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Permeation liquid membrane for trace metal speciation in natural waters
Transport of liposoluble Cu(II) complexes

Nalini Parthasarathy*, Michel Pelletier, Jacques Buffle

Department of Inorganic and Analytical Chemistry, Sciences II, University of Geneva, 30 Quai Ernest-Ansermet, CH-1211 Geneva 4, Switzerland

Abstract

In this paper, the transport of Cu(II) in the presence of lipophilic Cu(II) organic complexes through permeation liquid membranes (PLMs) have been investigated. In natural waters, small organic compounds, which form liposoluble neutral complexes with Cu(II), are potentially toxic and bioavailable. Hence, to understand the role of liposoluble Cu(II) complexes in natural waters, four organic ligands: phthalic acid, bipyridyl, pyrocatechol and hydroxyquinoline, which form uncharged or lipophilic Cu(II) complexes, were tested. The results showed that the transport of lipophilic Cu(II) complexes through PLM depends on the lipophilicity of the complex. Applications of PLMs in natural waters are presented.

Keywords: Water analysis; Environmental analysis; Permeation liquid membranes; Membranes; Copper; Metal cations

1. Introduction

The importance of speciation studies in environmental systems is widely recognised. Metal ions, in particular Cu(II), Pb(II), Cd(II) and Zn(II), exist in various forms such as free hydrated ions, inorganic and organic complexes. They play important role in the biogeochemical cycling of trace elements including transport, bioaccumulation and toxicity [1–4]. Although the free metal ions are the most toxic to organisms, labile metal species and lipophilic neutral metal–organic complexes are known to be bioavailable. In order to understand their role in the toxicity to organisms and the mechanism of uptake by the organism, methods allowing speciation studies at trace metal concentration level (nano or picomolar) under natural water conditions are needed. This remains a challenging problem to analytical chemist since very few techniques combine speciation determination and high sensitivity. Amongst the methods available are sophisticated in situ voltammetric probes and separation and preconcentration techniques such as liquid–liquid extraction, equilibrium dialysis, ultrafiltration [2] with their advantages and disadvantages. An alternative technique is the permeation liquid membrane (PLM), based on liquid–liquid extraction principles. Its attractive features are that separation and preconcentration of metals can be achieved in one step. It is a clean method for sample preparation. Its key features are minimisation of the sample handling, i.e. reduces contamination risks, and elimination of the matrix effects which pose problems in most instrumental analytical techniques. In addition, it is suitable for in situ preconcentration of trace metals. A major advantage of PLM is that it mimics somewhat biological membranes and hence trace metal speciation studies using PLM may provide insight into the mechanism of metal uptake by microorganisms.

PLM has been used for industrial applications in the separation of metal ions [5,6], for analytical separation and preconcentration of organic compounds in pharmaceutical drugs and in environmental systems for sample preparation for trace organics [6,7]. However, there are few studies on the application of PLM for trace metal speciation in natural water [8,9]. In our previous papers [2,10–12] the transport of heavy metal ions, e.g. Cu, Pb Cd and Zn, through a PLM containing a neutral macrocyclic carrier, and its capability for preconcentration and speciation of trace metals using flat sheet as well as hollow fibre support geometry

* Corresponding author.
E-mail address: nalini.parthasarathy@cabe.unige.ch (N. Parthasarathy).

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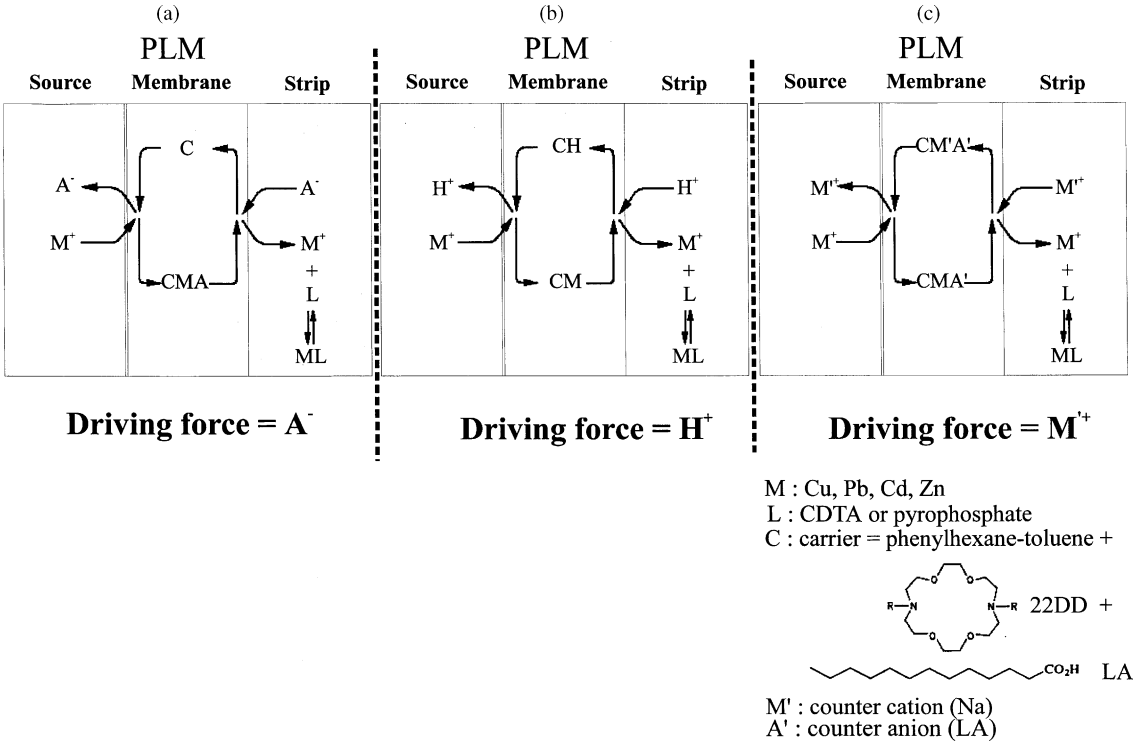


Fig. 1. Schematic representation of permeation liquid membrane system, using various driving forces (a–c) for uphill transport of metal ions. C: metal ion carrier in the membrane phase; L: metal ion complexant in the strip solution; A^-: coanion in the source solution; A′: lipophilic anion in the membrane phase; M'^+: counter cation; and M^+: test ion in the source solution.

was reported. A PLM consists of a microporous support impregnated with a hydrophobic organic solvent containing a cation carrier C. This membrane is placed between the sample (the source solution) and the receiver solution (the strip solution) (Fig. 1). The metal ion transport across the membrane occurs by (i) diffusion of the target metal ion to the sample/membrane interface, (ii) complexation of the metal ion, M, with carrier, C, to form MC, (iii) partitioning into the organic phase, (iv) diffusion of the MC complex to the membrane/strip solution interface and (v) decomplexation of MC at the strip/membrane interface. The metal ion transport can be driven by pH gradient; co-anion or counter cation gradient. In addition, in these systems, by using strip solution volumes much smaller than the sample volumes, very high preconcentration factors for the target species can be obtained. For making speciation measurements, perturbation of the test solution should be avoided. Thus counter cation gradient driven PLM system is the most suitable one.

Permeation liquid system containing species selective carrier 1,10-didecyldiaza crown ether (22DD) and lipophilic counter ion laurate dissolved in phenylhexane–toluene (1:1, v/v) was found to be selective to Cu(II), Pb(II), Cd(II) and Zn(II) ions. Previous report [11] showed that high preconcentration factors, e.g. 800 and 4000 in 120 min for Cu and Pb, respectively, can be obtained using hollow fibre supported liquid membrane. Cu(II) speciation measurements made in the presence of hydrophilic synthetic ligands (sulphosalicylic acid, tiron, hydroxyquinoline sulphonic acid, oxalic acid) and natural ligands (e.g. fulvic acid) showed that free metal ions are transported by this PLM system [2,12]. Recently, it was shown that by varying the hydrodynamic conditions in the measuring system, the transport flux is proportional to either the free metal ion concentration or to the labile Cu(II)–sulphosalicylic acid species [13]. However, small lipophilic organic metal complexes also play an important role in aquatic systems, since they are readily assimilated and they are toxic to the microorganisms [3,4,14,15]. Small low-molecular-mass organic compounds forming neutral lipophilic compounds may be found in natural water and these may pass through the PLM. The aim of this paper is therefore to investigate the Cu(II) transport characteristics of PLM in the presence of organic ligands forming lipophilic organic–Cu(II) complexes. For this purpose, phthalic acid, bipyridyl, pyrocatechol and 8-hydroxyquinoline, which form neutral or lipophilic complexes with Cu(II) were investigated. To the best of our knowledge, no such speciation studies using PLM has been reported previously.

2. Experimental

2.1. Reagents, membrane and apparatus

All chemicals used are reagent grade, unless otherwise stated.

2-(*N*-Morpholino)ethanesulphonic acid (MES, Sigma), *trans*-1,2-diaminocyclohexanetetraacetic acid (CDTA, Fluka), sodium hydroxide and lithium hydroxide monohydrate (Merck), 1,10-didecyl-diaza-18-crown-6 ether (22DD, Merck) and lauric acid (LA, Fluka), phthalic acid (pht, Merck). 2-2′-Bipyridyl (bipy), pyrocatechol (py), 8-hydroxyquinoline (HQ), 8-hydroxyquinoline sulphonic acid (HQSA), toluene and phenylhexane were all purchased from Fluka.

All aqueous solutions were prepared using Milli-Q water. Baker Instra HNO_3 was used for adjusting the pH of the solutions. All experiments were performed at room temperature.

The source solution consisted of desired concentration of Cu(II) in 10^{-2} mol/l MES, adjusted to pH 6.0 with LiOH. The strip solution consisted of 5×10^{-4} mol/l CDTA (pH 6.4). The membrane phase composition (the carrier) was as follows: 10^{-1} mol/l 1,10-didecyl-diaza-18-crown-6 and 10^{-1} mol/l lauric acid (LA) dissolved in mixture of phenylhexane–toluene (1:1, v/v).

Celgard 2500 hydrophobic flat sheet membrane (Hoescht), having a pore size of 0.04 μm, a porosity of 45% and a thickness of 25 μm, was used. Accurel ppq5/2 hydrophobic hollow fibre (HF) was used as supported liquid membrane for speciation studies in natural water. Accurel membrane has the following characteristics: inner diameter = 600 μm; pore size = 0.2 μm; porosity = 75%. A single fibre was used for transport experiments. Both Celgard and Accurel are polypropylene membranes.

The diffusion cells used for transport experiments with flat sheet were the same as those described previously (Fig. 2) [10]. Equal volume cells (100 ml) were used for transport measurements.

The copper concentrations were measured by flame atomic absorption spectrometry (AAS) or graphite furnace atomic absorption spectrometry (GFAAS).

3. Method

3.1. Metal ion transport experiments with flat sheet PLM

3.1.1. Cu(II) transport in the absence of complexing agent

The flat sheet membrane was impregnated with the carrier and, after rinsing it with water to remove the solvent excess, was placed between the two compartments of the diffusion cell. Eighty millilitres of source solution containing 5×10^{-5} mol/l Cu(II) in 10^{-2} mol/l MES (pH 6.0) was placed in one compartment and 80 ml of strip solution containing 5×10^{-4} mol/l CDTA (pH 6.46) in the other compartment. Aqueous solutions were stirred (480 rpm) and source and strip aliquots of solutions were periodically withdrawn and analysed by AAS. The flux of Cu(II) across the membrane was determined from the measured concentrations versus time graph.

3.1.2. Cu(II) speciation in Cu(II)–phthalic acid system

Flat sheet membrane was assembled as above and transport experiments were repeated by keeping the total Cu(II) concentration in the source solution constant (5×10^{-5} mol/l) and varying the phthalic acid concentration in the range of 5×10^{-3} to 2×10^{-2} mol/l. The pH was kept constant at 6.0. Fluxes of Cu(II) across PLM were also computed as before. Transport experiments with phthalic acid (2×10^{-2} mol/l) were done at pH 6.0 in the absence of Cu(II) and the concentration of the phthalate in the strip and source solution were determined by UV-Vis spectrometry ($\lambda_{max} = 280.6$ nm) to see if phthalate was transported through the PLM. In addition, in Cu(II) transport experiments, the presence of phthalate as Cu(II)–phthalate was checked in the strip at the end of each experiment by spectrophotometry.

3.1.3. Cu(II)transport studies in Cu(II)–2,2′-bipyridyl system

Cu(II) transport experiments in the presence of bipyridyl (bipy) were carried out in the same way as for those with pht

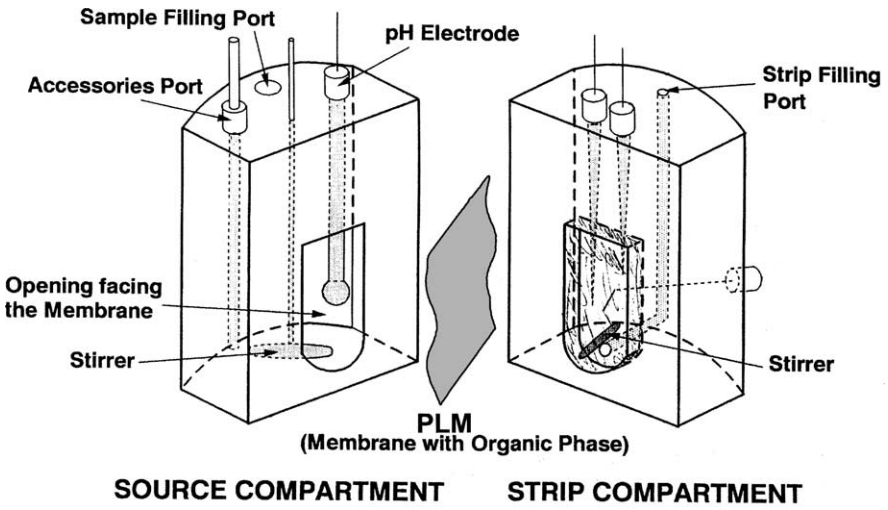


Fig. 2. Diagram of the diffusion cell used for performing transport experiments with flat sheet membrane. The cell is made of Plexiglas.

except that lower bipy concentrations (10^{-5} to 10^{-4} mol/l) were used in the source solution, due to its low solubility in water.

3.1.4. Cu(II) transport studies in Cu(II)–pyrocatechol system

Cu(II) transport experiments in the presence of pyrocatechol (pyro) were carried out in the same way as for pht, except that pyro concentration was varied in the range 5×10^{-5} to 1×10^{-3} mol/l, keeping Cu(II) concentration constant.

3.1.5. Cu(II) transport studies in Cu(II)–8-hydroxyquinoline

Cu(II) transport experiments in the presence of 8-hydroxyquinoline (HQ) were carried out as those for pht, except that stock solutions of HQ were made by first dissolving it in HCl 1.0 mol/l. Concentrations of HQ used, in the range of 10^{-5} to 10^{-4} mol/l, were lower than for pht, as HQ forms insoluble complexes with Cu(II).

Transport experiments were also performed at lower concentrations of Cu(II) and HQ to validate speciation capability of PLM at lower copper concentration.

For comparison, the transport experiments were done using 8-hydroxyquinoline sulphonic acid (HQSA) which, opposed to HQ, forms hydrophilic Cu(II)–HQSA complexes.

3.1.6. Cu(II) transport studies in Cu(II)–HQ system in the absence of carrier in the membrane

The membrane was impregnated with phenylhexane–toluene mixture (1:1, v/v) and, after rinsing it with water to remove the solvent excess, was placed between the two compartments of the diffusion cell. Eighty millilitres of source solution containing 6.8×10^{-7} mol/l Cu(II) and 1×10^{-5} mol/l HQ in 10^{-2} mol/l MES (pH 6.0) was placed in one compartment and 80 ml of strip solution containing 5×10^{-4} mol/l CDTA in the other compartment. Aqueous solutions were stirred (480 rpm) and source and strip aliquots of solutions were periodically withdrawn and analysed by AAS.

3.1.7. Extraction experiment

Five millilitres of a solution containing 5×10^{-5} mol/l Cu(II) and 10^{-2} mol/l phthalic acid in 10^{-2} mol/l MES buffer (pH 6) was placed in a glass bottle and 5 ml of toluene–phenylhexane mixture (1:1, v/v) was added to it. The mixture was shaken vigorously for 30 min in a shaker and transferred into separating funnel for phases to separate. The aqueous phase was withdrawn and Cu(II) determined by AAS. The initial Cu(II) concentration before extraction was also determined. The partition coefficient, K_p, was calculated as follows:

$$K_p = \frac{Cu_{org}}{Cu_{aq}}$$

where Cu_{org} is the concentration of Cu in the organic phase and Cu_{aq} is the concentration in the aqueous phase.

The same procedure was repeated for the determination of K_p of other Cu(II)–organic complexes, except that concentration of Cu(II) and organic ligands were different: Cu(II) = 4×10^{-5} mol/l and pyro = 1×10^{-3} mol/l; Cu(II) = 1.7×10^{-6} mol/l and HQ = 1×10^{-3} mol/l.

3.1.8. Precision of measurements

In transport experiments, the reproducibility of the measured fluxes was ca. 5%.

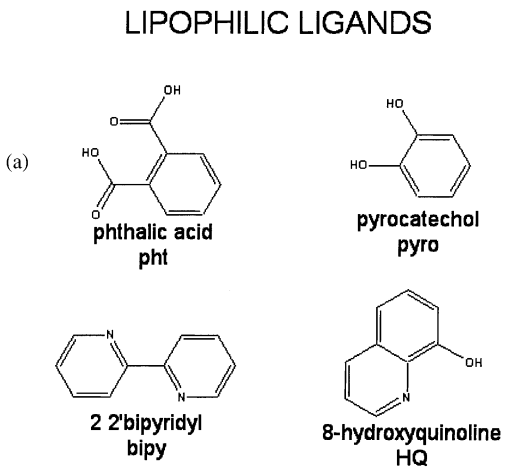
Similarly, the errors in extractions was about the same order of magnitude.

3.2. Results and discussion

3.2.1. Choice of organic ligands

The chemical structure of the ligands investigated in this work are shown in Fig. 3.

All these were chosen for several reasons: they form neutral or lipophilic complexes, except HQSA which forms hydrophilic anionic complexes with copper. The stability constants of these complexes are well known in the literature, the binding strengths of these ligands with Cu(II) are different and all of them have different functional groups. Small organic compounds bearing similar functional groups may be found in natural waters. Thus by making these studies, one may get insight into the factors governing the Cu(II) transport through the PLM in the presence of these complexes.



(b)

Ligand	log ß1	log ß2	log ß1H	log ß2H
pht	3.10	4.06	5.13	8.04
bipy	8.0	13.5	4.43	8.97
pyro	12.5	22.18	11.59	20.72
HQ	12.3	23.4	9.81	14.82

Fig. 3. The chemical structure of the selected lipophilic organic compounds (a); stability constants of metal complexes and acid–base formation constants (b) [18].

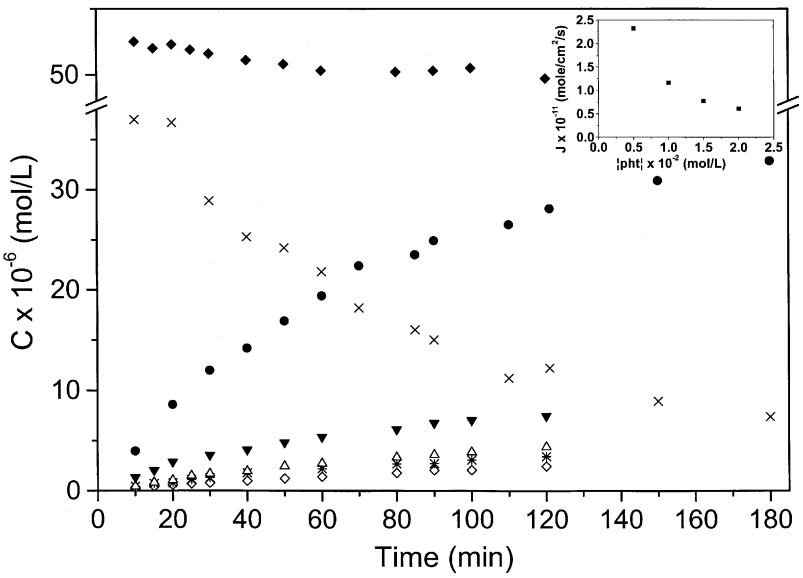


Fig. 4. Transport of Cu(II) through 22DD-LA-toluene–phenyl hexane supported PLM in the absence and presence of phthalic acid. Conditions used for Cu(II) without phthalic acid: source solution: 5×10^{-5} mol/l Cu(II) in 1×10^{-2} mol/l MES buffer (pH 6.0); strip solution: 5×10^{-4} mol/l CDTA (pH 6.4); carrier: 0.1 mol/l 22DD and 0.1 mol/l LA in phenylhexane–toluene mixture (1:1, v/v); volumes of source and strip solution: both 80 ml (LA: lauric acid). Symbols used (×) Cu(II) in the source solution and (●) Cu(II) in the strip solution. Conditions used for Cu(II) in the presence of phthalic acid: source solution: Cu(II) = 5×10^{-5} mol/l kept constant and pht concentration varied: (◇) pht = 2×10^{-2} mol/l; (✱) pht = 1.5×10^{-2} mol/l; (△) pht = 1×10^{-2} mol/l; (▼) pht = 5×10^{-3} mol/l. These symbols are for Cu(II) in the strip solution. Other conditions as without phthalic acid. (◆) is Cu(II) in the source solution for pht = 1.5×10^{-2} mol/l. For the sake of clarity, C vs. t in the source for other pht concentrations are not shown. The mass balance in all cases is respected. Inset: typical plot of flux, J, vs. pht concentration.

3.2.2. Cu(II)–phthalic acid system

Typical plots of Cu(II) concentration, C, versus time in the absence and presence of phthalic acid, pht, is shown in Fig. 4. It can be seen that much lower amounts of Cu(II) is transported across the membrane in presence of pht than in its absence. The Cu(II) concentration in the source solution decreases with time in the absence of pht where as it remains practically constant in its presence. Assuming that the Cu(II) transport is diffusion limited, the flux, J, under steady state conditions is given by [5]:

$$J = \left(-\frac{\mathrm{d}C}{\mathrm{d}t}\right)\frac{V}{A} = PC$$

where C is the metal concentration in the source solution, V the volume of the source solution, and A the surface area of the membrane. The rate of Cu(II) transport can be described by first order rate equation:

$$\ln\left(\frac{C}{C_0}\right) = -\frac{PA}{V}$$

where C_0 is the initial metal concentration in the source solution and P is the overall permeability coefficient.

P can be calculated from the initial portion of the $\ln(C/C_0)$ versus time plot and the flux can be computed from $J = PC_0$. J was computed for various pht concentrations using $V = 80$ ml and $A = 6.84\,\mathrm{cm}^2$ and the plot of J versus pht concentration (inset Fig. 4) shows that J decreases with increasing pht concentrations, indicating that probably only the free Cu(II) ion, with little contribution of neutral complexes, passes through the membrane. From the ratio of fluxes in the absence and presence of pht, the degree of complexation, defined as $\alpha = |\mathrm{Cu}|_t/|\mathrm{Cu}|$, can be calculated. $|\mathrm{Cu}|_t$ and $|\mathrm{Cu}|$ are the total Cu(II) and free Cu(II) concentration in the source solution. The flux is proportional to free metal concentration in carrier aided transport provided the rate controlling step is membrane diffusion controlled [2,12,16]. In this case, the ratio of the fluxes in the absence, J_0, and in the presence of ligand, J, for the same total concentration of Cu(II) is given by:

$$\frac{J_0}{J} = \frac{|\mathrm{Cu}|_t}{|\mathrm{Cu}|} = \alpha$$

In the absence of metal complexant, total metal concentration is equal to free metal ion concentration. Thus, experimentally measured degree of complexation α, (α_{exp}) can be computed and compared with the theoretical value of α (α_{th}) calculated using the programme Comics [17] and using the stability constants reported in the literature [18], for the complexes formed by Cu(II) with pht.

$$\mathrm{Cu}^{2+} + \mathrm{pht}^{2-} \Leftrightarrow \mathrm{Cu(pht)}$$

$$\mathrm{Cu}^{2+} + 2\mathrm{pht}^{2-} \Leftrightarrow \mathrm{Cu(pht)_2}^{2-}$$

The formation constant β_1 of Cu(pht) and β_2 of $\mathrm{Cu(pht)_2}^{2-}$ complexes are given by:

$$\beta_1 = \frac{|\mathrm{Cu(pht)}|}{|\mathrm{Cu}| \cdot |\mathrm{pht}|}$$

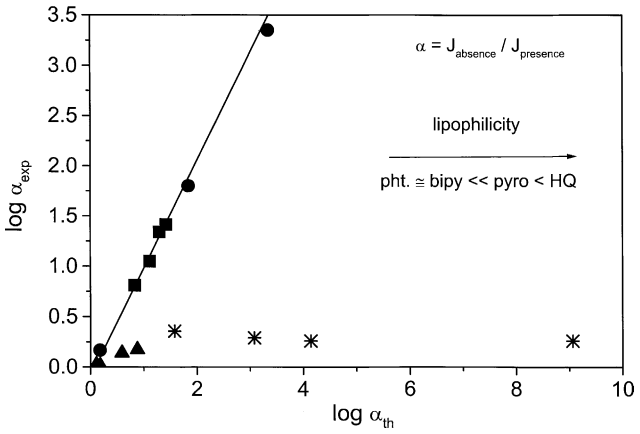


Fig. 5. Comparison of experimentally observed vs. theoretically computed values of the degree of complexation. α_{exp} vs. α_{th} for various lipophilic ligands tested. Symbols used: (■) pht; (●) bipy; (▲) pyro; and (✱) HQ.

$$\beta_2 = \frac{|\mathrm{Cu(pht)_2}|}{|\mathrm{Cu}| \cdot |\mathrm{pht}|^2}$$

The concentration of each species can be calculated by combining the mass balance equations for Cu(II) and pht.

$$|\mathrm{Cu}|_t = |\mathrm{Cu}^{2+}| + |\mathrm{Cu(pht)}| + |\mathrm{Cu(pht)_2}^{2-}|$$

$$|\mathrm{pht}|_t = |\mathrm{pht}^{2-}| + |\mathrm{H(pht)}^{-}| + |\mathrm{H_2(pht)}| + |\mathrm{Cu(pht)}| + 2|\mathrm{Cu(pht)_2}^{2-}|$$

where H(pht) and H_2(pht) are the protonated species of pht, whose formation constants are known in the literature [18].

The free Cu(II) concentration, under the experimental conditions used, was calculated using Comics programme. The values of complexation constants used [18] for the computation were as follows: $\log \beta_1 = 3.1$ and $\log \beta_2 = 4.06$ and the values of acid base constant $\log \beta_1^{\mathrm{H}} = 5.13$ and $\log \beta_2^{\mathrm{H}} = 8.04$. A plot of $\log \alpha_{exp}$ versus $\log \alpha_{th}$ (Fig. 5) shows a linear relation with a slope of 1 ± 0.01 indicating that flux depends on the free metal ion concentration under the conditions used. The salient feature of this study is that, although ca 80–85% of the Cu(II) is present as neutral Cu(pht) complex, very little or none of this species passes through the membrane.

3.2.3. Cu(II)–2,2′-bipyridyl system

Cu(II) forms much stronger complexes with bipy than with pht (Fig. 3). The complexes are charged but lipophilic and might pass as ion pair through the membrane. However, the *C* vs. *t* plots were similar to those obtained with pht. Like in the case of pht, the Cu(II) fluxes at various ligand concentrations were computed and plotted versus ligand concentrations and the results showed that the flux decreases with increasing ligand concentration. The degree of complexation α_{exp} was computed from the measured flux as described before and compared with the theoretical α_{th} value obtained using the stability constants (Fig. 3). A good linear plot for experimental versus theoretical $\log \alpha$ values, with a slope of 1, was observed (Fig. 5), indicating again that Cu(II) bipyridyl complexes do not pass through the membrane and that only free metal ions are measured in this case.

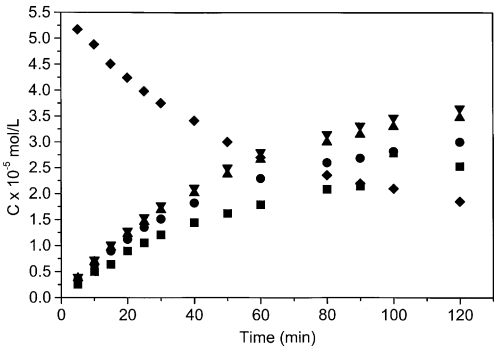


Fig. 6. Cu(II) transport in the presence of pyrocatechol (pyro). Typical plots of *C* vs. time. Conditions used: the same as in Fig. 3 except that source solution contained pyro in addition to Cu(II). Source solution: Cu(II) $= 5 \times 10^{-5}$ mol/l kept constant and pyro concentration varied: (■) pyro $= 1 \times 10^{-3}$ mol/l; (●) pyro $= 5 \times 10^{-4}$ mol/l: (▲) pyro $= 1 \times 10^{-4}$ mol/l; (▼) pyro $= 5 \times 10^{-5}$ mol/l. These symbols are for Cu(II) vs. time in the strip solution. (◆) is Cu(II) in the source solution for pyro $= 1 \times 10^{-4}$ mol/l. For the sake of clarity, *C* vs. *t* in the source for other pyro concentrations are not shown. The mass balance in all cases is respected.

3.2.4. Cu(II)–pyrocatechol system

Like bipy, pyrocatechol (pyro) also forms strong complexes with Cu(II) and typical plot of *C* versus time for Cu(II) transport in the presence of pyrocatechol is shown in Fig. 6. In contrast to pht and bipy, a larger proportion of Cu(II) is transported through the PLM in the presence of pyro, as seen by the increase of Cu(II) with time in the strip solution and hence a significant decrease in the Cu(II) concentration in the source solution with time is observed. In addition, the decrease in Cu(II) concentration is less marked than in the other two systems indicating that probably the lipophilic Cu(II)–pyro complex passes through the membrane. As before, the Cu(II) fluxes in the presence of pyro at various pyro concentrations were calculated. The results show that the decrease in Cu(II) flux with pyrocatechol concentration was significantly lower than those found with pht and bipy. The experimental degree of complexation α_{exp} was computed as before and its log plotted versus log of the theoretical value α_{th} and, although the graph (Fig. 5) is linear in the working range studied, its slope deviates from 1, indicating that in this system the free metal ions plus lipophilic complexes are transported. Indeed spectrophotometric measurements ($\lambda_{max} = 274.7$ nm) reveal that pyrocatechol, as well as Cu–pyrocatechol, are transported through the membrane. Theoretical calculations show that ca. 20–88% of Cu(II) is present as neutral Cu–pyro complex in the source solution.

3.2.5. Cu(II)–hydroxyquinoline

Cu(II) forms strong complexes with hydroxyquinoline (Fig. 3) and other research workers [14,15] have studied this system to understand the uptake of lipophilic metal complexes by microorganisms and these authors report that these complexes are assimilated by microorganisms. Therefore, we also tested this ligand. The transport of Cu(II) in the presence of HQ yielded similar *C* versus time profiles as found for Cu–pyro system, except that more Cu(II) ions were transported and Cu(II) fluxes were found to vary very little with HQ concentration. The log α_{exp} versus log α_{th} plot (Fig. 5) indeed shows that it is not linear and deviates considerably from the slope of 1, indicating that lipophilic Cu–HQ complex, which is the predominating species, passes through the PLM. UV-Vis measurements confirm that this complex passes through the membrane. The λ_{max} varies with time, making quantitation difficult. However, under the same conditions, in the presence of HQSA only free Cu(II) passes through the membrane [12].

3.2.6. Cu(II) transport through PLM containing no carrier

The lipophilic Cu(II) complexes can pass through the membrane by passive diffusion. To check this, Cu(II) transport in the absence and in the presence of HQ and HQSA were investigated. The results in Fig. 7 shows that practically no Cu(II) is transported by the solvent when HQ is absent, but Cu(II) passes through the membrane as lipophilic Cu(II)–HQ complex by passive diffusion. As one would expect, no Cu(II) is transported through PLM in the presence of HQSA. More studies need to be done regarding the kinetics of diffusion of these complexes compared to free metal ions transport in facilitated membranes.

3.2.7. General observations

The results of this study has shown that not all neutral lipophilic complexes pass through the membrane and their diffusion probably depends on their partition coefficient in the lipophilic membrane. The extraction results of Cu(II) by phenylhexane–toluene in the presence of the various ligands (Table 1) show that the partition coefficients, or percentage of Cu(II) extracted, varies with the lipophilicity of the ligand, indicating the following trend in the order of increasing lipophilicity

pht < bipy ≪ pyro < HQ.

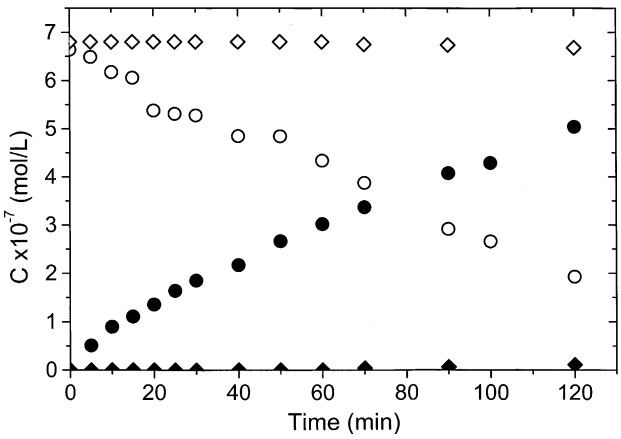


Fig. 7. Cu(II) transport in the absence and in the presence of hydroxyquinoline through PLM containing phenylhexane–toluene mixture (1:1, v/v). Conditions used: same as in Fig. 4 except that no carrier was used in the membrane phase. Source solution: (◇) Cu(II) = 6.8×10^{-7} mol/l in 10^{-2} mol/l MES (pH 6.0) strip solution: 5×10^{-4} mol/l CDTA (pH 6.4); (○) Cu(II) = 6.8×10^{-7} mol/l and 10^{-3} mol/l HQ in 10^{-2} mol/l MES buffer. The open and closed symbols are source and strip solutions, respectively.

Table 1
Partition coefficients (K_p) of various lipophilic Cu(II) organic complexes in phenylhexane–toluene mixture (1:1, v/v).

Ligand	|*L*| (mol/l)	|Cu| (mol/l)	K_p	Extracted (%)
Pht	1×10^{-2}	5.1×10^{-5}	0.03	3
Bipy	5×10^{-3}	4.5×10^{-5}	0.14	12
Pyro	1×10^{-3}	4.0×10^{-5}	3.9	77
HQ	1×10^{-3}	1.0×10^{-6}	5.98	86

3.3. Application of PLM for in situ preconcentration and speciation of trace metals in natural waters

Application of PLM to the speciation of Cu(II) and Pb(II) was tested with various types of natural water. For this purpose, a specially designed hollow fibre in situ

Table 2
Application of HFPLM for metal speciation in various water samples

Sample	Total dissolved metal (nmol/l)		Free metal ion (nmol/l)	
	Pb	Cu	Pb	Cu
Arve River (Geneva, Switzerland) (sampling date: 2001)	1.45 ± 0.03	33.5 ± 0.3	0.10 ± 0.01	2.1 ± 0.03
Rhone River (Geneva, Switzerland) (sampling date: 2001)	0.30 ± 0.06	12.6 ± 0.1	0.05 ± 0.01	2.95 ± 0.02
Seine River (Paris, France) (sampling date: 2002)	9.3 ± 0.1	49.0 ± 1.0	0.10 ± 0.01	1.1 ± 0.1
Cheneviers Brook (Geneva, Switzerland) (sampling date: 2000)	52.0 ± 0.7	234 ± 3	0.67 ± 0.02	1.9 ± 0.01
Greifen Lake (Zurich, Switzerland) (sampling date: 2000)	0.65 ± 0.01	53.2 ± 1.0	0.0008 ± 0.0001	0.12 ± 0.01
Ontario Lake (Toronto, Canada) (sampling date: 2001)	0.22 ± 0.02	29.34 ± 0.2	0.08 ± 0.02	2.2 ± 0.01
The English Channel (Plymouth, UK) (sampling date: 2002)	4.9 ± 0.1	47.0 ± 1.0	0.14 ± 0.01	1.05 ± 0.1

preconcentration PLM device (HFPLM) was used. Accurel hollow fibre of 15 cm length was impregnated with the carrier as described elsewhere [11], the excess of solvent removed by passing 3 ml of Milli-Q water through the lumen of the fibre and the outside of the fibre was rinsed by dipping it into a beaker containing Milli-Q water. Then, strip solution (5×10^{-4} mol/l CDTA) was filled in the lumen of the fibre and the device was dipped into surface waters for 120 min. After preconcentration of the sample, the strip solution was collected in a vial by pushing it with a syringe filled with the strip solution. The Pb(II) and Cu(II) in the preconcentrated sample was analysed by inductively coupled plasma (ICP) in the laboratory. The total concentration of Pb(II) and Cu(II) were measured by filtering the raw water sample through 0.45 μm filter and acidifying it to pH 2.0 with HNO_3 concentration. The analysis was also done by ICP-MS. The results in Table 2 clearly show the speciation capability of PLM. The PLM measured fraction, which is the free plus the very labile or liposoluble metal complexes, was always found to be less than the total metal concentration.

More work is needed to quantify different bioavailable fractions.

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References

[1] G.E. Butley, Trace Element Speciation: Analytical Methods and Problems, CRC Press, Boca Raton, FL, 1989.
[2] J. Buffle, H. P. Van Leeuwen, In Situ Monitoring of Aquatic Systems, IUPAC Series, vol. 6, Wiley, Chichester, 2000.
[3] P.G.C. Campbell, in: A. Tessier, D.R. Turner (Eds.), Metal Speciation and Bioavailability in Aquatic Systems, Wiley, Chichester, 1995, p. 45.
[4] T.M. Florence, Talanta 29 (1982) 345.
[5] P.R. Danesi, Sep. Sci. Technol. 19 (1984/1985) 857.
[6] J.-A. Jönsson, L. Mathiasson, Trends Anal. Chem. 11 (1992) 106.
[7] J.A. Jönsson, L. Mathiasson, Adv. Chromatogr. 41 (2001) 53.
[8] M. Papantoni, N.-K. Djane, K. Ndungu, J.-A. Jönsson, L. Mathiasson, Analyst 120 (1995) 1471.
[9] N.-K. Djane, K. Ndungu, F. Malcus, G. Johansson, L. Mathiasson, Fresenius J. Anal. Chem. 358 (1997) 822.
[10] N. Parthasarathy, J. Buffle, Anal. Chim. Acta 284 (1994) 649.
[11] N. Parthasarathy, M. Pelletier, J. Buffle, Anal. Chim. Acta 350 (1997) 183.
[12] N. Parthasarathy, J. Buffle, N. Gassama, F. Cuenod, Chem. Anal. (Warsaw) 44 (1999) 455.
[13] L. Tomaszewski, J. Buffle, J. Galceran, Anal. Chem. 75 (2003) 893.
[14] J. Phinney, K.W. Bruland, ES&T 28 (1994) 111.
[15] T.M. Florence, B.G. Lumsden, J.J. Fardy, Anal. Chim. Acta 151 (1983) 281.
[16] F. Guyon, N. Parthasarathy, J. Buffle, Anal. Chem. 71 (1999) 819.
[17] D.D. Perrin, L.G. Sayce, Talanta 14 (1967) 833.
[18] A.E. Martell, R.M. Smith, Critical Tables, vol. 3, Plenum Press, New York, 1976.