Available online at www.sciencedirect.com
ScienceDirect
Journal of Membrane Science 309 (2008) 182–188
journal of MEMBRANE SCIENCE
www.elsevier.com/locate/memsci

Transport of lipophilic ligands through permeation liquid membrane in relation to natural water analysis

Nalini Parthasarathy *, Michel Pelletier, Jacques Buffle

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

Received 4 September 2007; received in revised form 10 October 2007; accepted 14 October 2007
Available online 22 October 2007

Abstract

Trace metal ions can exist in many chemical forms, such as free metal, labile and liposoluble metal complexes in natural waters. Although, free metal ions are well known to be bioavailable, liposoluble species may also be potentially bioavailable and toxic. For understanding the metal uptake and toxicity to microorganisms, analytical tools are required to measure the various metal species under natural water conditions. Permeation liquid membrane (PLM) devices, comprising of 1, 10 dicecyl diaza 18 crown ether 6 and lauric acid in phenylhexane–toluene mixture, were demonstrated to be well suited for the trace metal speciation, in particular, for the free Cu(II), Pb(II) and Cd(II) concentration measurements in natural waters. In the presence of both free metal ions and lipophilic complexes, both these species will be transported across the membrane. In order to evaluate the contribution of the lipophilic species in the measured flux, the concentration of the lipophilic species must be determined. In this paper, transport characteristics of 8-hydroxyquinoline (HQ, also known as oxine) through a flat sheet PLM comprising a mixture of toluene/phenylhexane has been studied to obtain information on the permeability. HQ was chosen as model organic compound because its metal complexations are well known and it forms neutral lipophilic complex with Cu(II). Copper-oxine is used as a pesticide and may be present in natural waters. Important parameters such as diffusion coefficient in the membrane, D_m, partition coefficient, K_p, between the solution and the membrane, and permeability coefficient, P, have been evaluated by studying the effect of pH and membrane thickness on HQ transport. The results showed that the neutral HQ species is transported efficiently across the membrane and that the charged protonated species are not transported. Values of $D_m = 3.0 \times 10^{-7}$ cm^2 s^{-1} and $P = 2.47 \times 10^{-3}$ cm s^{-1} were found. The partition coefficient, K_p, of HQ in phenylhexane/toluene mixture and toluene were also determined using the classical liquid/liquid extraction method for comparison. The results revealed that partition coefficient in toluene was higher than that in phenylhexane/toluene mixtures. However, the two values obtained for K_p were comparable as expected.

Keywords: Permeation liquid membrane; Supported liquid membrane; Speciation; Lipophilic; Natural waters; 8-hydroxyquinoline

1. Introduction

In natural waters, metal ions are present in different chemical forms and their bioavailability or toxicity depends on their specific form. For instance, it is widely accepted that the free metal ion is a key species for metal transport through the membrane, but, labile and lipophilic metal complexes are potentially bioavailable and toxic to microorganisms [1–4]. In order to understand the metal uptake and toxicity to microorganism, methods are thus needed to measure the concentration and the trans-membrane flux of different metal species, under natural water conditions.

This requires the use of the so-called dynamic bioanalogical techniques of speciation [5,6] such as voltammetry [7], differential gradient on thin film (DGT) [8,9], Donan membrane technique (DMT) [10], and permeation liquid membrane (PLM) [11–14]. They have been used for measuring separately, the labile and free metal ion concentrations. The permeation liquid membrane (PLM) is a separation method based on liquid–liquid extraction principles and has been developed for in situ speciation measurements [12].

The attractive features of this advanced separation method are that extraction, back extraction and preconcentration of the target species can be done in one step and it mimics somewhat the

* Corresponding author. Tel.: +41 22 379 60 47; fax: +41 22 379 60 69.
E-mail address: nalini.parthasarathy@cabe.unige.ch (N. Parthasarathy).

0376-7388/$ – see front matter © 2007 Elsevier B.V. All rights reserved.
doi:10.1016/j.memsci.2007.10.015

biological membrane. It consists of a thin, hydrophobic, chemically inert macroporous membrane impregnated with a water immiscible organic solvent containing a carrier, selective to the target species, and placed between two aqueous solutions, the source and the strip solutions. The transport of metal ions across the membrane is a sequential process including diffusion of the metal ions to the source solution/membrane interface; complexation of metal ions with the carrier and its partitioning into the organic phase; diffusion of the metal carrier complex across the membrane to the membrane/strip solution interface where it is released by a complexing ligand present in the strip solution. The driving force for the metal flux is a chemical gradient between the two solutions, established by inclusion of a complexant in the strip solution, which is much stronger than that of the source solutions. The design of the PLM is such that the overall flux of metal transport may be source diffusion, membrane diffusion or chemical kinetics limited. Previous studies, using 1, 10 didecyl diaza 18, crown 6 ether as carrier dissolved in toluene–phenylhexane mixture have shown it to be selective to Cu(II), Pb(II), Cd(II) and Zn(II) [11]. For ligands forming hydrophilic complexes, the overall flux across the PLM was found to be limited by diffusion in the membrane, diffusion in the source solution or the chemical dissociation of the complex depending on the lability of the complexes [15–17]. Only preliminary studies using this technique have been preformed in solutions containing organic ligands forming lipophilic complexes. Phthalate, bipyridyl (bipy), 8-hydroxyquinoline (HQ) and diethyldithiocarbamate (DDC) have been used with Cu, to test if they can pass through the hydrophobic membrane [18]. The results revealed that transport of neutral complexes depends on the lipophilicity of the metal–ligand complex. Cu–phthalate complex did not pass through the membrane and the transport of the other complexes increased in the order: bipy < DDC < HQ. Thus, in the presence of both free metal ions and lipophilic metal complexes, both these species may be transported across the membrane and the measured metal flux will be a weighted average of the fluxes of the lipophilic complexes plus that of the free metal ion. In order to interpret the measured flux quantitatively and to determine the specific contribution of hydrophilic and lipophilic complexes, the transport of the latter across the membrane in the absence of carrier, but with only the organic solvent, should be investigated in detail. It must be pointed out that such studies are highly relevant in water analysis, since there are very few methods available for the determination of lipophilic complexes [1,18,19] and that none of them allows direct measurement.

In this work, 8-hydroxyquinoline has been chosen as a model ligand because (i) it forms a neutral lipophilic complex with Cu(II) and (ii) it is used as fungicide and is present as Cu(II) complex in aquatic systems. 8-Hydroxyquinoline is also used as antiseptic, disinfectant [20] and pesticide. Thus, 8-hydroxyquinoline may enter natural waters or soils through anthropogenic activities and react with trace metals present in natural waters, forming predominantly the neutral Cu(II) complex. Bioassay laboratory studies have shown that this neutral Cu(II) lipid soluble complex is toxic to microorganisms. For example, for Cu–8-hydroxyquinoline, the EC50 for diatom is 1.9 ppb [21]. In addition, HQ is also reported to be toxic to microorganisms, e.g. EC50 of HQ for diatom is 14.5 ppb [22]. However, little is known on the importance of lipid soluble complexes in aquatic systems and on the concentration of these complexes originating from anthropogenic sources. This stems from the lack of reliable and sensitive techniques available for the measurement of lipid soluble metal complexes. The permeation liquid membrane approach is well suited for this purpose. This paper focuses on the transport characteristics of 8-hydroxyquinoline (HQ) across PLM to obtain information on its permeability. This is required for the transport of its neutral complex with metals, which will be reported in a further work.

2. Experimental

2.1. Materials

All the reagents used were of analytical grade unless otherwise stated. 2-*N*-Morpholino 2-ethane sulphonic acid (MES) was purchased from Sigma–Aldrich, Buchs, Switzerland. 8-Hydroxyquinoline (HQ), *trans*-cyclohexane diamino tetra acetic acid (CDTA), toluene and phenylhexane were purchased from Fluka, Buchs, Switzerland. Concentrated nitric and hydrochloric acids used for acidifying solutions were Baker Instra products.

Stock solution of 0.1 mol L^{-1} HQ in 0.2 mol L^{-1} HCl was used for preparation of the desired concentration of hydroxyquinoline.

The Celgard 2500 flat sheet polypropylene membrane (thickness = 25 μm; pores size = 0.045 μm; porosity = 45%), was kindly supplied by Hoechst, Wiesbaden, Germany.

2.2. Determination of distribution coefficient of HQ in organic solvents

Five millilitres of 10^{-3} mol L^{-1} HQ in 10^{-2} mol L^{-1} buffer (pH 6.0) was added to 5 mL of toluene or a mixture of toluene + phenylhexane (1 + 1, v/v) and shaken for 15 min, left to stand for phase separation and centrifuged at 1000 rpm to remove any emulsion formed. The HQ in the aqueous phase before and after extraction was analysed by UV–vis spectrophotometry (Perkin-Elmer Lambda 35). The spectra of HQ in MES buffer at pH 6.0 shows a maximum at 239.6 nm. A linear calibration curve was observed in the concentration range 10^{-6} to 10^{-5} mol L^{-1} at pH 6.0 ($Y = 3.55 \times 10^4 X + 1.68.10^{-4}$, $r = 0.9999$). Assuming an absorbance of 0.004, the LOQ is about 10^{-7} mol L^{-1}.

2.3. Transport measurements with PLM

PLM device consists of two half Plexiglas cells as previously described [11,12,23]. Celgard 2500 flat sheet polypropylene membrane (thickness = 25 μm; pores size = 0.045 μm; porosity = 45%) was impregnated with a mixture of toluene + phenylhexane (1 + 1, v/v) and the excess solvent was removed by rinsing it with MilliQ water. The membrane was then placed between the two half cells. The desired concentration of HQ in 10^{-2} mol L^{-1} MES buffer (pH 6.0) (source solution) was placed in the source solution compartment