Structurally Simple Lipophilic Polyamines as Carriers of Cupric Ions in Bulk Liquid Membranes

Lucia Brinchi,[a] Pietro Di Profio,[a] Raimondo Germani,[a] Gianfranco Savelli,*[a] and Nicoletta Spreti[b]

Keywords: Ammine complexes / Copper / Membranes / N ligands

The carrier-mediated transport of copper ions through bulk liquid membranes has been examined and the transport capability of novel lipophilic polyamines investigated. The effects of hydrophilic/lipophilic balance, the nature of the membrane and buffer, the pH of the receiving phase, the carrier, and the metal salt concentration on the transport efficiency were examined and optimal conditions for transport established. High transport efficiency – 98% of Cu^{II} in the receiving phase after 48 h – was provided by carrier **2b** (1×10^{-3} M in CH_2Cl_2) with propionate buffer (pH = 4.60) as source phase, containing 5×10^{-3} M Cu^{II}, and 0.1 M HCl as stripping phase. Single-metal ion transport experiments showed potential transport selectivity for cupric ions over other ions such as Zn^{II}, Ni^{II}, and Co^{II}.

Introduction

Carrier-mediated transport of ionic species is an area of growing investigation, and involves such different fields as the modeling of biological transport and the search for waste water treatments and metal ion recovery.[1−6] Research into effective and selective separation of metal ions, and in particular the widely investigated copper, is still a challenging task from both a practical and a theoretical point of view, and has resulted in the study of several membrane types as well as many carriers.

Of all membrane systems, the bulk liquid membrane (BLM) is the one most frequently used to perform screening and modeling studies of specific carrier-mediated systems.[1,2,6] Their efficiency, selectivity, and cost make them the optimum solution to a number of technological issues such as noble metal recovery[7] and the removal of toxic heavy metal ions from waste waters or from the environment.[8]

The transport and separating capabilities of bulk liquid membranes are related to the nature of the carrier, which determines the nature of the substrate, the physico-chemical features (rate and selectivity), and the type of process.

The design and synthesis of more efficient and selective carriers represent a challenging task in this field of chemistry. Macrocycle carriers such as crown ethers (aza-crown ethers) have been used to transport alkali metal[9,10] (heavy metal) ions.[11,12] Acyclic polyethers (podands)[13,14] may also exhibit strong metal ion complexing abilities and a large number of these kinds of systems have demonstrated good abilities to transport ions through organic membranes.

Surfactant aggregates such as micelles have also demonstrated carrier properties,[15,16] not only for undesirable metal ions, but also, for example, for dyes, organic pollutants, amino acids,[17] or urea (for clinical applications[18]). Several studies by Tondre have shown that more than one mechanism can operate, and that the problem of transport effectiveness and selectivity is therefore quite complex.[16]

Long-chain ligands have been studied by Menger,[19] who suggested the necessity of a proper balance of properties (especially of the hydrophobic/hydrophilic character) of the carrier molecule, such as in surfactant molecules, to provide optimal results in transport.

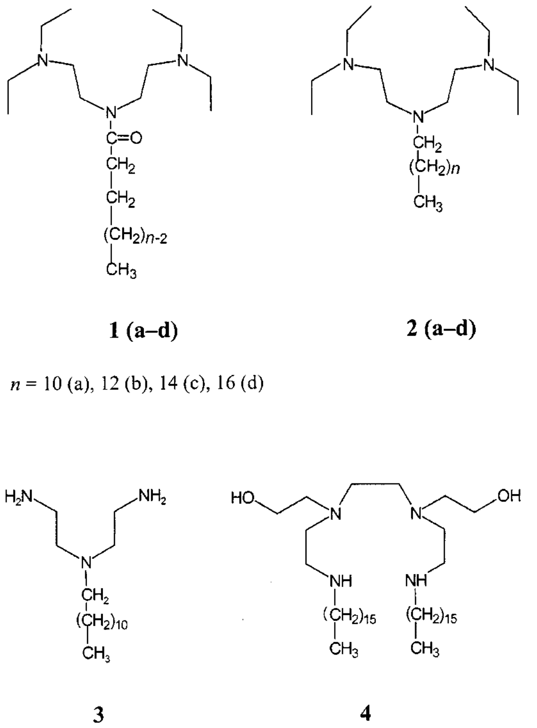
With these studies in mind, we were interested in finding an optimal carrier molecule, and optimal conditions for its efficacy and selectivity, for the transport of Cu^{II}. We used transport across BLMs for screening of several polyamines with a simple common backbone and slight modifications in their covalent structure, introduced by means of simple synthetic pathways, in order to examine how structural parameters may affect transport abilities. The carriers we synthesized, together with the best carrier found by Menger (which we prepared again and tested for comparison with our systems) are shown in Scheme 1.

An important modification relates to the variation of the functional group from amide (class **1**) to amine (class **2**), associated with, besides overall hydrophilicity and geometry, electron pair availability for coordination of metal ions, and hydrogen bonding ability of the molecule. The

---

[a] Dipartimento di Chimica, Università di Perugia,
Via Elce di Sotto 8, 06123 Perugia, Italy
Fax (internat.) + 39-075/585-5538
E-mail: savelli@unipg.it
[b] Dipartimento di Chimica, Ingegneria Chimica e Materiali, Università di L'Aquila,
Via Vetoio Coppito, 67100 L'Aquila, Italy

1434−193X/02/0305−0930 $ 17.50+.50/0



Scheme 1

hydrophobic/hydrophilic balance was also modulated by changes to the alkyl chain length (*n* = 10, 12, 14, 16, in molecule classes **1** and **2**), and changes from ethyl to H in the polyamine region (from molecule **2** to **3**).

The transport capability of these carriers was evaluated as a function of the following factors besides the covalent structure of the carrier: the pH of the receiving phase, the carrier concentration, the metal salt anion, the nature of the membrane, and the nature of the buffer.

Results and Discussion

Transport experiments were performed with a liquid membrane apparatus as shown in Figure 1. Cu^{II} was placed in an aqueous source phase buffered at pH = 4.60. The carriers were dissolved in a stirred organic "membrane". The Cu^{II} complex released its metal ion into the receiving phase at a lower pH, the process being driven by the pH difference. Although most liquid-membrane studies focussing on transport capability have monitored ion concentrations only in the receiving phase, we monitored the Cu^{II} concentrations in both aqueous compartments and, moreover, as function of time; this allowed us to obtain important mechanistic information and to make proper comparisons − also in terms of relative transport speeds − between different carriers. Furthermore, in order to obtain insight into the reasons for the different transport capabilities of various carriers, or of the same carrier under various conditions, experiments were often carried out to evaluate how effectively a carrier promoted Cu^{II} extraction from the source phase into the organic phase, in the absence of receiving phase ("dichloromethane uptake"). Various parameters were screened, and the results are presented below.

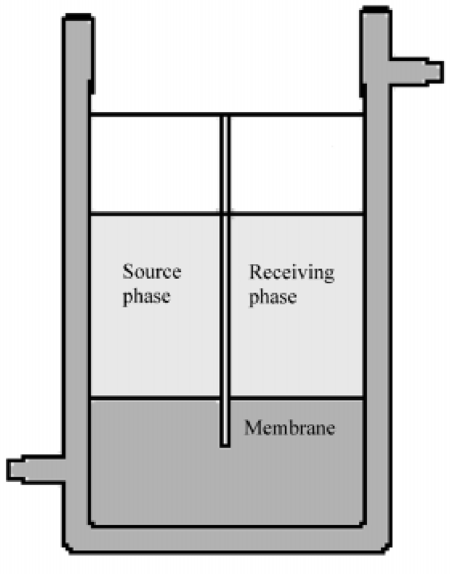


Figure 1. Representation of the bulk liquid membrane cell used

The Nature of the Carrier

With no carrier, but in the presence of 1,1,7,7-tetraethyldiethylenetriamine, no detectable transport of metal ions from the source phase to the receiving phase was observed: a carrier of relatively lipophilic nature is therefore necessary.

The ability of the ligands shown in Scheme 1 to transport Cu^{II} across organic membranes was tested. In these experiments, the concentrations of the carrier in the membrane (dichloromethane) and of the metal ion in the buffered source phase (0.15 м, pH = 4.6) were 1×10^{-3} м and 5×10^{-3} м, respectively; hydrochloric acid (0.1 м) was used as the receiving phase. Table 1 lists the percentage of Cu^{II} transported from the source phase to the receiving phase after 24 and 48 h as a function of carrier structure. The data clearly indicate the critical influence of the nature of the carrier: the ligand set **1** appears unable to transport Cu^{II} ions to the receiving phase. This could be due to inability of the carrier to extract ions from the source phase into dichloromethane or, alternatively, to a problem in the release of ions into the receiving phase. Determinations of partitioning of cupric ions between the dichloromethane and the source phases showed that they remained almost completely (98%) in the source phase, indicating a problem in their water-to-dichloromethane extraction capability.

The carriers **2**, in contrast, were excellent carriers for the transport of cupric ions through the liquid membrane, with only ca. 10% of Cu^{II} remaining in the source phase (Table 1). Partition experiments showed that the organic phase "uptake" of Cu^{II} was ca. 9%, and so not high, but enough to give efficient transport thanks to the "in continuum" nature of the process. A change from an amido to an amine group significantly changed the carrier ability. In particular, the central nitrogen atom in the amido group

Table 1. Mol percentage of Cu^{II} transported through dichloromethane membrane at 25.0° C

Carrier[a]	mol-% Cu^{II} transported (receiving phase) 24 h	48 h	mol-% Cu^{II} remaining (source phase) 24 h	48 h
1b	2	4	96	95
1c	2	4	96	95
1d	3	5	95	94
2a	56	82	40	16
2b	78	89	19	8
2c	76	89	19	10
2d	79	91	18	8
3	33	42	66	58
4	67	90	28	10

[a] Conditions: source phase, 8.0 mL of 5.0×10^{-3} M $CuCl_2$ in acetate buffer (pH = 4.60); receiving phase, 8.0 mL of 0.1 M HCl; membrane phase, 20.0 mL of 1.0×10^{-3} M carrier.

displayed a weakened ability to extract Cu^{II} from dichloromethane, probably due both to geometrical constraints and to decreased nitrogen electron availability. It is therefore not only the hydrophobic/hydrophilic balance that has a key role, but also all the factors involved in complex formation with the metal ion.

The transport capabilities of the carriers in set **2** seem to be dependent on alkyl chain length; a significant improvement in efficiency was observed as the number of methylene groups went from 12 to 14, but then no further improvements with increasing chain length were observed.

Concentration/time profiles of Cu^{II} transport were also studied. Figure 2 shows a rapid rise in metal ion concentration in the receiving phase (and a sharp decrease in Cu^{II} in the source phase corresponding to it, not shown in Figure 2) after short intervals, after which concentrations tended to reach a limiting value and level off. Plots of mM Cu^{II} in the receiving phase vs. time are linear in the first part, which gives an indication of the transport speed. As regards carriers in set **2**, the transport speed was significantly dependent on the alkyl chain length, and increased as the number of methylene groups went from 12 to 14, but then further increases of hydrophobicity did not affect transport speed, as had also been the case for the transport efficiency.

N-Tetradecylethylenetriamine, carrier **3**, is very similar to the previous carrier, but its chelating region has a character more hydrophilic (primary amino groups) than in carrier set **2** (tertiary amino groups). The initial transport speed did not change with respect to carrier **2b**, but the subsequent speed was reduced (Figure 2), as was the overall transport capability of the carrier **3**, with respect to **2b** (Table 1). This demonstrates the importance of a proper balance of hydrophilic and hydrophobic properties in the carrier and can be explained in terms of a small capability of the Cu^{II}−carrier complex for back diffusion in the membrane phase.

N,*N′*-Bis(hydroxyethyl)-*N*,*N′*-bis[2-(hexadecylamino)-ethyl]ethylenediamine (**4**) (Scheme 1) is well known as Menger's carrier. It was also tested under our experimental conditions, and the results are shown in Table 1 and Figure 2. Menger found that carrier **4** was an excellent carrier and that 80% of the Cu^{II} was transferred to the receiving phase through a chloroform membrane after only 10 h[19] with an efficiency much higher than that provided by the industrial extractant LIX-63. In our experiment in dichloromethane it remained a good carrier; as can be seen from Table 1, the amount of Cu^{II} transported by our carrier **2b** was similar to that transported by carrier **4**.

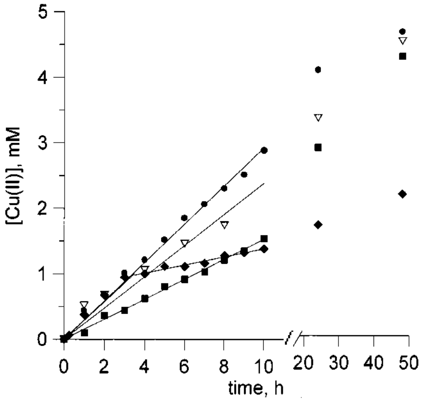


Figure 2. Concentrations of Cu^{II} vs. time in the receiving phase for carriers **2a** (■), **2b** (●), **3** (◆), and **4** (▽); lines are only intended to help the eyes in following the points; experimental conditions: source phase: 8 mL of $CuCl_2$ (5 mM) at pH = 4.6 for acetate buffer; liquid membrane phase: 20 mL of carrier (1 mM) in CH_2Cl_2; receiving phase: 8 mL of HCl (0.1 M); T = 25.0 °C

Carrier **2b** was found to be the most effective, and was selected for further experiments intended to improve its transport ability.

Effect of the pH of the Receiving Phase

Transport by this set of carriers was pH-driven, and took place when a pH gradient was applied between the two aqueous phases.[3] Transfer of Cu^{II} into the receiving phase is accompanied by a carrier-mediated "reverse flow" of protons from the receiving phase to the source phase; indeed, a decrease of the pH of the latter was observed. As already outlined, most experiments were carried out with a source phase at pH = 4.6 and a receiving phase at pH = 1: these values were selected, as in Menger's investigations, for their similarity to large-scale operations. Variation of the pH of the receiving phase was examined for carrier **2b**, in the range from 0.30 to 4.60. Figure 3 shows the profiles of the percentage of Cu^{II} transported across the dichloromethane membrane after 10 h, 24 h, and 48 h as a function of the pH of the stripping phase, and Figure 4 shows the variation of Cu^{II} concentration with time in the receiving phase at different pH values. The results indicate an optimum pH value of ca. 0.9, at which the transport rate is 2.5 times faster than at pH = 2.0. This kind of variation of transport efficiency with pH (the presence of a maximum) has been observed in other systems,[13,19] and can be related to the fact that the process of transfer of cupric ions from the membrane bulk to the receiving phase is governed not only by diffusion but also by the rate of chemical reaction between the Cu^{II}-carrier complex and the hydrogen ions of the stripping phase.

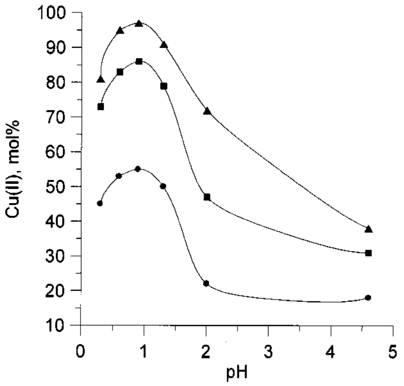


Figure 3. Mol percentage of Cu^{II} in the receiving phase vs. pH of receiving phase for carrier **2b** after 10 (●), 24 (■), and 48 (▲) h; lines are only intended to help the eyes in following the points; experimental conditions: source phase: 8 mL of $CuCl_2$ (5 mM) at pH = 4.6 for acetate buffer; liquid membrane phase: 20 mL of carrier (1 mM) in CH_2Cl_2; receiving phase: 8 mL of HCl at various concentrations; T = 25.0 °C

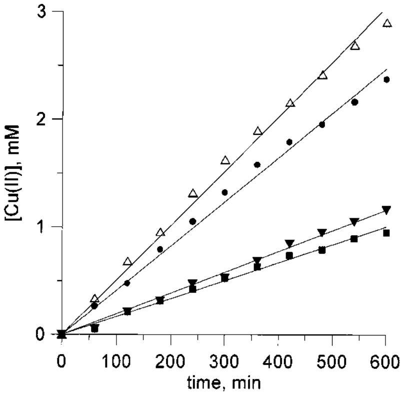


Figure 4. Mol percentage of Cu^{II} in the receiving phase vs. time at different pH values, 0.3 (●), 0.9 (Δ), 2 (▼), and 4.6 (■) of the receiving phase for carrier **2b**; lines are only intended to help the eyes in following the points; experimental conditions as for Figure 2

The Concentration of the Carrier

The concentration of the carrier **2b** in the dichloromethane membrane was varied from 1×10^{-3} M to 0.1 M and the results are shown in Figure 5. As can be seen, when the carrier concentration was increased, the percentage of Cu^{II} transported into the receiving phase decreased. It is very important to note that speed and efficiency of the decrease in concentration in the source phase do not correspond to the speed and efficiency of the increase in concentration in the receiving phase. In particular, at a carrier concentration of 0.1 M, the cupric ions are extracted very rapidly from the source phase into the membrane phase but their release from the Cu^{II}−ligand complex in the stripping phase is strongly impeded by the high concentration of protonated carrier in this phase (Figure 5, D). We may therefore legitimately speak about a "saturation" effect due to the high concentration of the carrier.

The Nature of the Organic Phase

The effect of the nature of the organic phase was also investigated, with tetrachloromethane, chloroform, and chlorobenzene being screened as organic membranes for carrier **2b**. With carbon tetrachloride and chlorobenzene membranes, no detectable transport of Cu^{II} ions from the source phase to the receiving phase was observed, and partitioning experiments indicated that no extraction of Cu^{II} from the source phase into membrane was operative. This effect can be explained by considering the low polarities of these two solvents, as compared to those of dichloromethane and chloroform. The carrier was able to transport the metal ions through dichloromethane and chloroform, and Figure 6 reports the percentage of Cu^{II} in the source phase and the receiving phase as a function of time in the presence of carrier **2b**. The dichloromethane membrane appeared to provide the better results, since after 48 h 90% of the Cu^{II} had been transferred to the receiving phase, compared to 72% with the chloroform membrane. A rationale for this was provided by our extraction experiments showing that dichloromethane took up the Cu^{II} ion better than chloroform did (9% vs. 3%).

The Nature of the Metal Salt

The rate of cation transport through liquid membranes by macrocyclic ligands,[23] Schiff bases,[24] and surfactants[25] has been shown to be influenced by the nature of the anion accompanying the cation−ligand complex. Different cupric salts were therefore deployed (chloride, bromide, acetate, sulfate, nitrate), but no difference in transport efficiency was observed. The nature of the accompanying anion probably did not influence the transport process because of the higher acetate concentration (with respect to metal salt) in the source phase, acetate anion thus effectively being the accompanying anion of Cu^{II} in all the experiments.

Selectivity in Cu^{II} Transport

Selectivity in the transport of metal ions has become increasingly of interest,[1−6] and only a few carriers are both efficient and selective.[26,27] In particular, the different methods for the specific transport of Cu^{II} ions across a liquid membrane have the drawbacks of slow rates of transport or lack of high selectivity.[28] The transport capabilities of carriers **2b** and **3** towards Zn^{II}, Ni^{II}, and Co^{II} ions were studied, and the results of single-ion transport experiments are shown in Table 2. None of these metal ions was transported by the carrier **2b**, which was therefore both efficient and selective. On the other hand, carrier **3** showed similar behavior towards Ni^{II} and Cu^{II}, when the percentage of the metal ion in the receiving phase was lower than 50%: this carrier can therefore selectively transport Cu^{II} over Zn^{II} and Co^{II}, or selectively transport Ni^{II} over Zn^{II} and Co^{II}. These

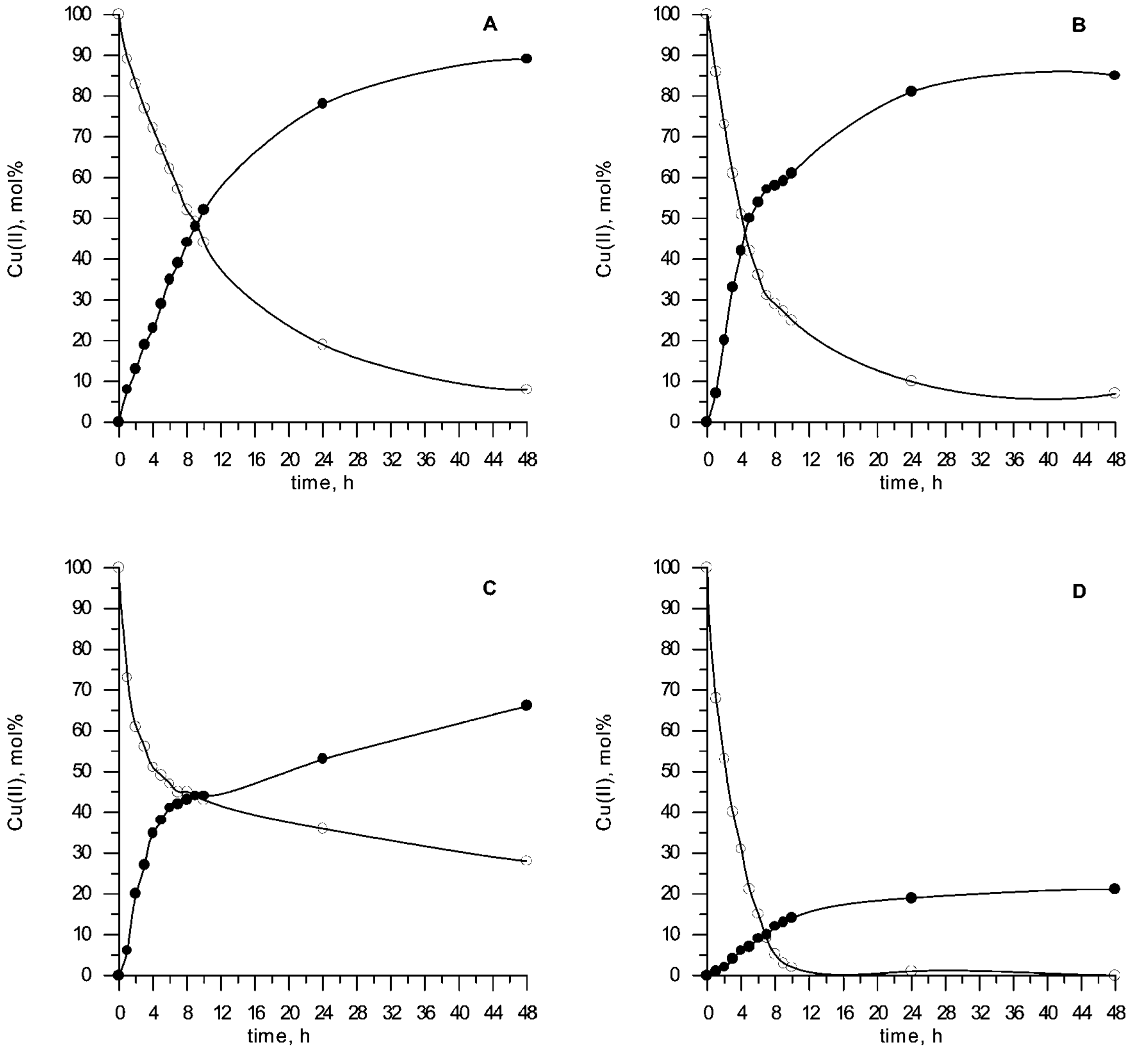


Figure 5. Mol percentage of Cu^{II} in the receiving (●) and source (O) phases at various concentrations of carrier **2b** in the membrane phase: 1 (A), 3 (B), 10 (C), and 100 (D) mM; lines are only intended to help the eyes in following the points; experimental conditions: source phase: 8 mL of $CuCl_2$ (5 mM) at pH = 4.6 for acetate buffer; liquid membrane phase: 20 mL of carrier at specified concentrations in CH_2Cl_2; receiving phase: 8 mL of HCl (0.1 M); T = 25.0 °C

results are only preliminary in any case, because competitive experiments would be necessary for proper discussion of transport selectivity.

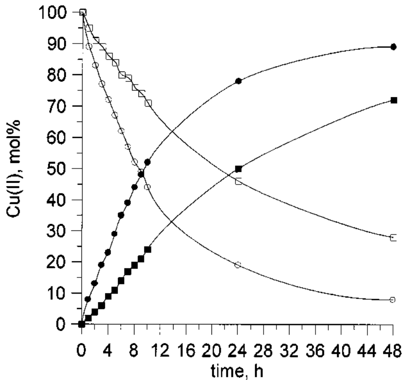


Figure 6. Percentage of Cu^{II} vs. time in the receiving (filled symbol) and source (open symbol) phases with carrier **2b** (1 mM) and different liquid membrane: dichloromethane (●, O) and chloroform (□, ■); lines are only intended to help the eyes in following the points

Table 2. Mol percentage of M^{II} transported through dichloromethane membrane after 48 h at 25.0° C

Carrier	% M^{II} transported into the receiving phase[a]			
	Cu^{II} [b]	Zn^{II} [b]	Ni^{II} [c]	Co^{II} [c]
2b	89	4	< 1	< 1
3	42	–	42	< 1

[a] Conditions: source phase, 8.0 mL of 5.0×10^{-3} M MCl_2 in acetate buffer; receiving phase, 8.0 mL of 0.1 M HCl; membrane phase, 20.0 mL of 1.0×10^{-3} M carrier. [b] pH of the source phase = 4.60. [c] pH of the source phase = 6.00.

The Nature of the Buffer

As reported above, we did not observe any effect of the nature of the metal salt, as Lamb[23] and others[24,25] did with different carriers, mostly because the accompanying anion seemed to be that provided by the more concentrate buffer (0.15 M), and not that provided by the Cu^{II} salt (5 mM). Transport experiments with different buffered solutions at the same pH (4.6) as the source phase were therefore carried out. Sodium acetate, sodium propionate, and potassium phthalate buffers were chosen: acetate and propionate have the same organic chemical group but different hydrophobicities, whereas phthalate is a bifunctional molecule that might complex Cu^{II} differently. The results given in Table 3 clearly indicated that the carrier was unable to transport cupric ions in the presence of phthalate buffer, while there was a small but significant difference when propionate was used instead of acetate.

Table 3. Mol percentage of Cu^{II} transported through dichloromethane membrane by carrier **2b** in different buffered source phases at 25.0° C

Buffer	mol% Cu^{II} transported into receiving phase[a]		
	10 h	24 h	48 h
Acetate	52	78	89
Propionate	69	85	95
Phthalate	1	2	2

[a] Conditions: source phase, 8.0 mL of 5.0×10^{-3} M $CuCl_2$ in buffer (pH = 4.60); receiving phase, 8.0 mL of 0.1 M HCl; membrane phase, 20.0 mL of 1.0×10^{-3} M carrier **2b**.

Partitioning equilibria showed that no extraction of Cu^{II} from the phthalate-buffered source phase into the membrane took place. We can ascribe that to the formation of Cu^{II} phthalate complex, consistently with the experimental observation of quite different colors in the Cu^{II} solutions when the buffer was phthalate (light blue) from when it was acetate or propionate (very light blue). This may explain why the carrier was not able to transport Cu^{II} into the membrane.

The difference between acetate and propionate may be ascribed to the nature of the accompanying anion, the more hydrophobic being the more effective, consistently with data of Lamb et al.[23] showing a correspondence between the transport of a cation and the free energy of hydration of the accompanying anion.

Conclusions

We have synthesized new carriers and characterized optimal experimental conditions for coupled transport of cupric ions. Carriers were prepared by facile synthetic procedures, several parameters in the covalent structures of the carriers were introduced, and their effects upon transport properties were investigated. These transport experiments demonstrated the ability of the carrier **2b** to transfer Cu^{II} across a liquid membrane, and also a potential selectivity for Cu^{II} over Ni^{II}, Co^{II}, and Zn^{II}. External factors influencing transport efficiency were examined and optimal conditions were found, with carrier **2b** showing a high capability to transfer Cu^{II} across a bulk liquid membrane, superior to that of commercially available chelating agents of the LIX series. The mol percentage of Cu^{II} ions remaining in the membrane phase was very low (< 5%).

Several parameters played important and interconnected roles, and the prediction of structural features that could improve transport activity and selectivity of the carriers is still a hard task. Our results clearly indicate that attention must be paid to the HLB of the molecules, but further investigations involving the synthesis of several carriers with subtle variations in covalent structure are necessary. Our polyamine carriers had a simple backbone and other subtle modifications in their covalent structures (simple to achieve by the synthetic routes used here) aimed at improving transport may be imagined, such as further lengthening of the alkyl group in the polar amine or its functionalization.

Experimental Section

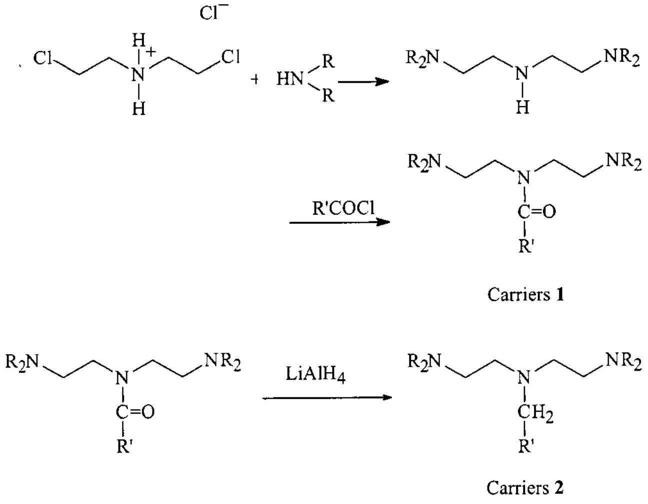
Liquid Membrane: Experiments were performed with a thermostatted (25.0 ± 0.1 °C) bulk liquid membrane cell[19] as shown in Figure 1. Under standard conditions the aqueous source phase (8 mL) contained Cu^{++} (5×10^{-3} M) in sodium acetate buffer (0.15 M) at pH = 4.60 and the receiving phase (8 mL) contained HCl (0.1 M). Doubly distilled deionized water was used for preparing solutions. The organic layer (20 mL), containing 1×10^{-3} M carrier, was slowly stirred (150 rpm) with a Teflon-coated magnetic bar. Under these conditions, the interfaces between the organic membrane and the two aqueous phases remained flat and were well defined.

Dichloromethane "Uptake": Dichloromethane "uptake" experiments were carried out under the same experimental conditions as used for transport. After the source phase (3 mL of 5 mM $CuCl_2$) had been vigorously shaken with the organic solvent containing 3 mL of 1 mM carrier, complete phase separation was awaited (24 h). Concentrations were then measured by the spectrophotometric method reported below.

Metal Ion Analysis: The metal ion concentrations in both aqueous phases were monitored as a function of time by a colorimetric method, by using a methanolic stock solution of sodium *N*,*N*-diethyldithiocarbamate, as described by Menger for Cu^{II},[19] and also for other cations such as Ni^{II}, Co^{II}, and Zn^{II} by Sandell.[20] Absorbance data were converted into concentration by using a linear standard curve, experimentally determined under the same experimental conditions, and with a correlation coefficient better than 0.999. Each reported result is given as the arithmetic mean of three separate experiments; reproducibly was confirmed as ± 5% or better. In this study, most of the transport data are discussed in terms of mol % Cu^{II} transported across the membrane phase.

Materials: Solvents and metal ion salts were of analytical grade, purchased from Carlo Erba, and used as received. The following were purchased from Aldrich and used as received: sodium diethyldithiocarbamate, diethylamine, bis(chloroethyl)amine hydrochloride, diethylenetriamine, and various alkanoyl chlorides. The phthalic anhydride was 99.5% from BDH. ^1H NMR spectra were recorded with a Bruker instrument at 200 MHz; chemical shifts (δ) are referred to $(CH_3)_4Si$ internal standard. 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. Colorimetric measures were made with a double-beam Kontron Uvikon 923 spectrophotometer.

Carriers: The synthesis of carriers **1** and **2** was carried out as in Scheme 2. The simplicity of the synthetic scheme, and its flexibility, should be outlined in consideration of scaling-up for industrial application of the systems, and also in view of possible other variations in the covalent structure of the carriers, which can be simply introduced by the same synthetic procedure. Carriers **1** were prepared by treatment of 1,1,7,7-tetraethyldiethylenetriamine with suitable alkanoyl chlorides in diethyl ether. Carriers **2** were obtained from **1** by reduction with $LiAlH_4$ in anhydrous THF. The substituted diethylenetriamine was prepared according to a literature procedure,[21] by treating bis(chloroethyl)amine hydrochloride with diethylamine in refluxing water for 6 h. After workup of the reaction mixture, the crude material was purified by vacuum distillation at 120 °C (10 mm). The distillation gave a colorless oil in 34% yield (GLC 99%). ^1H NMR ($CDCl_3$): δ = 1.05 (t, 12 H, 4 CH_3), 2.45−2.60 (m, 12 H, 6 CH_2), 2.65−2.75 (m, 4 H, 2 CH_2).



Scheme 2. Synthetic pathways for carriers **1** and **2**: R = Et, R′ = $CH_3(CH)_{n-1}CH_2-$, with n = 10, 12, 14, 16

General Procedure for the Synthesis of Amino-amide Compounds (Carriers 1a-d): 1,1,7,7-Tetraethyldiethylenetriamine (21.5 g, 0.1 mol) was dissolved in anhydrous diethyl ether in a 250 mL two-necked, round-bottomed flask, equipped with a magnetic stirring bar, a constant-pressure dropping funnel, and a nitrogen inlet adapter. To this solution, stirred at room temperature, the alkanoyl chloride (0.11 mol) was added dropwise over ca. 30 min; a precipitate rapidly formed. The reaction mixture was stirred overnight at ambient temperature. The white solid was collected by filtration through a Büchner funnel, and washed with ether to remove traces of reactants. The hydrochloride thus obtained was dissolved in a separating funnel containing a 10% solution of NaOH, and the free amino-amide was extracted three times with diethyl ether. The organic solution, after drying with Na_2SO_4, was concentrated in a rotary evaporator. Yields of the pale yellow oils were, respectively, 71% for **1a**, 75% for **1b**, 81% for **1c**, and 79% for **1d**. The purity by glc was 98%. ^1H NMR ($CDCl_3$): δ = 0.90 (t, 3 H, CH_3), 1.03 (t, 12 H, 4 CH_3), 1.25 [br. s, 2 (n − 2) H, (n − 2) CH_2], 1.63 (m, 2 H, CH_2), 2.31 (t, 2 H, CH_2), 2.53 (m, 12 H, 6 CH_2), 3.38 (m, 4 H, 2 CH_2).

General Procedure for the Synthesis of Amino-amine Compounds (Carriers 2a-d): The appropriate amino-amide (0.05 mol) was dissolved in anhydrous THF (100 mL) in an oven-dried, 250-mL, two-necked flask, equipped with a reflux condenser, a constant-pressure dropping funnel, and a magnetic stirring bar. A solution of $LiAlH_4$ in THF (1 M, 60 mL) was added dropwise over ca. 15 min to this solution, stirred at 0 °C in an ice bath. The resulting mixture was refluxed overnight under N_2. After the reflux period, the mixture was quenched with 10% NaOH solution at 0 °C to destroy the unreacted $LiAlH_4$. The white solid was filtered and washed several times with ether. The resulting mixture was concentrated in a rotary evaporator and the residue was extracted four times with diethyl ether. Standard workup gave the crude amino-amines. The crude products were purified by column chromatography on silica gel with diethyl ether as eluent to give the pure materials as pale yellow oils. Yields were, respectively, 83% for **2a**, 86% for **2b**, 76% for **2c**, and 80% for **2d**. They were stored at 0 °C in the dark in a refrigerator. ^1H NMR ($CDCl_3$): δ = 0.90 (t, 3 H, CH_3), 1.05 (t, 12 H, 4 CH_3), 1.25 (br. s, $2n$ H, n CH_2), 2.50 (m, 18 H, 9 CH_2).

4-Tetradecyldiethylenetriamine Carrier 3: This carrier was prepared by treatment of bis(2-phthalimidoethyl)amine with tetradecyl bromide in refluxing CH_3CN; the protected derivative was then treated with hydrazine hydrate in refluxing absolute ethanol to give the product. The bis(2-phthalimidoethyl)amine was prepared according to a literature procedure.[22] White solid, m.p. 180−181 °C (80% yield); the ^1H NMR and IR data agreed with those in the literature.

***N*,*N*-Bis(2-phthalimidoethyl)tetradecylamine:** Bis(2-phthalimidoethyl)amine (10 g), tetradecyl bromide (8.5 g), KI (0.5 g), and K_2CO_3 (anhydrous, 10 g) were placed in a 1000-mL, round-bottomed flask, equipped with a reflux condenser, and refluxed in CH_3CN (600 mL) for 36 h. After cooling to room temperature, the solid was filtered, and the acetonitrile was evaporated under reduced pressure. The residue was treated with water, and then extracted several times with diethyl ether. After the usual workup, a viscous liquid that solidified at 0 °C was obtained. The product was obtained in 68% yield as a white solid after two recrystallizations from methanol, m.p. 62−63 °C. ^1H NMR ($CDCl_3$): δ = 0.90 (t, 3 H, CH_3), 1.03−1.36 (m, 24 H, 12 CH_2), 2.5 (t, 2 H, CH_2), 2.80 (t, 4 H, 2 CH_2), 3.75 (t, 4 H, 2 CH_2), 7.64−7.81 (m, 8 H, 2 Ph).

4-Tetradecyldiethylenetriamine: *N*,*N*-Bis(2-phthalimidoethyl)tetradecylamine (4 g), hydrazine monohydrate (1 mL), and absolute ethanol (50 mL) were placed in a 100-mL, round-bottomed flask equipped with a reflux condenser. The reaction mixture was heated to reflux for 1 d. After the mixture had cooled to room temperature, the ethanol and hydrazine were removed under reduced pressure. The residue was treated with ethanol (20 mL) and conc. HCl (10 mL) and was heated to reflux for 8 h. The mixture was cooled to 3−5 °C, the precipitate was filtered, and the filtrate was concentrated to a few mL. The remaining material was treated with KOH (3 g), to generate the free base, and extracted four times with dichloromethane. After standard workup, a pale yellow syrup was obtained; this crystallized from petroleum ether as a white solid with m.p. ca. 30 °C (yield 94%). ^1H NMR ($CDCl_3$): δ = 0.90 (t, 3 H, CH_3), 1.18−1.50 (m, 24 H, 12 CH_2), 1.90 (br. s, 4 H, 2 NH_2, D_2O exchanges), 2.41 (t, 4 H, 2 CH_2), 2.49 (t, 4 H, 2 CH_2), 2.75 (t, 4 H, 2 CH_2).

Carrier 4: This carrier, Menger's one, was prepared by his procedure.[19] The IR and ^1H NMR spectra confirmed the structure.

---

[1] R. D. Noble, J. D. Way, in *Liquid Membranes: Theory and Applications*, American Chemical Society, Washington D. C., **1987**.

[2] R. M. Izatt, J. S. Bradshaw, J. D. Lamb, R. L. Brueing, in *Liquid membranes: Chemical Applications* (Eds.: T. Araki, H. Tsukube), CRC Press, Boca Raton, **1990**.

[3] J. M. Lehn, in *Supramolecular Chemistry. Concepts and Perspectives*, VCH, Weinheim, **1995**.

[4] P. R. Danesi, *Sep. Sci. Technol.* **1984**, *19*, 857−894.

[5] E. S. Matulevicius, N. N. Li, *Sep. Purif. Methods* **1973**, *4*, 73−96.

[6] H. C. Visser, D. N. Reinboudt, F. de Jong, *Chem. Soc. Rev.* **1994**, 75−81.

[7] J. W. Frankenfeld, R. P Cahn, N. N. Li, *Sep. Sci. Technol.* **1981**, *16*, 385−402.

[8] T. Kitagawa, Y. Nishikawa, J. W. Frankenfeld, N. N. Li, *Environ. Sci. Technol.* **1977**, *11*, 602−605.

[9] M. Kirck, J. M. Lehn, *Angew. Chem. Int. Ed. Engl.* **1975**, *14*, 555−556.

[10] M. Dozol, in *New Separation Chemical Techniques for Radioactive Waste and other Specific Applications*, Elsevier, London, **1991**.

[11] R. M. Izatt, J. S. Bradshaw, S. A Nielsen, J. D. Lamb, J. J. Christensen, *Chem. Rev.* **1985**, *85*, 271−339.

[12] R. M. Izatt, K. Pawlak, J. S. Bradshaw, R. L. Bruening, *Chem. Rev.* **1991**, *91*, 1721−2085.

[13] J. S. Kim, M. H. Cho, S. C. Lee, J. H. Pang, J. H. Lee, A. Ohki, *Talanta* **1999**, *49*, 69−75.

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

[15] J. F. Schameron, S. D. Christian, R. T. Ellington, in *Surfactant-based Separation Process. Surfactant Science Series* (Eds.: J. F. Schameron, J. H. Harwell), Dekker, New York, **1989**.

[16] C. Tondre, H. Hebrant, *J. Mol. Liquids* **1997**, *72*, 279−294 and references therein.

[17] P. Scrimin, P. Tecilla, U. Tonellato, *Tetrahedron* **1995**, *51*, 217−230.

[18] W. J. Asher, N. N. Li, A. L. Shrier, *Detoxifying-medicinal emulsion*, U. S. Patent 4,183,918, **1980**.

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

[20] E. B. Sandell, in *Colorimetric Determination of Traces of Metals*, Interscience, New York, **1950**.

[21] A. Marxer, K. Miescher, *Helv. Chim. Acta* **1951**, *34*, 924−931.

[22] A. Onopchenko, J. J. Harrison, C. Y. Chan, *Bull. Chem. Soc. Jpn.* **1998**, *71*, 717−721.

[23] J. D. Lamb, J. J. Christensen, S. R. Izatt, K. Bedke, M. S. Astin, R. M. Izatt, *J. Am. Chem. Soc.* **1980**, *102*, 3399−3403.

[24] S. Upadhyay, V. A. Varghese, L. Mishra, S. N. Singh, R. C. Srivastava, *J. Membrane Sci.* **1994**, *93*, 149−156.

[25] V. A. Varghese, S. Upadhyay, R. C. Srivastava, *J. Membrane Sci.* **1994**, *93*, 229−235.

[26] A. Safavi, E. Shams, *Talanta* **1999**, *48*, 1167−1172.

[27] T. Nabeshima, T. Aoki, Y. Yano, *Tetrahedron Lett.* **1997**, *38*, 8323−8326.

[28] A. Safevi, S. Rastegarzadeh, *Talanta* **1995**, *42*, 2039−2049.

Received October 12, 2001
O01494]