concentrations had levelled off, small amounts of concentrated HCl were added in the stripping phase and, despite the system becoming heterogeneous, the concentrations of the two metal ions rose significantly.

Experiments with more concentrated HCl solution as receiving phase (pH = 0.3) were then carried out, and percentages/time profiles are shown in Figure 1. Data relating to transport at pH = 2.5 are also displayed.

The extraction curves in the early hours of the process are very similar, independently of the pH of the receiving phase, but the more efficient release of the metal ions allowed further extraction. Notwithstanding the improvement in the transport and the low amount of metal ions in the membrane (ca. 15%) for both Cu^{2+} and Hg^{2+}, bis-*p*ODET was far more effective for Hg^{2+} than for Cu^{2+}, the percentages in the receiving phase after 48 h being 80% and 46%, respectively.

Simultaneous Transport of Hg^{2+}/M^{2+} Mixtures

On the basis of single ion transport experiments, different operational conditions could potentially allow sequential separation of Hg^{2+}/Cd^{2+} and Hg^{2+}/Pb^{2+} mixtures. Initially, with a pH = 2.5 receiving phase, Cd^{2+} and Pb^{2+} should be efficiently transported, with Hg^{2+} stored in the membrane as metal ion−carrier complex. Then, after the removal of the concentrated Cd^{2+} (or Pb^{2+}) solution, the addition of a new aqueous phase at pH = 0.3 should allow the release of all Hg^{2+} ions present in the membrane.

Equimolar mixtures of Cd^{2+} (or Pb^{2+}) and Hg^{2+} were therefore used as source phase for these experiments, and $[M^{2+}]_{tot}$ was 5×10^{-3} M, as in the single ion transport experiments. The carrier concentration was doubled, since the affinity of bis-*p*ODET for Hg^{2+} was much higher than for Cd^{2+} (and Pb^{2+}) and the amount of the carrier was not enough to transport Cd^{2+} and Pb^{2+} ions through the membrane (data not shown). Results relating to Hg^{2+}/Cd^{2+} mixtures are shown in Figure 2. In the first part of the process (0−48 h), both Hg^{2+} and Cd^{2+} were efficiently extracted from the source phase, and, as expected, only Cd^{2+} ions were transported in the receiving phase (ca. 90%). Then, Hg^{2+} ions, stored in the membrane, were quickly transferred into the new aqueous stripping phase at pH =

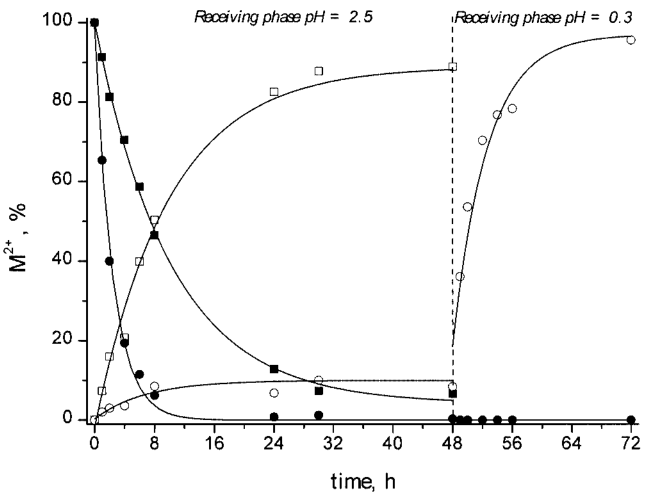

Figure 2. Mol percentages of Hg^{2+} (circles) and Cd^{2+} (squares) vs. time in the source phase (filled symbols) and receiving phase (open symbols) in simultaneous transport; [bis-*p*ODET] = 2×10^{-3} M in chloroform; [$CdCl_2$] = [$HgCl_2$] = 2.5×10^{-3} M in 0.15 M acetate buffer, pH = 4.68; T = 25 °C; see text for the experimental procedure

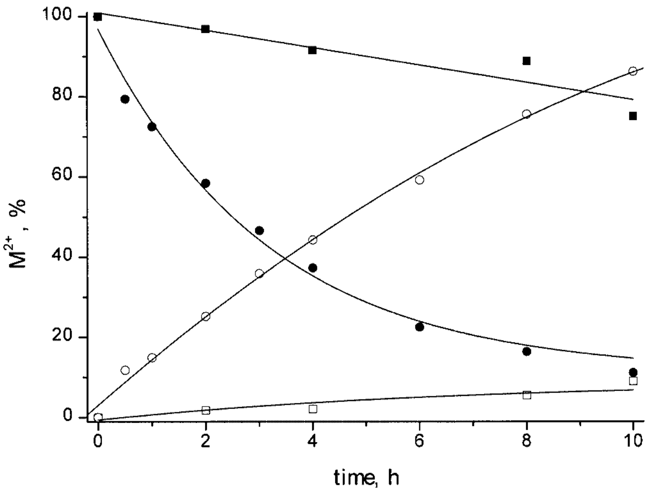

Figure 3. Mol percentage of Hg^{2+}(circles) and Pb^{2+} (squares) vs. time in the source phase (filled symbols) and receiving phase (open symbols) in the simultaneous transport; [bis-*p*ODET] = 1×10^{-3} M in chloroform; [$PbCl_2$] = [$HgCl_2$] = 2.5×10^{-3} M in 0.15 M acetate buffer, pH = 4.68; receiving phase: 0.5 M HCl, pH = 0.3; T = 25 °C

0.3. In this way, sequential separation of Cd^{2+} and Hg^{2+} was carried out.

Similar experiments were performed with equimolar mixtures of Pb^{2+} and Hg^{2+}, but lower selectivity was obtained. After 48 h, only 67% of Pb^{2+} had been transferred into the receiving phase, with more than 25% remaining in the membrane. When the receiving phase was replaced with the more acidic one, besides the quantitative transport of Hg^{2+} ions, the total release of Pb^{2+} present in the organic phase was observed. Moreover, a further increase in carrier concentration decreased the efficiency of the whole process: both metal ions were extracted more rapidly, but their release into the stripping phases was strongly inhibited. Metal ion/carrier ratio therefore also plays an important role: as already reported, an excess carrier concentration either has no significant effect[20,21] or causes a slight decrease in transport efficiency.[11,18,22]

In view of the high affinity of bis-*p*ODET for Hg^{2+} with respect to Cd^{2+} and Pb^{2+} ions observed in these last experiments, a different separation method was used. The use of a more acidic solution as receiving phase should allow the fast transport of Hg^{2+}, most of the competitive ions remaining in the source phase. In this way, there is a “real competition” between Cd^{2+} (or Pb^{2+}) and Hg^{2+} ions for the carrier. Figure 3 displays the actual separation of Pb^{2+}/Hg^{2+} mixture (the results with Cd^{2+}/Hg^{2+} ions were very similar).

After 10 h, the stripping phase contained ca. 80% Hg^{2+} and only 10% Pb^{2+} (or Cd^{2+}), while in the source phase there remained ca. 10% Hg^{2+} and more than 75% Pb^{2+} (or Cd^{2+}). Hence, from a starting equimolar binary solution, we obtained (in a few hours) an Hg^{2+}/Pb^{2+} (or Cd^{2+}) ratio of ca. 8:1 in the receiving phase and the reciprocal in the source.

Finally, the separation of an Hg^{2+}/Cu^{2+} mixture was attempted. Both metal ions were efficiently transported by use of the more acidic solution as receiving phase, and so only a much higher carrier affinity for either of the metal ions could allow selective transport.

Experiments were carried out with 1×10^{-3} M and 2×10^{-3} M carrier. A very fast decrease in Hg^{2+} concentration in the source phase was observed and, after the first 8−10 h, all the metal ions had been extracted by the carrier. Conversely, the extraction of Cu^{2+} ions was dependent on carrier concentration, being more rapid with 2×10^{-3} M bis-*p*ODET (41% and 18% in the source phase after 8 h with 1×10^{-3} M and 2×10^{-3} M carrier, respectively). In both experiments, however, 24−48 h were necessary to remove all Cu^{2+} ions from the source phase. Therefore, bis-*p*ODET showed a greater affinity for Hg^{2+} than Cu^{2+} ions.

On the other hand, the release of both metal ions into the receiving phase was more effective with the lower carrier concentration. After 24 h, quantitative transport of Hg^{2+} was observed, while the amount of Cu^{2+} transferred into the stripping phase reached 60% and remained constant in the next hours. A similar Hg^{2+}/Cu^{2+} ratio, but lower respective percentages (80% for Hg^{2+} and 50% for Cu^{2+}), were obtained in the stripping phase with 2×10^{-3} M carrier.

On the basis of these results, carrier concentration could play an important role in increasing the selectivity of Hg^{2+} transport. In the presence of a smaller amount of the carrier, stronger competition between the metal ions should be achieved, due to more rapid transport of the metal ion showing the greater affinity for the carrier. Experiments with 5×10^{-4} M bis-*p*ODET were then carried out. More than 70% of Hg^{2+} ions was transported by the carrier, while both Cu^{2+} extraction and release proved to be inhibited, although 30% of the Cu^{2+} had been transferred to the stripping phase after 24 h and the Hg^{2+}/Cu^{2+} ratio was only slightly increased.

Thus, notwithstanding that bis-*p*ODET exhibited a higher affinity for Hg^{2+} than for Cu^{2+} ions, no effective mixture separation was accomplished under the experimental conditions used, and therefore alternative methods would appear necessary.

The separation of Hg^{2+} from metal ion mixtures is a challenging problem in this field of chemistry, and some highly efficient and selective carriers have been reported in the literature.[10,11,23] However, the competitive metal ions are often insoluble in the source phase[11] or are not extracted by the carrier,[23] so their transport is negligible. In our system all the competitive ions are transported by the carrier and the experimental conditions can be modified depending on the nature of the contaminated aqueous solutions.

Simultaneous Transport of Cu^{2+}/Cd^{2+} and Cu^{2+}/Pb^{2+}

Selectivity tests were also performed with binary equimolar mixtures of Cu^{2+} and Cd^{2+} or Pb^{2+}. The HCl concentration in the receiving phase could also be an useful means to control selectivity in these transports. Cu^{2+} ions, as previously seen for Hg^{2+}, were extracted by the carrier, but, for their release, the more acidic receiving phase had to be used.

Two different sets of experiments in which the pH of the stripping phase was varied (i.e., 2.5 and 0.3) were then performed. The carrier affinity for Cu^{2+} was always much higher than for Cd^{2+} or Pb^{2+}, and in order to allow the transport of these ions across the membrane, the concentration of the carrier was doubled when a pH = 2.5 solution was used as receiving phase (Table 3).

Table 3. Mol percentages of M^{2+} in the receiving (R) and source (S) phases in simultaneous transports (Cu^{2+}/Cd^{2+} and Cu^{2+}/Pb^{2+} at 25 °C)

Time [h][a]	Cu^{2+}/Cd^{2+}				Cu^{2+}/Pb^{2+}			
	Cu^{2+}		Cd^{2+}		Cu^{2+}		Pb^{2+}	
	R	S	R	S	R	S	R	S
2	1	48	7	67	1	55	3	57
4	1	23	22	42	1	36	13	47
8	2	9	39	23	1	18	23	34
24	3	8	49	21	1	12	41	24
48	5	5	56	15	1	6	53	18

[a] Conditions: source phase: 8 mL of a solution of 2.5×10^{-3} M $CuCl_2$ and 2.5×10^{-3} M $CdCl_2$ (or $PbCl_2$) in 0.15 M acetate buffer pH = 4.68; membrane: 20 mL of 2×10^{-3} M carrier in chloroform; receiving phase: 8 mL of 3.2×10^{-3} M HCl (pH = 2.5).

The extraction of Cu^{2+} from both mixtures was very fast and, after 8 h, 90% of the metal ion had been accumulated in the organic phase (only ca. 10% in the aqueous phases). A moderate rise in Cd^{2+} and Pb^{2+} concentration in the receiving phase was observed, with over 50% of the metal ions being transported. These results are not very satisfactory, since 30% of the Cd^{2+} or Pb^{2+}, in addition to Cu^{2+}, is stored in the membrane.

Results obtained with the other receiving phase (pH = 0.3) are reported in Table 4. In this case the transport of Cu^{2+} was promoted and, after 48 h, most of the metal ion had been delivered into the stripping phase. It is noteworthy that the Cu^{2+}/Cd^{2+} and Cu^{2+}/Pb^{2+} ratios in the receiving phase decreased as the process was in progress. In fact, on short timescales, a sharp decrease in Cu^{2+} concentration in the source phase was observed, along with a rapid rise in the receiving one; concentrations then tended to a limiting value and to level off. On the other hand, Pb^{2+} and Cd^{2+} ions were gradually transported with a consequent lowering of selectivity.

Table 4. Mol percentages of M^{2+} in the receiving (R) and source (S) phases in simultaneous transports (Cu^{2+}/Cd^{2+} and Cu^{2+}/Pb^{2+} at 25 °C)

Time [h][a]	Cu^{2+}/Cd^{2+}				Cu^{2+}/Pb^{2+}			
	Cu^{2+}		Cd^{2+}		Cu^{2+}		Pb^{2+}	
	R	S	R	S	R	S	R	S
2	11	68	5	89	13	55	1	95
4	16	53	5	86	23	35	2	88
8	32	35	9	80	42	18	6	80
24	61	22	22	73	78	8	22	58
48	71	12	39	56	85	4	39	38

[a] Conditions: source phase: 8 mL of a solution of 2.5×10^{-3} M $CuCl_2$ and 2.5×10^{-3} M $CdCl_2$ (or $PbCl_2$) in 0.15 M acetate buffer pH = 4.68; membrane: 20 mL of 1×10^{-3} M carrier in chloroform; receiving phase: 8 mL of 0.5 M HCl (pH = 0.3).

Simultaneous Transport of Pb^{2+}/Cd^{2+}

Simultaneous transport of Cd^{2+} and Pb^{2+} was then examined. Both metal ions were effectively transported across the membrane in the receiving phase at pH = 2.5, and the ability of bis-*p*ODET to complex more efficiently, and therefore to transport, either of the metal ions was evaluated. The data reported in Table 5 clearly indicate that no selectivity between Cd^{2+} and Pb^{2+} was observed, the percentages being very similar to those of the single ion transport (see Table 2). The use of two differently concentrated HCl solutions as receiving phase did not improve carrier selectivity, since either no significant effect or a decrease in the transport of both metal ions were observed in receiving phases at pH = 3.3 and pH = 0.3, respectively.

Carrier Recycling

As previously reported, a strongly acidic aqueous solution must be used to allow the release of Hg^{2+} ions from the membrane into the receiving phase, in which bis-*p*ODET and Hg^{2+} formed a very stable complex. Consequently, the three N atoms of the chelating region were highly protonated and the use of the carrier for further transports could be compromised. On the other hand, besides the high efficiency and selectivity of bis-pODET for Hg^{2+} ions, the capability to perform many consecutive processes should increase its potential applicability in Hg^{2+} removal from polluted aqueous solutions.

Table 5. Mol percentages of M^{2+} in the receiving phase in simultaneous transports (Cd^{2+}/Pb^{2+} as function of the pH of the receiving phase at 25 °C)

Time [h][a]	Cd^{2+}			Pb^{2+}		
	pH = 2.5	pH = 3.3	pH = 0.3	pH = 2.5	pH = 3.3	pH = 0.3
4	16	21	7	7	10	8
24	73	66	13	44	42	24
48	77	73	14	55	46	28

[a] Conditions: source phase: 8 mL of a solution of 2.5×10^{-3} M $CdCl_2$ and 2.5×10^{-3} M $PbCl_2$ in 0.15 M acetate buffer pH = 4.68; membrane: 20 mL of 1×10^{-3} M carrier in chloroform; receiving phase: 8 mL of HCl at different concentrations.

Experiments to evaluate the capability of the carrier to transport Hg^{2+} efficiently for several cycles were therefore carried out, both aqueous phases being removed and replaced with fresh solutions after the first transport process. Figure 4 reports the profile of μmols of Hg^{2+} in the source phase and receiving phase observed over three consecutive cycles.

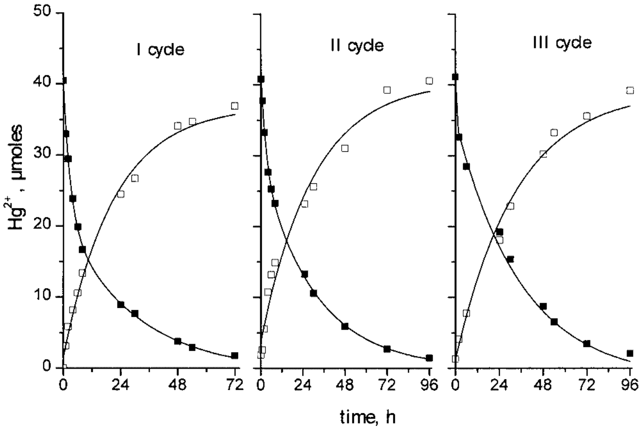

Figure 4. μmols of Hg^{2+} in the source phase (filled squares) and receiving phase (open squares) in three consecutive cycles; [bis-*p*ODET] = 1×10^{-3} M in chloroform; [$HgCl_2$] = 5×10^{-3} M in 0.15 M acetate buffer, pH = 4.68; receiving phase: 0.5 M HCl, pH = 0.3; T = 25 °C.

Over 90% of the Hg^{2+} was transported in every process and only in the last cycle did the rate of the metal ion transport seem to be slower than in the first ones.

Conclusion

The transport capability of a new carrier, bis-*p*ODET, for the selective removal of heavy metal ions is reported. Cadmium, lead and mercury were chosen for this study, owing to their high toxicity, along with copper for comparative purposes.

Single ion transport experiments showed that the carrier was able to complex and transfer all the metal ions from the source phase to the receiving phase. On the other hand, bis-*p*ODET displayed different affinities for the selected metal ions, in the order $Hg^{2+} > Cu^{2+} > Cd^{2+} \approx Pb^{2+}$, and the release of the metal ions from the membrane was dependent on the pH of the receiving phase. Selective metal ion transport was therefore examined, and two different separation procedures were optimized.

For Cd^{2+}/Pb^{2+} and Hg^{2+}/Cu^{2+} mixtures, the inefficacy of separation was due to two different reasons: (i) the carrier is able to extract the metal ions with similar degrees of ability, and (ii) the carrier−metal ion complexes require the same acidity of the receiving phase to release the metal ions.

Finally, the capability of the carrier to transport Hg^{2+} efficiently over consecutive cycles increases its potential applicability to selective removal of mercury from wastewater solutions.

Experimental Section

Membrane "Uptake": A glass test tube, fitted with a screw cap, was filled with both the source phase (3 mL, 5×10^{-3} M MCl_2) and the organic membrane (3 mL, 1×10^{-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.[19] An organic solution (20 mL, 1×10^{-3} M carrier) was used as liquid membrane separating an aqueous solution (source phase) containing the metal salt or a mixture of metal salts (8 mL, 5×10^{-3} M MCl_2), and a receiving phase (8 mL, 3.2×10^{-3} M or 0.5 M HCl). The liquid membrane phase was slowly stirred (250 rpm) with the aid of 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 single ion transport experiments were measured by the sensitive spectrophotometric method described in an earlier publication.[19] A diode array Hewlett Packard 8452 A spectrophotometer was used for the quantitative determinations. Graphite furnace atomic absorption spectrophotometers for the measurements of metal ion concentrations in competitive experiments were used: Perkin−Elmer Model Zeeman 3030 for Cu^{2+}, Cd^{2+} and Pb^{2+} and Varian-Spectra 200 with a GTA100 graphite furnace for Hg^{2+} 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 diethylenetriamine were analytical grade, purchased from Aldrich and used as received. Solvents, purchased from Carlo−Erba, were ACS-certified quality. ^1H NMR spectra were recorded with a Bruker instrument at 200 MHz;

chemical shifts (δ ppm) are referred to internal standard $(CH_3)_4Si$. Melting points were measured with a Büchi 510 melting point apparatus and are uncorrected. IR spectra were recorded with a Paragon 500 FT-IR Perkin−Elmer spectrophotometer. GLC was carried out with an HP 5890 (FID) instrument with a 30 m × 0.53 mm capillary column (HP-5, 1.5-μm film thickness) or a 15 m × 0.53 mm capillary column (HP-INNOVAX, 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), and with petroleum ether/Et_2O (8:2) as eluent. TLC was carried out on silica gel (ALUGRAM® SIL G/UV_{254}) with petroleum ether/Et_2O (8:2) as eluent.

Synthesis of the Carrier

Preparation of *p*-Octyloxybenzaldehyde: Freshly recrystallized (from water) and dried 4-hydroxybenzaldehyde (0.24 mol, 29.31 g), anhydrous potassium carbonate (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. As reflux was reached, octyl bromide (0.23 mol, 44.42 g) was added dropwise over 1 h. 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, giving a pale yellow oil. The yield of this oil was 98% (52.82 g), and the purity by GLC 98%. No treatment of the oil followed. ^1H NMR ($CDCl_3$): δ = 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_2O), 7.00 (d, 2 H, Ar), 7.85 (d, 2 H, Ar), 9.01 (s, 1 H, COH) ppm. $C_{15}H_{22}O_2$ (234.3): calcd. C 76.88, H 9.46, found, C 76.90, H 9.50.

Preparation of 2,2′-Bis(*p*-octyloxybenzylimine)diethylamine [*N*′-(*p*-Octyloxybenzylidene)-*N*-{2-[(*p*-octyloxybenzylidene)amino]ethyl}-1,2-ethanediamine]: Diethylenetriamine (0.086 mol, 8.87 g) was added to a solution of *p*-octyloxybenzaldehyde (0.178 mol, 41.71 g) 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. Once distillation had finished, a reflux condenser was substituted for the separator, and molecular sieves (4 Å; 15 g) were added. After the system had been heated at reflux for 12 h and cooled to room temperature, molecular sieves were removed by filtration. The organic solution was concentrated in a rotary evaporator to give a yellow semisolid. This was crystallized from petroleum ether, and recrystallized from methanol to give, after drying under vacuum, a crystalline white solid. The yield of this solid was 80% (36.86 g). M.p. 48−49 °C. ^1H NMR ($CDCl_3$): δ = 0.88 (t, 6 H, 2 CH_3), 1.20−1.45 (m, 20 H, 10 CH_2), 1.69−1.82 (m, 4 H, 2 CH_2), 2.97 (t, 4 H, 2 N−CH_2), 3.71 (t, 4 H, 2 =N−CH_2), 3.90 (t, 4 H, 2 CH_2−O-Ar), 6.80 (d, 4 H, Ar), 7.57 (d, 4 H, Ar), 8.22 (s, 2 H, 2 CH=N) ppm.

Preparation of 2,2′-Bis(*p*-octyloxybenzyl)diethylenetriamine {*N*′-(*p*-Octyloxybenzyl)-*N*-[2-(*p*-octyloxybenzylamino)ethyl]-1,2-ethanediamine}: $NaBH_4$ (0.035 mol) was added in small aliquots to a stirred mixture of 2,2′-bis(*p*-octyloxybenzylimine)diethylamine (0.015 mol, 8.04 g) in methanol (200 mL), in a round-bottomed flask fitted with a reflux condenser. The mixture was heated at reflux for 10 h and allowed to cool to room temperature. It was then transferred to a separating funnel, treated with water (200 mL) and extracted twice with diethyl ether. The organic layer was washed 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, giving a colourless oil, which solidified on a water/ice bath. The yield of this product was 70% (5.67 g). ^1H NMR ($CDCl_3$): δ = 0.86 (t, 6 H, 2 CH_3), 1.13−1.42 (m, 20 H, 10 CH_2), 1.58−1.76 (m, 7 H, 2 CH_2 + 3 NH), 2.67 (s, 8 H, 2 N$(CH_2)_2$N], 3.66 (s, 4 H, 2 N−CH_2−Ar), 3.90 (t, 4 H, 2 CH_2−O−Ar), 6.81 (d, 4 H, Ar), 7.15 (d, 4 H, Ar) ppm. $C_{34}H_{57}N_3O_2$ (539.8): calcd. C 75.64, H 10.64, N 7.78; found C 75.60, H 10.59, N 7.82.

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