Carrier-Mediated Transport of Toxic Heavy Metal Ions in Bulk Liquid Membranes

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Keywords: Cadmium / Carriers / Lead / Lipophilicity / Membranes / Mercury

Transport through a dichloromethane liquid membrane has been studied to investigate the ability of 1,1,7,7-tetraethyl-4-tetradecyldiethylenetriamine (TE14DT), previously tested for the transport of copper, to act as a carrier for toxic heavy metal ions such as Cd^{2+}, Pb^{2+} and Hg^{2+}. The carrier displayed a remarkable capability to extract all the metal ions from the source to the organic phases but only cadmium was efficiently transported across the membrane. The experimental conditions optimised for the transport of copper are inadequate for lead and mercury. In fact, the inefficacy of their transport could be due, as regards lead, to the slow diffusion of the complex through the membrane, while mercury remained in the organic phase because of the high stability of the mercury-carrier complex. Selectivity tests using binary mixtures of the metal ions showed TE14DT's capability to transport copper or cadmium also in the presence of lead in the source phase.

Introduction

Wastewater decontamination is of great concern in the environmental field of waste and pollution reduction. The presence of traces of heavy metals in wastewater streams is particularly dangerous, since most of them are toxic and persistent.[1−4] In fact, heavy metal biodegradation pathways do not exist in nature and biological and chemical remediation processes cannot render them harmless;[5] traditional treatment systems, such as flocculation, precipitation and filtration, or biological processes, are usually effective in reducing organic pollutants, but they often fail to lower heavy metal ion concentrations below permissible limits.[6] Furthermore, only toxic heavy metals, and not other innocuous cations, often need to be removed, as in the production of, for example, potable water; selectivity is therefore quite important. Among the most harmful heavy metals, cadmium, lead and mercury are some of the most important because of their massive use, pronounced toxicity and large-scale distribution.[7]

Liquid-membrane separation is an attractive and promising technology for the selective extraction and recovery of heavy metal ions from aqueous solutions.[8] Three different types of liquid membrane are known: bulk (BLM), supported (SLM) and emulsion (ELM) liquid membranes.[9] SLMs and ELMs present a number of practical advantages in view of industrial applications, whereas BLMs are more suitable for screening novel carrier-mediated transport systems on a laboratory scale.[10] BLMs are the most frequently used membrane systems thanks to their high efficiency and selectivity and their low costs and energy consumption. Their metal-ion-transport capability relies essentially on the complexation properties of an opportune carrier added to the membrane: the design and synthesis of efficient and selective carriers represent a challenging task in this field of chemistry.[11] Many different carriers have been employed in bulk liquid membranes to perform the transport of Pb^{2+}, Cd^{2+} and Hg^{2+} ions: macrocyclic crown ethers,[12−14] macrocyclic aza- and thio-crown ethers,[15,16] acyclic polyethers,[17] and reversed micelles[18] are only a few examples.

We have recently reported our studies on carrier structure design and optimisation for the transport of copper through bulk liquid membranes. Several lipophilic polyamines with different hydrophilic/lipophilic balances were screened and 1,1,7,7-tetraethyl-4-tetradecyldiethylentriamine (TE14DT; Scheme 1) showed the best ability.[19] In this work we report the complexation and transport properties of this carrier for the toxic heavy metal ions Pb^{2+}, Cd^{2+} and Hg^{2+}, using the optimal conditions previously found for transport of Cu^{2+}. Diffusion processes and actual carrier-mediated transport of Pb^{2+}, Cd^{2+} and Hg^{2+} across the membrane were compared and carrier selectivity was also evaluated with regard to binary mixtures of the metal ions. Moreover,

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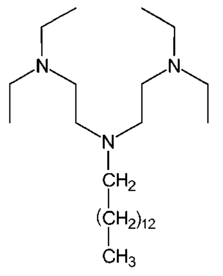
DOI: 10.1002/ejoc.200300622

a very sensitive method for metal ion determination has been developed by using a chelating organic reagent and ionic surfactants, as reported in the Exp. Sect.



1,1,7,7-tetraethyl-4-tetradecyldiethylentriamine

(TE14DT)

Scheme 1

Results and Discussion

Transport experiments were made using the liquid-membrane apparatus reported previously.[19] The metal ion was placed in an aqueous source-phase buffered at pH 4.68. The carrier was dissolved in a stirred organic "membrane". The metal complex released its metal ion into the receiving phase at a lower pH, and the process is driven by the pH difference between the two aqueous phases. The metal ion concentration was monitored in both aqueous compartments as a function of time: this allows the recording of important mechanistic information in order to be able to make proper comparisons between different carriers in terms of relative speeds of transport.

Partition Measurements and Diffusion Processes

Initially, "membrane uptake" experiments were carried out to evaluate the ability of the ligand to extract metal ions from the source phase. The quantitative determination of the ion in the aqueous phase was performed and the percentages of M^{2+} extracted from the source phase are reported in Table 1. For comparative purposes, this test was also made in the absence of carrier.

Table 1. Mol percentage of M^{2+} extracted from the source phase to the organic phase[a]

Carrier	Cu^{2+}	Cd^{2+}	Pb^{2+}	Hg^{2+}
None	<1	<1	<1	11
TE14DT	23	10	12	31

[a] Conditions: 25 °C; source phase: 3 mL of 5×10^{-3} M MCl_2 in 0.15 M acetate buffer, pH 4.68; organic phase: 3 mL of 1×10^{-3} M TE14DT in dichloromethane.

It is evident that TE14DT is active towards all the ions, especially Hg^{2+} and Cu^{2+}, whereas, apart from Hg^{2+}, there is no partition of the ions in dichloromethane in the absence of carrier. However, to separate the different effects due to the actual carrier-mediated transport and the spontaneous process, diffusion experiments were also carried out.

The metal ion concentration in buffered source phase was 5×10^{-3} M, and 0.1 or 1 M HCl was used as the receiving phase. No detectable passage of Cu^{2+}, Pb^{2+} or Cd^{2+} from the source phase to the receiving phase was observed, which is consistent with the absence of partition reported in Table 1, while Hg^{2+} ions showed a marked diffusion ability through the membrane. Furthermore, a significant difference in uptake from the source phase and release in the receiving one was found with 0.1 M and 1 M HCl (Figure 1). After 48 h, 46% of Hg^{2+} was found in the receiving phase at pH 1, versus 70% released at pH 0; the percentages of Hg^{2+} in dichloromethane were nearly the same in both experiments (ca. 20%). This behaviour — the different diffusion rates with receiving phases at different pH — could be dependent either on H_3O^+ or on Cl^- concentration.

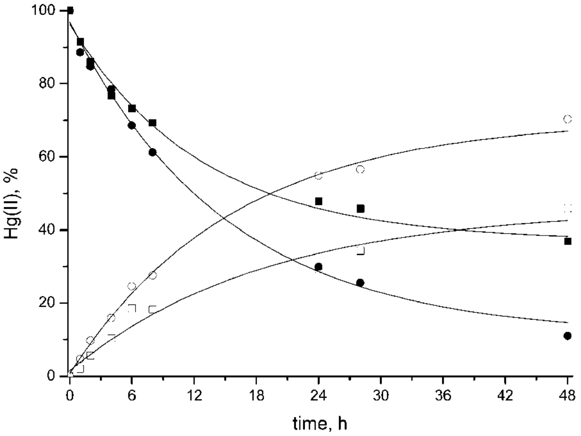


Figure 1. Mol percentage of Hg^{2+} vs. time in the source (filled symbols) and receiving (open symbols) phases with 0.1 M HCl (■/□) and 1 M (●/○) as the receiving phase; the lines are only drawn to help the eyes to follow the points; experimental conditions: source phase, 8 mL of 5×10^{-3} M MCl_2 in 0.15 M acetate buffer, pH 4.68; liquid membrane phase, 20 mL of dichloromethane; receiving phase, 8 mL of 0.1 and 1 M HCl; T = 25 °C

As regards mercury complexes, it is known that Hg^{2+} ions show a strong preference for Cl, Br, I, 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. In particular, solid mercury chloride has an essentially molecular (linear Cl−Hg−Cl) structure. In common with the other halides of mercury, it shows a low solubility in water, apparently mainly in the molecular form. Moreover, Hg^{2+} dissolves in polar and moderately polar organic solvents such as ethanol and ethyl acetate and in apolar solvents such as benzene, although to only a small extent.[20]

Since an accompanying ion is necessary for the charge balance in the membrane, Hg^{2+} could partition in dichloromethane from the source phase either as the acetate, derived from the buffer, or as the chloride itself: the first should be favourite because of the higher concentration with respect to metal salt, but the large affinity of mercury for chloride ions could play a relevant role.

In the case where acetate is the accompanying ion, the release of Hg^{2+} in the receiving phase should be due to the protonation of acetate itself at the membrane-receiving phase interface; then the diffusion process should be pH dependent. Conversely, if Hg^{2+} goes through the membrane as $HgCl_2$, the release could be due to the higher concentration of Cl^- ions in the receiving phase.

To test which hypothesis is correct, the receiving phase was modified in further experiments: in order to eliminate the H_3O^+ effect, 0.1 and 1 M NaCl were used, whereas to check the pH role, 0.05 and 0.5 M H_2SO_4 were used as receiving phases, respectively. A significant increase in Hg^{2+} diffusion from the source to the receiving phases was observed when the NaCl concentration was varied from 0.1 to 1 M, with a similar behaviour found with HCl as the receiving phase. On the other hand, the diffusion process through the membrane was independent of H_2SO_4 concentration: it was lower than that observed with HCl and NaCl and is probably driven by the $HgCl_2$ concentration gradient between the two aqueous phases. These results suggest that the main accompanying ion of Hg^{2+} in the partition in dichloromethane is Cl^-, so that the different behaviour observed with 0.1 and 1 M HCl is due to the different concentration of Cl^- in the receiving phase.

Single-Ion Transport

The ability of TE14DT to transport metal ions across the organic membrane was tested and the concentration/time profiles of M^{2+} transports were also studied. In these experiments, the concentration of the carrier in dichloromethane and of the metal ion in the buffered source-phase were 1×10^{-3} M and 5×10^{-3} M, respectively; 0.1 M HCl was used as the receiving phase. In Table 2 the percentages of M^{2+} present in the source and the receiving phases after 24 and 48 h are listed; the corresponding profiles of the percentage in the source and the receiving phases of Cd^{2+}, Pb^{2+} and Hg^{2+} vs. time are reported in Figure 2. The data for the related Cu^{2+} transport previously determined[19] are also shown for comparative purpose.

Table 2. Mol percentage of M^{2+} in the receiving phase and source phase after 24 and 48 hours at 25 °C[a]

	Cu^{2+}		Cd^{2+}		Pb^{2+}		Hg^{2+}	
Time (h)	R.P.	S.P.	R.P.	S.P.	R.P.	S.P.	R.P.	S.P.
24	78	19	53	37	2	92	14	28
48	89	8	72	19	4	90	15	26

[a] Conditions: 25 °C; source phase: 8 mL of 5×10^{-3} M MCl_2 in 0.15 M acetate buffer, pH 4.68; organic phase: 20 mL of 1×10^{-3} M TE14DT in dichloromethane; receiving phase: 8 mL of 0.1 M HCl.

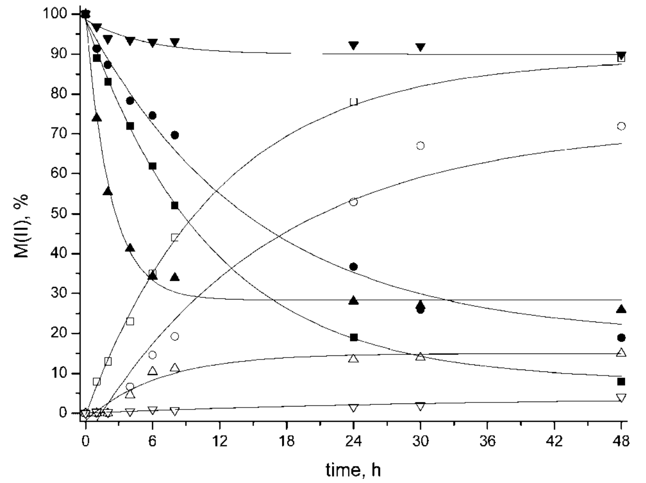


Figure 2. Mol percentage of M^{2+} vs. time in the source (filled symbols) and receiving (open symbols) phases for Cu^{2+} (■/□), Cd^{2+} (●/○), Pb^{2+} (▼/▽) and Hg^{2+} (▲/△) in single transport experiments; experimental conditions: source phase, 8 mL of 5×10^{-3} M MCl_2 in 0.15 M acetate buffer, pH 4.68; liquid membrane phase, 20 mL of 1×10^{-3} M TE14DT in dichloromethane; receiving phase, 8 mL of 0.1 M HCl; T = 25 °C

Despite the ability of TE14DT to complex all the metal ions from the source phase (see Table 1), the transport efficiency was very different both in uptake and in release processes and not related to the extraction percentages. Furthermore, the high efficiency of the carrier to transfer Cu^{2+} across the membrane was not verified for the other metal ions. Indeed, as regards Cd^{2+}, Figure 2 shows a moderate rise in metal ion concentration in the receiving phase and a corresponding decrease in the source phase; after 48 h, the percentage in the receiving phase was 72%, with very low amounts of metal ion in dichloromethane (9%). On the contrary, notwithstanding the ability of TE14DT to extract both Pb^{2+} and Hg^{2+} ions from the source phase (see Table 1), their concentrations in the receiving phase at the end of the process were very low, i.e. 5 and 15% respectively. Actually, the transport efficacy of a carrier depends not only on the complexation of the metal but also on its easy release into the receiving phase.

However, the measurements of metal ion concentrations in the source phases suggested a significant difference in the uptake of Pb^{2+} and Hg^{2+}. In fact, a slight decrease in Pb^{2+} concentration was observed, with 90% in the source phase after 48 h. On the contrary, the Hg^{2+} extraction curve was very sharp and after 6 h only 35% remained in the source phase; moreover, its percentage in the membrane was always more than 50%.

Therefore, as regards Pb^{2+}, the lack of transport could probably be due to the slow diffusion of the Pb-carrier complex through the membrane. On the other hand, TE14DT showed a high affinity for Hg^{2+}, even higher than for Cu^{2+}, although the metal-ion release in the stripping phase, which is lower than that observed during the diffusion process, could be prevented by the stability of the Hg-carrier complex in the organic phase.

A variation of transport efficiency with pH has been observed in other systems,[11,21] and it can be related to the fact that the process of transfer of metal ions from the membrane bulk to the receiving phase is controlled by several factors, including the rate of chemical reaction between the carrier-M^{2+} complex and the hydrogen ions of the stripping phase. The pH lowering should determine, at the membrane-receiving phase interface, a further protonation of the N atoms of the chelating region of the carrier, allowing the release of metal ions. Therefore, progressive addition of small amounts of concentrated HCl in the receiving phase was carried out after 48 h; despite the remarkable decrease of the pH of the receiving phase, the percentage of Hg^{2+} in the receiving phase did not rise significantly.

Both the comparison of diffusion and transport releasing data, and the lack of the effect of H_3O^+ addition in the stripping phase, allow us to conclude that the inefficacy of Hg^{2+} transport is essentially due to the high stability of the metal ion-carrier complex in the membrane.

Selectivity of Bulk Liquid Membrane System

Selectivity in the transport of metal ions has become increasingly important, and competitive experiments are necessary to verify transport selectivity. Therefore simultaneous transports were performed using the same conditions as for the single-ion transport, with a buffered mixture of two ions as the source phase. The total metal ion concentration was 5×10^{-3} M, so that each ion was present in half the concentration of the corresponding single-ion transport.

Taking into account the high affinity of TE14DT for Hg^{2+}, observed in both extraction and single-ion transport experiments, tests of simultaneous partition of Hg^{2+} with Cu^{2+}, Cd^{2+} and Pb^{2+} were performed. The presence of Hg^{2+} in the mixture, in fact, could diminish the amount of carrier available for the transport of the competitive metal ion, because it remains in the membrane as the Hg^{2+}-carrier complex. Actually, the Hg^{2+} amounts partitioned in the membrane increased, with the mol ratio of Hg^{2+}/M^{2+} in the organic phase being about double that of the values determined in the single ion tests.

Table 3. Mol percentages of metal ions transported by TE14DT in competitive experiments[a]

Metals	Time (h)	Receiving phase		Source phase	
Cd^{2+}/Pb^{2+}		Cd^{2+}	Pb^{2+}	Cd^{2+}	Pb^{2+}
	8	27 (19)	<1 (1)	68 (70)	96 (93)
	24	54 (53)	2 (2)	40 (37)	95 (92)
	48	74 (72)	5 (4)	21 (19)	83 (90)
		Cu^{2+}	Pb^{2+}	Cu^{2+}	Pb^{2+}
Cu^{2+}/Pb^{2+}	8	32 (42)	<1 (1)	50 (55)	97 (93)
	24	67 (78)	1 (2)	26 (19)	96 (92)
	48	88 (89)	4 (4)	11 (8)	91 (90)
		Cd^{2+}	Cu^{2+}	Cd^{2+}	Cu^{2+}
Cd^{2+}/Cu^{2+}	8	34 (19)	31 (42)	64 (70)	48 (55)
	24	53 (53)	72 (78)	39 (37)	28 (19)
	48	76 (72)	85 (89)	21 (20)	13 (8)

[a] Conditions: 25 °C; source phase, 8 mL of 5×10^{-3} M MCl_2 (total metal ion concentration) in 0.15 M acetate buffer, pH 4.68; organic phase, 20 mL of 1×10^{-3} M TE14DT in dichloromethane; receiving phase, 8 mL of 0.1 M HCl; values in parentheses are relative to transport of each ion in single ion experiments.

The selectivity of TE14DT for Cu^{2+}, Cd^{2+} and Pb^{2+} using equimolar binary mixtures of the metal ions was then evaluated (Table 3). The presence of Pb^{2+} ions in the source phase did not alter significantly the amount of Cu^{2+} and Cd^{2+} transported by the carrier, being nearly the same as that observed in the corresponding single-ion transport. On the other hand, Pb^{2+} ions were not transported in either case. This result highlights the ability of TE14DT to extract (and to release) Cu^{2+} or Cd^{2+} ions selectively from a mixture also containing Pb^{2+}.

Simultaneous transport of Cu^{2+} and Cd^{2+} shows that the carrier is not able to distinguish between them. Both metal ions were transported across the membrane without marked mutual influence, the amount of Cu^{2+} and Cd^{2+} ions in the source and receiving phases being almost the same as that observed in the corresponding single-ion transports.

Conclusion

Liquid-membrane chemistry is a complex process involving the interplay of several parameters, and the capability of a carrier to complex a metal ion is not enough for an efficient transport. The stability of a metal ion-carrier complex in the membrane, its slow diffusion through the organic phase or the lack of metal ion release into the receiving phase, can negatively influence the carrier-mediated transport of metal ions across liquid membranes.

TE14DT, a structurally simple lipophilic polyamine, could be successfully used for the selective transport of Cu^{2+} or Cd^{2+}, also in the presence of Pb^{2+} ions in the source phase. On the other hand, the experimental conditions previously optimised for the transport of Cu^{2+} are inadequate for Pb^{2+} and Hg^{2+} ions. Their transport could be performed by changing external system features, such as the nature of the organic solvent, the pH gradient between the two aqueous phases, or the presence of a specific chelating agent in the stripping phase. Subtle modifications in the structure of the carrier are also in progress in order to obtain more efficient and selective transports.

Experimental Section

Transport Experiments: Experiments were made using the thermostatted (25 °C) bulk liquid-membrane cell[19] shown in Figure 3. The cylindrical membrane cell was 3 cm inner diameter and 12 cm in height. It was divided into two equal compartments by a glass partition that runs vertically from the opening to within 1.2 cm of the flat bottom plate. The cell was filled with the three phases: an aqueous source phase (8 mL, 5×10^{-3} M MCl_2 in 0.15 M sodium acetate buffer at pH 4.68), a dichloromethane layer (20 mL of 1×10^{-3} M carrier) and a receiving phase (8 mL, 0.1 M HCl). Doubly distilled deionised water was used for preparing the solutions. The membrane was slowly stirred (250 rpm) by a Teflon™-coated magnetic bar. Under these conditions, the interfaces between the organic membrane and the two aqueous phases remained flat and

Table 4. Conditions for formation and detection of metal-dithizone complexes in dichloromethane[a]

Metal ion	Surfactant	pH[b]	λ_{max} (nm)	ε ($M^{-1}\cdot cm^{-1}$)	R^2
Cu^{2+}	SB3−14 5×10^{-2} M	1	514	26200	0.9996
Hg^{2+}	SB3−14 5×10^{-2} M	1	498	45300	0.9998
Cd^{2+}	SDS 5×10^{-3} M	13	418	10400	0.9993
Pb^{2+}	SDS 5×10^{-3} M	11	548	7500	0.9991

[a] [Dithizone] = 1.5×10^{-4} M. [b] pH for addition of HCl or NaOH.

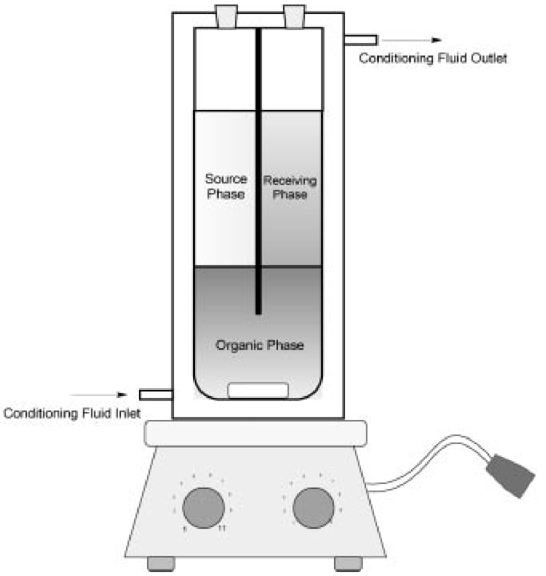


Figure 3. Representation of the device used for the transport experiments

were well defined. The metal ion concentrations in both aqueous phases were monitored as a function of time.

Partition Experiments: Dichloromethane "uptake" experiments were carried out by vigorous shaking of the source phase (3 mL, 5×10^{-3} M MCl_2 in sodium acetate buffer 0.15 M, pH 4.68) with the organic solvent (3 mL, 1×10^{-3} M carrier) for a few minutes. The organic layer was then slowly stirred (250 rpm at 25 °C) and the mixture was left to stand until complete phase separation had occurred (12−18 h). The concentrations were then measured by the method described below.

Metal Ion Analysis: A simple spectrophotometric method for the determination of the metal ion concentration in both aqueous phases has been developed, and measurements were made using a diode array Hewlett−Packard 8452A spectrophotometer.

An organic colourimetric reagent [diphenylthiocarbazone (dithizone)], which combines with metal ions and forms non polar coloured complexes, was used.[22] Both dithizone and its complexes are soluble in organic solvents, such as alcohols, hydrocarbons and chlorinated hydrocarbons, and in alkaline aqueous media, but they are insoluble in water at neutral and acidic pHs. In order to avoid the use of toxic organic solvents, surfactants can be successfully used to enhance the solubility of organic compounds in water. Surfactants possess both lipophilic and hydrophilic moieties and, above a certain concentration, the critical micelle concentration (cmc), form micelles, roughly spherical aggregates with a hydrocarbon core and a polar surface. Micellar solutions are optically transparent and macroscopically homogeneous and their apolar interior can solubilize dithizone and metal-dithizone complexes.

This technique has already been reported in the literature[23] and here the surfactant Triton X-100, a non-ionic surfactant, was used; the pH of the aqueous solutions was adjusted to an optimal value for the formation of the complexes, and metal-ion concentrations were then determined. Under these conditions, however, the stability of the solution of dithizone in Triton X-100 is very low (about 60 min) and it should be freshly prepared before each analysis. We tested solutions of different surfactant at different concentrations and different pHs, in order to find the experimental conditions which allow stability for prolonged periods of time (1−2 days). Myristyldimethylammonium propanesulfonate (SB3−14) and sodium *n*-dodecyl sulfate (SDS) were selected for acidic and alkaline pHs, respectively, and Table 4 gives the best conditions for the formation of various metal dithizonates in surfactant solutions, along with their wavelengths of maximum absorbance and their molar extinction coefficients. This method is suitable for the analysis of individual metal ions, and it can be successfully used in single-ion transport experiments.

A graphite furnace atomic absorption spectrophotometer (Perkin−Elmer Model Zeeman 3030) was used for the measurements of metal ion concentrations in competitive experiments.

Each reported result is given as the arithmetic mean of three separate experiments; reproducibility was confirmed as ±5% or better.

Materials: Metal salts and diphenylthiocarbazone were obtained from Aldrich and used without further purification. The commercial grade surfactants sodium *n*-dodecyl sulfate (SDS) and myristyldimethylammonium propanesulfonate (SB3−14) were purchased from Fluka and purified by recrystallisation from ethanol and acetone/methanol, respectively. The synthesis of the carrier has been reported previously.[19] All other chemicals were of analytical grade, purchased from Carlo−Erba and used as received.

Acknowledgments

Support of this work by Ministero dell'Istruzione, Univesità e Ricerca, Rome (COFIN 2001) is gratefully acknowledged.

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Received October 3, 2003