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Selective Bulk Liquid Membrane Transport of Metal Ions Using Dibenzopyridinio-18-Crown-6 as Ionophore

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The transport experiments standardized 'concentric cells' in which the aqueous source and receiving phases were separated by an organic phase *viz.*, chloroform ($CHCl_3$), 1,2-dichloroethane (1,2-DCE), dichloromethane (DCM), nitrobenzene (NB) and chloroform-nitrobenzene binary mixed solvents. The aqueous source phase consisted of a buffer solution (CH_3COOH/CH_3COONa) at pH = 4.9 and containing an equimolar mixture of Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, Cd^{2+}, Ag^+ and Pb^{2+} metal cations. The organic phase contained the macrocyclic ligand, dibenzopyridinio-18-crown-6 (DBPY18C6) as an ionophore and the aqueous receiving phase consisted of a buffer solution (HCOOH/HCOONa) at pH = 3. The obtained results show that dibenzopyridinio-18-crown-6 is a highly selective ionophore for silver ion and under the employed experimental conditions, it transport only this metal cation among the seven studied metal cations. The influence of the stearic acid, palmitic acid and oleic acid in the membrane phase on the silver ion transport was also investigated. The results show that the transport efficiency of the Ag^+ ion increases in the presence of stearic and palmetic acids. The sequence of transport efficiency for Ag^+ ion in organic solvents is: NB > DCM > 1,2-DCE > $CHCl_3$. The non-linear behaviour was observed for variations of the transport rate of silver ion *vs.* the composition of chloroform-nitrobenzene binary mixtures was discussed in terms of changing the chemical and physical properties of the constituents solvents when they mixed with one another.

Key Words: Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, Cd^{2+}, Ag^+ and Pb^{2+}, Dibenzopyridinio-18-crown-6, Liquid membrane transport, Chloroform, 1,2-Dichloroethane, Dichloromethane, Nitrobenzene, Chloroform-nitrobenzene binary mixtures.

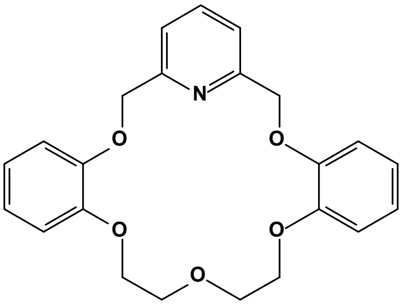
INTRODUCTION

The silver content of environmental samples is increased with the increasing use of silver compounds and silver-containing preparations in industry and in medicine[1,2]. Silver can enter the environment *via* industrial water because it is often as an impurity in copper, zinc, arsenic and antimony ores[3]. It is noteworthy that recent information about the interaction of silver cation with essential nutrients, especially Se, Cu, vitamin E and vitamin B_{12}, have focused attention on potentially toxic nutrients[4]. The separation, preconcentration and sensitive determination of silver ion are of increasing interest[5].

The liquid membrane technique has been emerging as an alternative technique for the separation and preconcentration of several chemical species. It has several advantages over conventional solvent extraction and ion exchange methods[6].

There have been a number of investigations of the transport of some alkali and alkaline earth metal ions[7] and also transition and post-transition metal cations through bulk liquid membranes using various synthetic ionophores. The latter include macrocyclic[8,9] as well as acyclic derivatives[10-12].

In this study, the transport of Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, Cd^{2+}, Ag^{+} and Pb^{2+} metal cations with dibenzopyridinio-18-crown-6 (DBPY18C6) (**I**) as carrier was performed using chloroform ($CHCl_3$), 1,2-dichloroethane (1,2-DCE), dichloro-methane (DCM), nitrobenzene (NB) and chloroform-nitrobenzene binary mixture as liquid membranes. The effect of the stearic acid, oleic acid and palmetic acid as surfactants on transport efficiency of the metal cations was also investigated.



Structure of dibenzopyridino-18-Crown-6 (**I**)

EXPERIMENTAL

Dibenzopyridinio-18-crown-6 (Merck), cobalt(II) nitrate (Riedel), nickel(II) nitrate (G.P.R), copper(II) nitrate (Fluka), zinc(II) nitrate (Merck), silver(I) nitrate (G.P.R), cadmium(II) nitrate, lead(II) nitrate, sodium acetate, sodium hydroxide (all from Merck), stearic acid (BDH), palmitic acid (Riedel) and oleic acid (Merck) were used without further purification. Chloroform (AnalR), nitric acid (BDH), 1,2-dichloroethane, nitrobenzene, dichloromethane, acetic acid and formic acid (all from Merck) were used with the highest purity. All aqueous solutions were prepared using deionized double distilled water.

Apparatus and procedure: For transport study of the heavy metal cations across a liquid membrane, two bulk type 'concentric cells' in which the aqueous source phase (10 mL) and receiving phase (30 mL) were separated by an organic phase (50 mL) were used in this study (Fig. 1). Details of the cell design have been reported elsewhere[13]. Both aqueous and organic phases were stirred separately at 20 rpm and the cells were enclosed by a water jacket and thermostated at 25 ºC.

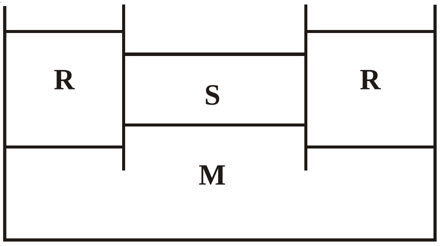


Fig. 1. Liquid membrane apparatus (S = source phase, R = receiving phase, M = membrane phase)

The aqueous source phase consisted of a buffer solution at pH = 4.9 ± 0.1 (6.95 mL of 2 mol dm^{-3} sodium acetate solution and 3.05 mL of 2 mol dm^{-3} acetic acid made up to 100 mL)[14] containing an equimolar mixture of the metal cations (0.01 M). The organic solvents: chloroform, 1,2-dichloroethane, nitrobenzene, dichloromethane and chloroform-nitrobenzene binary mixtures were used as membrane phase, were presaturated with water by shaking a two-phase mixture and removing the aqueous phase. The organic phase contained the macrocycle ionophore (0.001 M) and the receiving phase consisted of a buffer solution at pH = 3 ± 0.1 (56.6 mL of 1 mol dm^{-3} formic acid and 10 mL of 1 mol dm^{-3} sodium hydroxide made up to 100 mL)[14]. After 24 h, the metal ions concentrations of both aqueous phases were measured by atomic absorption spectroscopy (Shimadzu-670) along with a series of standard solutions which were made similary, in order to convert the atomic absorption signals to concentration units.

RESULTS AND DISCUSSION

Effect of solvent upon fluxes and selectivity: The data for competitive transport of Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, Cd^{2+}, Ag^{+} and Pb^{2+} metal cations from an aqueous source phase through chloroform, 1,2-dichloroethane, dichloromethane and nitrobenzene membranes containing dibenzopyridinio-18-crown-6 ligand at 25 ºC are given in Table-1 (Fig. 2). As is seen from this Fig. 2, the rate of transport of silver ion by this ligand is varied in order: NB > DCM > 1,2-DCE > $CHCl_3$. The higher polarity of nitrobenzene ($\mu = 4$)[15] compared to the other organic solvents results in

TABLE-1
DATA FOR SEVEN-METAL IONS COMPETITIVE TRANSPORT ACROSS ORGANIC SOLVENTS AS BULK MEMBRANE WITH DBPY18C6 LIGAND AT 25 ºC

Solvent	Co(II)	Ni(II)	Cu(II)	Zn(II)	Cd(II)	Ag(I)	Pb(II)
$CHCl_3$							
%(Receiving)[a]	–	–	–	–	–	3.86	–
%(Membrane)[b]	75.69	88.52	84.42	91.50	–	86.44	94.45
J (mol per 24 h)[c]	–	–	–	–	–	4.83	–
1,2-DCE							
%(Receiving)[a]	–	–	–	–	–	7.07	–
%(Membrane)[b]	–	–	67.81	9.29	99.18	–	0.88
J (mol per 24 h)[c]	–	–	–	–	–	8.84	–
NB							
%(Receiving)[a]	–	–	–	–	–	19.03	–
%(Membrane)[b]	–	–	71.79	20.65	98.20	17.31	16.07
J (mol per 24 h)[c]	–	–	–	–	–	23.79	–
DCM							
%(Receiving)[a]	–	–	–	–	–	12.71	–
%(Membrane)[b]	–	6.64	16.24	24.45	21.35	38.43	14.46
J (mol per 24 h)[c]	–	–	–	–	–	15.88	–

[a] Per cent of total metal cations in the receiving phase after 24 h.
[b] Per cent of total metal cations in the membrane phase after 24 h.
[c] All values are × 10^{-7}.

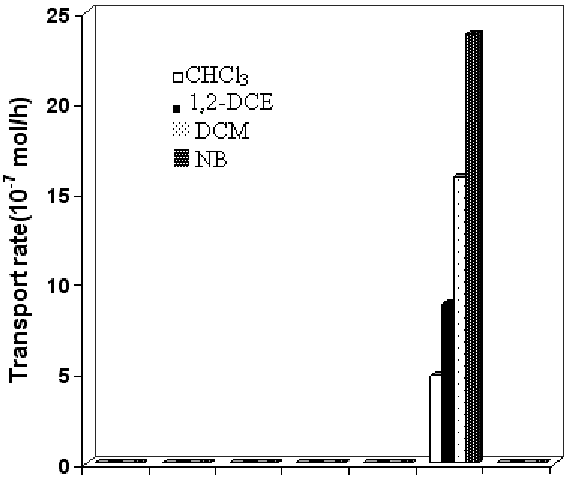


Fig. 2. Comparison of the results of metal ion transport (water/organic solvent/ water) studies with DBPY18C6 ligand. Source phase: pH = 4.9 (CH_3COOH/ CH_3COONa) containing metal ions at 0.01 M (10 mL). Membrane phase: contains DBPY18C6 (0.001 M) (50 mL). Receiving phase: pH = 3.0 (NaOH/ HCOOH), (30 mL) stirred for 24 h; enclosed in a water jacket at 25 ºC

higher solubility of the $(DBPY18C6.Ag)^+$ complex in membrane phase and, therefore, the transport rate of Ag^+ ion in this organic phase is higher than the other organic solvents[16].

Although the dipole moment of DCM (μ = 1.55) is lower than that of 1,2-DCE (μ = 1.88), but the J value for silver ion transport is larger in DCM with respect to 1,2-DCE. The lower dielectric constant of DCM (ε = 8.93) than that of 1,2-DCE (ε = 10.1) may aid the ion-pair formation in DCM which results in a better transfer rate in dichloromethane membrane phase[17].

As is evident from Table-1, the selectivity of dibenzopyridinio-18-crown-6 for Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, Cd^{2+}, Ag^+ and Pb^{2+} metal cations does not depend on the identity of organic solvents that used as membrane phase.

Effect of time: Some experiments were performed for investigation of the effect of time on the values of the Ag^+ ion transport from source phase into the receiving phase through NB solvent as membrane phase (Fig. 3). As is shown in this Figure, the optimum time for transport of silver ion under the employed experimental conditions is *ca.* 20 h.

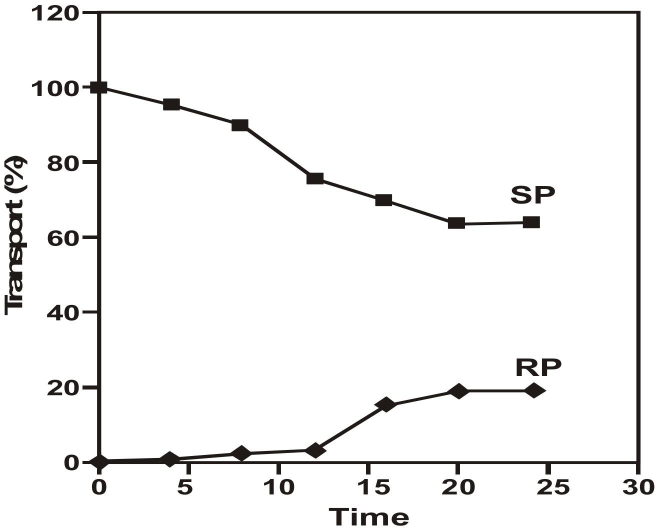


Fig. 3. Time dependence of silver(I) transport (water/nitrobenzene/water) with DBPY18C6. Source phase: pH = 4.9 (CH_3COOH/CH_3COONa) containing metal ions at 0.01 M (10 mL). Membrane phase: contains DBPY18C6 (0.001 M) (50 mL). Receiving phase: pH = 3.0 (NaOH/HCOOH), (30 mL) stirred for 24 h; enclosed in a water jacket at 25 °C

Effect of the surfactants on transport efficiency: The influence of the stearic acid, palmetic acid and oleic acid as surfactants in the membrane phase on the silver ion transport was also investigated. The results are summarized in Table-2. As is evident from this Table, the efficiency of Ag^+ ion transport increases in the presence of stearic and palmitic acids. This confirms the cooperative action of the two components as carriers. A possible explanation for this cooperative behaviour would be the existence of some proton-donor and proton-accepter interactions between surfactant (as proton donor) and nitrogen atom of DBPY18C6 (as proton acceptor) which can impart a greater dgree of lipophilicity to the crown-cation complex, in order to facilitate the cation transport through liquid membrane[18].

TABLE-2
EFFECT OF SURFACTANTS ON SILVER ION TRANSPORT[a]

Fatty acid	%Transport into receiving phase	%Remaining in source phase
–	3.86	87.24
Stearic acid	8.29	73.02
Palmetic acid	5.18	62.11
Oleic acid	1.57	85.55

[a] Experimental conditions: Source phase: pH = 4.9, containing metal ions 0.01 M (10 mL), Membrane phase: contain DBPY18C6 (0.001 M) and surfactant (0.004 M) (50 mL) in chloroform. Receiving phase: pH = 3 (30 mL) stirred for 24 h, enclosed in a water jacket at 25 ºC.

In addition, the nature of the fatty acid used in this study would also influence the flux of Ag^+ ion transport. As is seen from Table-2, the rate of silver ion transport varies in the order: stearic acid > palmitic acid > oleic acid. It seems that both the acidity and lipophlicity of the fatty acids influence the transport efficiency of the Ag^+ ion through chloroform as membrane phase.

Effect of ligand: The results showed that the transport of the metal cations into the receiving phase was undetectable in absence of DBPY18C6 in the organic liquid membranes.

The selectivity and fluxes of the metal cations are strongly influenced by the nature of macrocyclic ligand. The relative size of the metal ion to the cavity size of the macrocyclic ligand can play an important role in the selectivity of the ligand for the metal cations[19]. The observed J values for Ag^+ ion transport (Table-1) show that DBPY18C6 effectively transports the Ag^+ ion into the aqueous receiving phase. Since the ionic size of Ag^+ cation (ionic radius = 1.15 Å) is very close to the cavity size of the ligand (2.6-3.2 Å)[20] and in addition, since the interaction between the Ag^+ cation as a soft acid with the nitrogen atom of DBPY18C6 ligand as a soft base[21] is stronger than the other studied metal cations and the Ag^+ cation may also interact with the π-electron system of aromatic substituents present in the macrocyclic ligand[22], therefore, the Ag^+ ion forms a stronger complex with this ligand which results in a higher transfer rate for this metal cation with respect to the other studied metal cations. This result is in agreement with stability of the complex which is formed between the Ag^+ ion and PY18C6[19].

TABLE-3
DATA FOR SEVEN-METAL IONS COMPETITIVE TRANSPORT ACROSS $CHCl_3$-NB BINARY SYSTEMS AS BULK MEMBRANE WITH DBPY18C6 AT 25 ºC

Solvent	Co(II)	Ni(II)	Cu(II)	Zn(II)	Cd(II)	Ag(I)	Pb(II)
Pure $CHCl_3$							
%(Receiving)[a]	–	–	–	–	–	3.86	–
%(Membrane)[b]	75.69	88.52	84.42	91.50	–	86.44	94.45
J (mol per 24 h)[c]	–	–	–	–	–	4.83	–
75%$CHCl_3$+25%NB							
%(Receiving)[a]	–	–	–	–	–	3.86	–
%(Membrane)[b]	18.85	–	19.35	24.76	21.22	27.08	19.95
J (mol per 24 h)[c]	–	–	–	–	–	4.83	–
60%$CHCl_3$+40%NB							
%(Receiving)[a]	–	–	–	–	–	7.62	–
%(Membrane)[b]	–	–	–	–	–	51.65	10.28
J (mol per 24 h)[c]	–	–	–	–	–	9.53	–
50%$CHCl_3$+50%NB							
%(Receiving)[a]	–	–	–	–	–	15.95	–
%(Membrane)[b]	5.87	–	9.21	18.13	–	44.84	6.28
J (mol per 24 h)[c]	–	–	–	–	–	19.95	–
40%$CHCl_3$+60%NB							
%(Receiving)[a]	–	–	–	–	–	16.56	–
%(Membrane)[b]	–	–	90.74	85.34	–	35.02	95.03
J (mol per 24 h)[c]	–	–	–	–	–	20.72	–
25%$CHCl_3$+75%NB							
%(Receiving)[a]	–	–	–	–	–	12.88	–
%(Membrane)[b]	18.85	–	19.35	21.22	–	40.12	16.95
J (mol per 24 h)[c]	–	–	–	–	–	16.09	–
Pure NB							
%(Receiving)[a]	–	–	–	–	–	19.03	–
%(Membrane)[b]	–	–	71.79	–	98.20	17.31	16.07
J (mol per 24 h)[c]	–	–	–	–	–	23.79	–

[a] Per cent of total metal cations in the receiving phase after 24 h.
[b] Per cent of total metal cations in the membrane phase after 24 h.
[c] All values are × 10^{-7}.

Effect of binary mixed solvents upon fluxes and selectivity: The data for competitive transport of Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, Cd^{2+}, Ag^{+} and Pb^{2+} metal cations with DBPY18C6 ligand in $CHCl_3$-NB binary systems as membrane phase are shown in Table-3. As an example, the graphical results for the transport of the studied metal cations by DBPY18C6 in a binary mixture of $CHCl_3$-NB system (mol % NB = 50) are shown in Fig. 4.

As is evident in Fig. 5, the change of the transport rate of the Ag^{+} ion *vs.* the solvent composition in $CHCl_3$-NB binary mixture is not monotonic. This behaviour may be related to the interactions between chloroform and nitrobenzene molecules in their binary solutions[23] which result in changing some of the chemical and physical properties of each of the solvents such as acidity, basicity, polarity and relative permittivity which will affect the log K_f values for formation of the cation-ligand complex in organic membrane phase. In addition, the composition of the boundary layers and also the partition coefficients of the ligand and the cation-ligand complex may change with the composition of the binary mixed solvent[24].

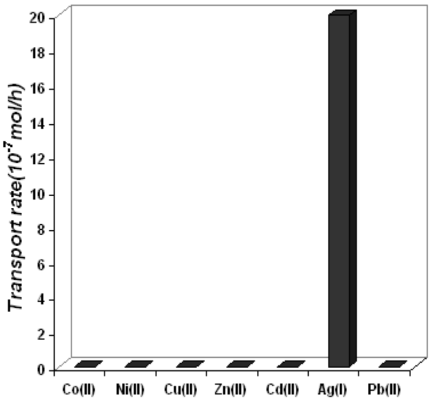


Fig. 4. The results of metal ion transport (water/$CHCl_3$-NB binary solvents/water) with DBPY18C6. Source phase: pH = 4.9 (CH_3COOH/CH_3COONa) containing metal ions at 0.01 M (10 mL). Membrane phase: contains DBPY18C6 (0.001 M) (50 mL) in $CHCl_3$-NB binary solvents (mol % NB = 50). Receiving phase: pH = 3.0 (NaOH/HCOOH), (30 mL) stirred for 24 h; enclosed in a water jacket at 25 ºC

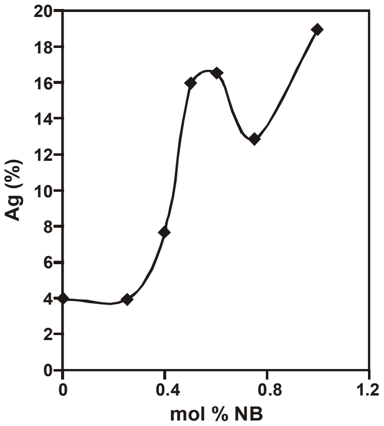


Fig. 5. Changes of silver(I) ion transport with the composition of the $CHCl_3$-NB binary systems. Source phase: pH = 4.9 (CH_3COOH/CH_3COONa) containing metal ions at 0.01 M (10 mL). Membrane phase: contains DBPY18C6 (0.001 M) (50 mL) in $CHCl_3$-NB binary solvents. Receiving phase: pH = 3.0 (NaOH/HCOOH), (30 mL) stirred for 24 h; enclosed in a water jacket at 25 ºC

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