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## ORIGINAL ARTICLE

# Separation study of some heavy metal cations through a bulk liquid membrane containing 1,13-bis(8-quinoly)-1,4,7,10,13-pentaoxatridecane

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Received 13 March 2011; accepted 8 June 2011

## KEYWORDS

Bulk liquid membrane transport;  
Kryptofix5;  
Transition metal cations;  
Nitrobenzene;  
Chloroform;  
Dichloromethane;  
1,2-Dichloroethane

**Abstract** Competitive permeation of seven metal cations from an aqueous source phase containing equimolar concentrations of  $\text{Co}^{2+}$ ,  $\text{Fe}^{3+}$ ,  $\text{Cd}^{2+}$ ,  $\text{Cu}^{2+}$ ,  $\text{Zn}^{2+}$ ,  $\text{Ag}^+$  and  $\text{Pb}^{2+}$  metal ions at pH 5 into an aqueous receiving phase at pH 3 through an organic phase facilitated by 1,13-bis(8-quinoly)-1,4,7,10,13-pentaoxatridecane (Kryptofix5) as a carrier was studied as bulk liquid membrane transport. The obtained results show that the carrier is highly selective for  $\text{Ag}^+$  cation and under the employed experimental conditions, it transports only this metal cation among the seven studied metal cations. The effects of various organic solvents on cation transport rates have been demonstrated. Among the organic solvents involving nitrobenzene (NB), chloroform ( $\text{CHCl}_3$ ), dichloromethane (DCM) and 1,2-dichloroethane (1,2-DCE) which were used as liquid membrane, the most transport rate was obtained for silver (I) cation in DCM. The sequence of transport rate for this cation in organic solvents was:  $\text{DCM} > \text{CHCl}_3 > 1,2\text{-DCE} > \text{NB}$ . The competitive transport of these seven metal cations was also studied in  $\text{CHCl}_3\text{-NB}$  and  $\text{CHCl}_3\text{-DCM}$  binary solvents as membrane phase. The results show that the transport rate of  $\text{Ag}^+$  cation is sensitive to the solvent composition and a non-linear relationship was observed between the transport rate of  $\text{Ag}^+$  and the composition of these binary mixed non-aqueous solvents. The influence of the stearic acid,

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Peer review under responsibility of King Saud University.

doi:10.1016/j.arabjc.2011.06.013



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palmitic acid and oleic acid as surfactant in the membrane phase on the transport of the metal cations was also investigated.

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## 1. Introduction

The use of liquid membranes (LMs) as a sample pretreatment technique is related to their ability to perform analyte enrichment as well as sample-matrix separation. Among the different advantages of LMs, when compared to the liquid liquid extraction (LLE) and solid phase extraction (SPE) techniques, are the lower sample volume and cost of analysis (Jonsson and Mathiasson, 1992). Besides, LMs enable higher analyte-enrichment factors and selectivity (Cordero et al., 2000). Furthermore, LMs are greener than LLE and SPE, since they involve lower volumes of organic reagents, and are suitable for easy miniaturization and automation, offering an excellent sample treatment alternative for “green” analytical chemistry (Armenta et al., 2008; Keith et al., 2007).

Membranes can be defined as selective barriers between two phases with mass transfer taking place from the donor phase to the acceptor phase. In the case of LMs, this barrier comprises a liquid phase separating two immiscible solutions, with the transport of some chemical species across the barrier. The LM is usually made of an organic solution, and the donor and acceptor phases are aqueous solutions (Kislik, 2009; Dzygiel and Wiczorek, 2002), which can be arranged in different configurations, thus providing different types of LM.

The design and development of selective reagents to bind the metal cations is very important in the areas of analytical chemistry and separation science. With regard to molecular recognition and selective binding, macrocyclic and chelating ligands are extensively studied in the transport of alkali and alkaline earth metal cations across liquid membranes (Izatt et al., 1986a,b; Dozol, 1991). However, since fewer studies have been reported on transition and post-transition heavy metal ions, the development of selective techniques for the separation and determination of these metal cations is still a challenging task (Zolgharnein et al., 2008; Vajda et al., 2000; Rounaghi and Khoshnood, 2006). In this paper, a good transport selectivity has been observed for  $\text{Ag}^+$  cation over several cations by using an appropriate ligand. Silver is an important element that is mainly used in photographic and imaging industry, dental and medical products, electrical and electronic equipment and other products like jewelry, coins, and mirrors (Purcell and Peters, 1998). Thus, the determination of this metal cation in various media is of importance.

In this work, we report the results of competitive seven metal membrane transport experiments involving  $\text{Co}^{2+}$ ,  $\text{Fe}^{3+}$ ,  $\text{Cd}^{2+}$ ,  $\text{Cu}^{2+}$ ,  $\text{Zn}^{2+}$ ,  $\text{Ag}^+$  and  $\text{Pb}^{2+}$  metal cations with 1,13-bis(8-quinolyl)-1,4,7,10,13-pentaoxatridecane (Kryptofix5) (Scheme 1) as a carrier, using nitrobenzene (NB), chloroform ( $\text{CHCl}_3$ ), dichloromethane (DCM) and 1,2-dichloroethane (1,2-DCE) as liquid membrane. The effect of binary mixtures of chloroform-nitrobenzene ( $\text{CHCl}_3$ -NB) and chloroform-dichloromethane ( $\text{CHCl}_3$ -DCM) as liquid membrane on the transport of these metal cations was also studied. The influence of the stearic acid, palmitic acid and oleic acid as surfactant on the transport efficiency of the metal cations was also investigated.

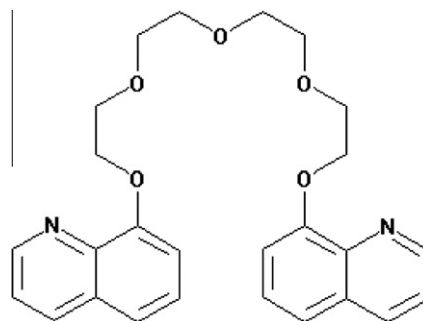
## 2. Experimental

### 2.1. Reagents and solvents

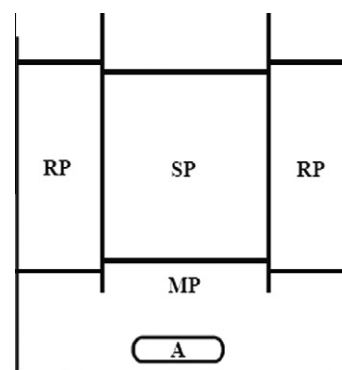
1,13-bis(8-quinolyl)-1,4,7,10,13-pentaoxatridecane (Kryptofix5) (Merck), silver (I) nitrate (Merck), iron (III) nitrate (Merck), cadmium (II) nitrate (Merck), zinc (II) nitrate (Merck), copper (II) nitrate (BDH), cobalt (II) nitrate (BDH), lead (II) nitrate (BDH), sodium acetate (Merck), sodium hydroxide (Riedel), stearic acid (BDH), palmitic acid (Riedel) and oleic acid (Merck) were used without further purification. The solvents nitrobenzene (BDH), chloroform (Merck), dichloromethane (Merck) and 1,2-dichloroethane (Merck) with the highest purity were used as liquid membranes. Acetic acid (Merck), formic acid (Riedel) and nitric acid (Merck) were also used with the highest purity. All aqueous solutions were prepared using double distilled deionized water.

### 2.2. Apparatus

A Shimadzu AA-670 atomic absorption spectrometer (AAS) was used for measurement of metal ions concentration. The



**Scheme 1** Structure of 1,13-bis(8-quinolyl)-1,4,7,10,13-pentaoxatridecane (Kryptofix5).



**Scheme 2** Representation of the bulk type liquid membrane cell used: SP = source phase, RP = receiving phase, MP = membrane phase, A = magnetic stirrer.

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