

Selective Transport of Copper(II) Ion across a Polymer Membrane Incorporating a Difunctional Schiff-base Ionophore

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Abstract

The selective polymer membrane transport of Cu(II) from an aqueous solution containing seven metal cations, Co(II), Ni(II), Cu(II), Zn(II), Ag(II), Cd(II) and Pb(II), was studied. The source phase contained equimolar concentrations of the above-mentioned cations, with the source and receiving phases being buffered at pH 4.9 and 3.0, respectively. Cu(II) ion transport occurred ($J = 2.82 \times 10^{-7}$ mol/h at 25 °C) from the aqueous source phase across the polymer membrane (derived from cellulose triacetate) containing ligand (I) as the ionophore, into the aqueous receiving phase. Clear transport selectivity for Cu(II) was observed.

Introduction

An effective way to use the molecular recognition capability of macrocycles for metal ion separations is to incorporate such ligands into solvent extraction and liquid membrane systems.

During the past years, the separation of heavy metals and organic substances has become more important in water purification applications owing to the drastic strengthening of environmental protection laws. In this field, various separation techniques, precipitation, extraction, distillation and electrodialysis have all been employed. Membrane processes such as liquid-membrane transport systems are potentially quite important in this area [1]. In practical applications three main types of liquid membranes containing a mobile carrier have been studied: liquid surfactant, supported liquid and solvent polymeric membranes [1–5] – the latter based on a polymer film containing the ionophore and a plasticizer.

There have now been many reports of the transport of transition and post-transition metal ions through bulk liquid membranes using synthetic ionophores [6–13]. For example, the competitive extraction and transport of transition and post-transition metal ions using mixed-donor cyclic and acyclic ligands as ionophores have now received considerable attention [14–17].

In the present report, the results of competitive metal polymer inclusion transport involving Co(II), Ni(II), Zn(II), Cu(II), Ag(I), Cd(II) and Pb(II) using carrier I [18, 19] are presented.

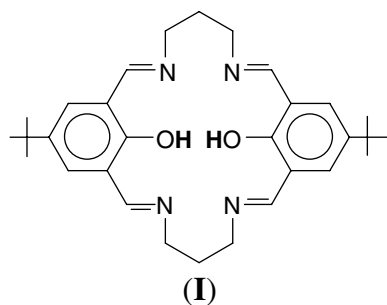
Experimental

The preparation and characterization of I has been described previously [19].

Transport experiments:

The transport cell was based on that described previously [20]. The source phase was buffered at pH 5.0 (CH₃COOH/CH₃COONa). The metal ions present at a concentration of 0.01 M were cobalt(II), nickel(II), copper(II), zinc(II), silver(I), cadmium(II) and lead(II), all as their nitrate salts. The receiving phase was buffered at pH 3.0 (HCOOH/HCOONa). The volume of each of the source and receiving phases was 130 ml. The transport runs were carried out for a period of 24 h and the stirring speed was 50 rpm at 25 °C. The polymer membrane was synthesized as described elsewhere [21]: 4.0 ml of a solution of 3.125 g of cellulose triacetate in 250 ml of dichloromethane, 3.0 ml of a 0.01 M solution of ligand in dichloromethane, 1.5 ml of a 10% (v/v) solution of 2-nitrophenyl octyl ether in dichloromethane and 0.5 ml of a 10% (v/v) solution of tris(2-butoxyethyl) phosphate in dichloromethane were mixed and 9.0 ml of this mixture was set aside in a 4-cm Petri dish and left to evaporate for 18 h. After this time the gel-like polymer membrane was removed from the Petri dish and placed between the two half glass cell compartments so that the side exposed to the air during evaporation was facing the source solution. When not in use, individual polymer membranes were stored submerged in a solution of MilliQ water. The membrane surface exposed to the source and receiving phases was circular and of 3.5 cm diameter. The metal ion concentrations in the receiving phase after each transport experiment were determined using a Varian spectra AA-800 atomic absorption

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spectrometer. The extraction results are quoted as average values obtained from duplicate runs.

Results and discussion

A monomeric oxime ligand related to **I** is used commercially as a selective extractant for Cu(II) *via* the formation of a 1:2 metal: ligand complex [18] and, in part, this provided a motivation for the present study. The competitive metal ion transport experiment contained the seven metals, Co(II), Ni(II), Cu(II), Zn(II), Ag(I), Cd(II) and Pb(II) in the aqueous source phase, with **I** as the ionophore in the polymer membrane. Under the conditions employed, this ditopic ligand **I** yielded highly selective transport of Cu(II) (see Figure 1). Ligand **I** and its unsubstituted derivative have been well established previously to bind two Cu(II) ions on loss of two protons [18, 19] and similar coordination behaviour appears likely to occur in the polymer membrane phase in the present case.

The observed Cu(II) transport rate ($J = 3.14 \times 10^{-7}$ mol/h at 25 °C) is the average taken

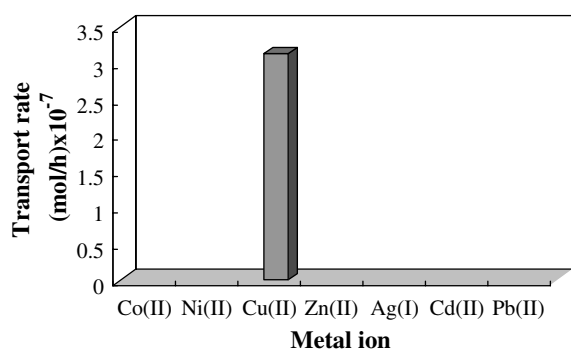


Figure 1. The rate of transport [(mol/h) × 10⁻⁷] for a competitive metal-ion transport (source/membrane/receiving) study using **I** incorporated into a polymer inclusion membrane. Aqueous source phase: 130 ml, contains seven metal ions, each with initial concentration 0.01 M prepared in a buffer solution (CH₃COOH/CH₃COONa) pH 5.0. Membrane polymer phase contain ligand (0.01 M). Aqueous receiving phase: a buffer solution of HCOOH/HCOONa, pH 3.0 (130 ml); both liquid phases stirred for 24 h at 25 °C. The transport rate for Cu(II) is the average taken from duplicate runs (duplicates differed by less than 5%).

from duplicate runs (duplicates differed by less than 5%) over 24 h. No evidence for transport of any of the remaining six metals present was observed within the detection limits of the experiment.

Previously reported parallel competitive ligand membrane and two-phase extraction experiments gave parallel results to those of the present study [21]. Namely, high selectivity for Cu(II) was observed in each case. All these results confirm that **I** is an efficient reagent showing high specificity for Cu(II) in each of bulk membrane transport, polymer inclusion transport and solvent extraction experiments under the conditions employed.

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