

Study of competitive transport of metal cations through bulk liquid membrane using 4'-nitrobenzo-18-crown-6 and diaza-18-crown-6

Gholam Hossein Rounaghi · Malihe Sadat Hosseiny · Mahmud Chamsaz

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Abstract The competitive metal ion transport experiments of copper(II), cobalt(II), zinc(II), cadmium(II), silver(I), chromium(III) and lead(II) were carried out by 4'-nitrobenzo-18-crown-6 (NB18C6) and diaza-18-crown-6 (DA18C6) as carrier in organic membrane phase. The source phase contained equimolar concentrations of metal ions at pH 5 and the receiving phase being buffered at pH 3. Fluxes and selectivities for competitive metal cations transport across bulk liquid membranes by the lipophilic crown ethers have been determined in a variety of chlorinated hydrocarbon and aromatic hydrocarbon solvents. The membrane solvents include: dichloromethane (DCM), chloroform (CHCl_3), 1,2-dichloroethane (1,2-DCE), nitrobenzene (NB), chloroform–nitrobenzene (CHCl_3 –NB) and chloroform–dichloromethane (CHCl_3 –DCM). The obtained results show that the selectivity and efficiency of transport for these heavy metal cations change with the nature of the ligand and also the organic solvents, which were used as liquid membrane in these experiments. Although a good selectivity was observed for lead(II) cation by 4'-nitrobenzo-18-crown-6 in all membrane systems, but the highest transport rate for this cation was obtained in DCM. Also, no transport was observed for these metal cations by diaza-18-crown-6 in all membrane systems. A linear relationship was observed between the transport rate of lead(II) cation by 4'-nitrobenzo-18-crown-6 and the composition of CHCl_3 –DCM binary solution, but a non-linear behavior was found in the case of CHCl_3 –NB binary solution. The influence of the stearic, palmitic and oleic acids as surfactant in the membrane phase on the transport of metal cations was also investigated.

Keywords Bulk liquid membrane transport · Cobalt(II) · Copper(II) · Chromium(III) · Silver(I) · Cadmium(II) · Zinc(II) · Lead(II) · 4'-nitrobenzo-18-crown-6 · Diaza-18-crown-6

Introduction

Selective transport of cationic substrates by membrane carriers is of great importance in industrial, analytical chemistry, biology, and separation sciences. In most cases, various interfering species must be removed and/or the species of interest must be enriched before detection is possible. Carrier mediated transport through liquid membrane is well known as one of the most powerful tools for such concentration, separation and recovery. The liquid membrane consists of an organic phase, which contains the carrier responsible for the transport of metal ions, placed between two aqueous phases. Compared with conventional separation processes, such as liquid–liquid extraction, membrane techniques are characterized by the technical simplicity and high efficiency in separating or enriching material from gaseous or liquid mixtures.

The bulk liquid membrane techniques have been widely used for metal ion separations [1–8], and to a lesser degree for separation of organic substances [9–11]. The principle of such separation techniques was explained by Danesi [12]. Over the past 40 years, a large number of macrocyclic receptors have been synthesized and evaluated for their abilities to transport cations [13, 14]. Macrocyclic compounds such as crown ethers, azacrowns, cryptands, and calixarenes have been well known for selective recognition of specific metal ions or molecules [15–19]. In these respects, they resemble the naturally occurring antibiotic macrocycles, which have been shown to alter the

G. H. Rounaghi (✉) · M. S. Hosseiny · M. Chamsaz
Department of Chemistry, Faculty of Sciences, Ferdowsi
University of Mashhad, Mashhad, Iran
e-mail: ghrounaghi@yahoo.com

permeability of biological membranes to certain cations [20–22]. As pointed out by Menger and Lee [23], liquid organic solvents bear very little similarity with biological membranes; however, they may be useful for evaluating the factors playing a role in the translocation from and to aqueous pools through an organic phase.

Although many carriers on the transport of alkali and alkaline earth metal cations through liquid membranes have been reported so far [24–27], relatively few carriers have been reported for the selective and efficient transport of transition- or heavy-metal ions [28–34], while it is important from biological, medical, environmental and industrial points of view.

The aim of the present study, is to investigate the selectivity of two macrocyclic ligands i.e. 4'-nitrobenzo-18-crown-6 (NB18C6) (**I**) and diaza-18-crown-6 (DA18C6) (**II**) (Scheme 1) as carriers towards seven metal ions that are present together in solution at equimolar concentrations across bulk liquid membrane. In this paper, we report the results of competitive of seven-metal membrane transport experiments involving Cr^{3+} , Co^{2+} , Cu^{2+} , Ag^+ , Cd^{2+} , Zn^{2+} and Pb^{2+} metal cations with NB18C6 and DA18C6 as carriers, using dichloromethane (DCM), chloroform (CHCl_3), 1,2-dichloroethane (1,2-DCE), nitrobenzene (NB) as liquid membrane. The effect of the stearic, oleic and palmitic acids as surfactants on transport efficiency of the metal cations was also investigated. The effect of binary mixtures of chloroform–nitrobenzene (CHCl_3 –NB) and chloroform–dichloromethane (CHCl_3 –DCM) as liquid membrane on transport of Pb^{2+} cation by NB18C6 was also investigated.

Experimental

Reagents

4'-nitrobenzo-18-crown-6 (Merck), diaza-18-crown-6 (Merck), cobalt(II) nitrate (BDH), copper(II) nitrate

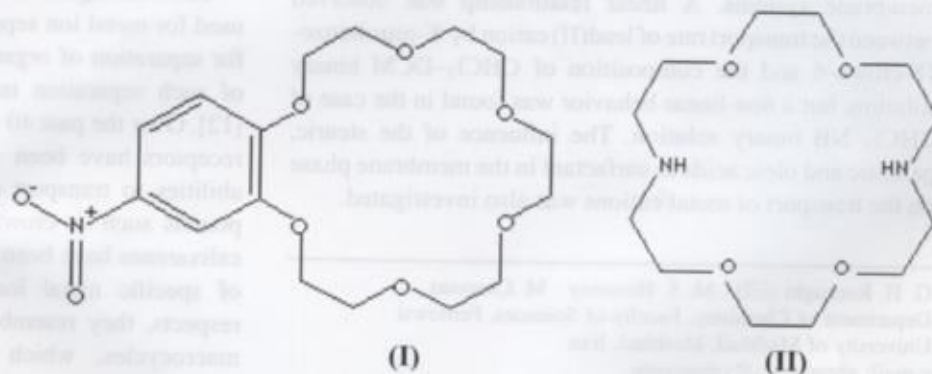
(BDH), zinc(II) nitrate (Merck), silver(I) nitrate (Merck), cadmium(II) nitrate (Riedel), lead (II) nitrate (BDH), chromium(III) nitrate (BDH), sodium acetate, sodium hydroxide, palmitic acid (all from Riedel), stearic acid (BDH) and oleic acid (Merck) were used without further purification. Chloroform (BDH), 1,2-dichloroethane, dichloromethane and nitrobenzene (all from Merck) with highest purity were used as liquid membranes. Acetic acid (Merck), formic acid (Riedel) and nitric acid (Merck) were used as received. All aqueous solutions were prepared using deionized double distilled water.

Procedure

The transport experiments employed standardized concentric cells in which the aqueous source phase (10 cm³) and receiving phase (30 cm³) separated by an organic phase (50 cm³) (Fig. 1). All transport experiments were carried out at ambient temperature. The organic layer was stirred by a Teflon-coated magnetic bar. Speed of stirrer was adjusted so that the phases did not mix with each other. Under these conditions, not only the mixing process is perfect, but also the interfaces between the organic membrane and the two aqueous phases remained flat and were well defined.

The inner aqueous phase (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) containing an equimolar mixture of the metal cations (0.01 M). 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) [35]. In the course of the transport experiment, after 24 h, samples of both aqueous phases were analyzed for metal content by atomic absorption spectroscopy using a Shimadzu-670 atomic absorption spectrophotometer.

Scheme 1 Structure of 4'-nitrobenzo-18-crown-6 (**I**) and diaza-18-crown-6 (**II**)



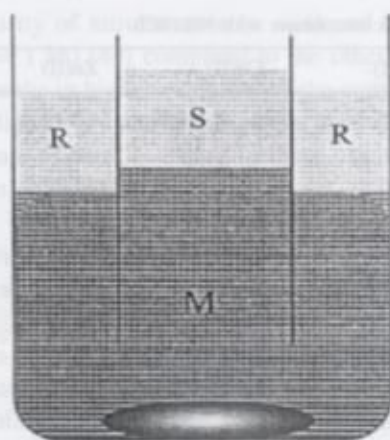


Fig. 1 Liquid membrane apparatus (S: source phase; R: receiving phase; M: liquid membrane)

Results and discussion

Effect of carrier structure on cation transport

The nature of a macrocyclic ionophore such as the ring size, the kind of donor atoms and substituting groups present in the ring has an important effect on cation transport [36, 37]. When a ligating agent complexes with a specific metal ion, the major factors which influence the stability constant are the radius of the metal ion, the

oxidation state of the metal ion, the identity of the donor atoms, the solvation effect, the anion effect, and the dipolar interaction between the organic ligand and the metal ion [18]. In order to evaluate the potential of the crown ethers as ion carriers, liquid membrane transport of transition metal cations were conducted.

The data for competitive of Cr³⁺, Co²⁺, Cu²⁺, Ag⁺, Cd²⁺, Zn²⁺ and Pb²⁺ metal cations from aqueous source phase through dichloromethane, chloroform, 1,2-dichloroethane, nitrobenzene membranes containing DA18C6 and NB18C6 are shown in Tables 1 and 2, respectively. The results obtained in this study with average relative standard deviation of ±0.03%, show that NB18C6 system preferentially transports the Pb²⁺ cation. Although the size of Ag⁺ cation (r = 1.26 Å) is bigger than the size of the Pb²⁺ cation (r = 1.18 Å) and, therefore, it can attain a more convenient fit condition for the crown ether cavity, but since the Pb²⁺ cation has a less soft character than Ag⁺ cation [38], it seems that according to the hard and soft acid–base concept, it can form a more stable complex with the oxygen donor atoms of NB18C6 as a hard base. The use of DA18C6 as ion carrier in the organic membrane resulted no efficient and selective transport of these metal cations through membranes (Table 1). This is probably related to bleeding of this ionophore to aqueous phases through boundary layers because of its low lipophilicity [39].

Table 1 Data for seven-metal ions competitive transport across organic solvents as bulk membrane with DA18C6

Solvent	Cr(III)	Cu(II)	Co(II)	Ag(I)	Cd(II)	Zn(II)	Pb(II)
DCM							
%(Receiving) ^a	– ^d	–	–	–	–	–	–
%(Membrane) ^b	12.77	11.53	20.51	7.19	1.17	31.15	5.14
J (mol per 24 h) ^c	–	–	–	–	–	–	–
CHCl₃							
%(Receiving) ^a	–	–	–	–	–	–	–
%(Membrane) ^b	17.72	13.61	22.68	9.44	7.86	37.16	6.00
J (mol per 24 h) ^d	–	–	–	–	–	–	–
NB							
%(Receiving) ^a	–	–	–	–	–	–	–
%(Membrane) ^b	10.52	10.48	20.51	3.03	1.76	3.15	3.87
J (mol per 24 h) ^c	–	–	–	–	–	–	–
1,2-DCE							
%(Receiving) ^a	–	–	–	–	–	–	–
%(Membrane) ^b	17.25	10.14	24.31	14.27	3.51	36.24	3.87
J (mol per 24 h) ^c	–	–	–	–	–	–	–

The average relative standard deviation for cations transport is obtained ±0.03%

^a Percent of total metal cations in the receiving phase after 24 h

^b Percent of total metal cations in the membrane phase after 24 h

^c All values are × 10⁻⁷

^d The hyphenated symbols mean that the values are about zero

Table 2 Data for seven-metal ions competitive transport across organic solvents as bulk membrane with NB18C6

Solvent	Cr(III)	Cu(II)	Co(II)	Ag(I)	Cd(II)	Zn(II)	Pb(II)
DCM							
%(Receiving) ^a	– ^d	–	–	–	–	–	1.79
%(Membrane) ^b	–	4.00	13.40	6.74	1.58	20.27	8.68
J (mol per 24 h) ^c	–	–	–	–	–	–	2.23
CHCl₃							
%(Receiving) ^a	–	–	–	–	–	–	0.83
%(Membrane) ^b	–	8.17	12.83	12.15	–	14.12	11.40
J (mol per 24 h) ^d	–	–	–	–	–	–	1.04
NB							
%(Receiving) ^a	–	–	–	–	–	–	1.30
%(Membrane) ^b	8.97	16.20	20.10	17.95	8.84	15.30	19.55
J (mol per 24 h) ^c	–	–	–	–	–	–	1.62
1,2-DCE							
%(Receiving) ^a	–	–	–	–	–	–	1.13
%(Membrane) ^b	–	4.55	6.40	9.46	–	–	7.03
J (mol per 24 h) ^c	–	–	–	–	–	–	1.42

The average relative standard deviation for cations transport is obtained $\pm 0.03\%$

^a Percent of total metal cations in the receiving phase after 24 h

^b Percent of total metal cations in the membrane phase after 24 h

^c All values are $\times 10^{-7}$

^d The hyphenated symbols mean that the values are about zero

Effect of solvent upon fluxes and selectivity

According to Izatt and coworkers [40], several parameters whose values depend on the membrane solvent can affect transport of metal cations. These are the thickness of the unstirred boundary layers in the membrane (i.e., the diffusion path length), diffusion coefficients of all mobile species in these boundary layers, and the $\log K_f$ value for formation of the cation–ligand complex in the organic phase. Additional parameters are the partition coefficients of the macrocycle and the cation–ligand complex. The thickness of the boundary layers is a function of the rate at which the solvent is stirred, as well as, its viscosity. The composition of the boundary layers is a function of the mutual water–solvent solubilities. The partitioning of ions into the organic phase should also be affected by the dielectric constant [41].

The data for competitive transport of seven metal cations from an aqueous source phase through different membranes which are listed in Tables 1 and 2, show that the rate of transport of the metal cations depends on the nature of the membrane solvent. As is seen from Fig. 2, the rate of transport of lead(II) cation by NB18C6 is varied in order: DCM > 1,2-DCE > NB > CHCl₃. According to the physicochemical properties of the solvents, this result may be attributed to the lower viscosity of dichloromethane ($\eta = 0.39$) than the other organic solvents (chloroform

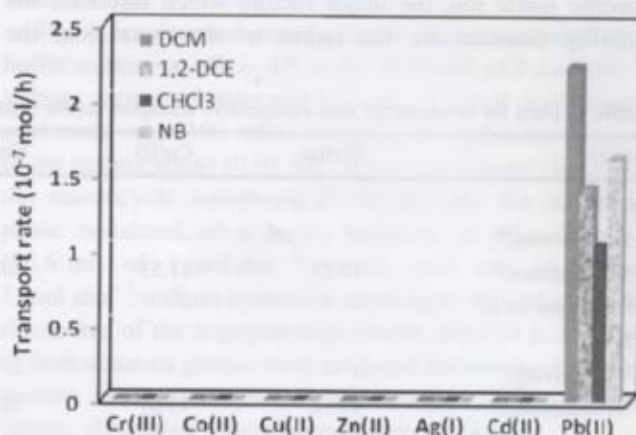


Fig. 2 Comparison of the results of metal ion transport (water/organic solvent/water) studies for NB18C6. Source phase: pH 5.0 (CH₃COOH/CH₃COONa) containing metal ions at 0.01 M (10 mL). Membrane phase: contains NB18C6 (0.001 M) (50 mL). Receiving phase: pH 3.0 (NaOH / HCOOH), (30 mL) stirred for 24 h

($\eta = 0.58$), 1,2-dichloroethane ($\eta = 0.73$), nitrobenzene ($\eta = 1.62$)) which leads to increase the rate of transport in this organic solvent compared to the other three solvents [42].

Although the viscosities of nitrobenzene and 1,2-dichloroethane are higher than that of chloroform, but the J value for lead(II) cation transport is larger in 1,2-dichloroethane and nitrobenzene with respect to chloroform. The

higher polarity of nitrobenzene ($\mu = 4$) and 1,2-dichloroethane ($\mu = 1.86$) [43] compared to the other two organic solvents results in higher solubility of the complex of Pb^{2+} with this ligand in membrane phase and, therefore, the transport rate of lead(II) cation in these organic phases is higher than chloroform.

Effect of binary mixed solvents upon fluxes and selectivity

The results of transport from a source phase containing seven metal cations through chloroform–dichloromethane and chloroform–nitrobenzene binary mixtures containing NB18C6 are listed in Tables 3 and 4. As is evident from

results in Fig. 3, the rate of transport of lead(II) cation is sensitive to the composition of $CHCl_3$ –NB binary solution and a non-linear relationship is observed for variation of the transport rate of this metal cation with the composition of this binary mixed solvent. This behavior may be due to the interactions between the chloroform and nitrobenzene molecules, via formation of an intermolecular hydrogen bond [44] in their binary mixtures, which may result in changing some of the chemical and physical properties of each of the solvents in their binary solutions.

Also, as is evident from Fig. 3, the transport rate of Pb^{2+} cation increases as the concentration of chloroform is lowered in $CHCl_3$ –DCM binary mixed solvent. According to the physicochemical properties of the solvents, the

Table 3 Data for seven-metal ions competitive transport across $CHCl_3$ –DCM binary systems as bulk membrane with NB18C6

Solvent	Cr(III)	Cu(II)	Co(II)	Ag(I)	Cd(II)	Zn(II)	Pb(II)
Pure $CHCl_3$							
%(Receiving) ^a	– ^d	–	–	–	–	–	0.83
%(Membrane) ^b	–	8.17	12.83	12.15	–	14.12	11.40
J (mol per 24 h) ^c	–	–	–	–	–	–	1.04
75% $CHCl_3$ + 25%DCM							
%(Receiving) ^a	–	–	–	–	–	–	0.99
%(Membrane) ^b	–	10.86	11.97	15.87	3.96	15.79	10.95
J (mol per 24 h) ^c	–	–	–	–	–	–	1.24
60% $CHCl_3$ + 40%DCM							
%(Receiving) ^a	–	–	–	–	–	–	1.16
%(Membrane) ^b	–	11.34	12.50	19.05	–	21.40	11.76
J (mol per 24 h) ^c	–	–	–	–	–	–	1.45
50% $CHCl_3$ + 50%DCM							
%(Receiving) ^a	–	–	–	–	–	–	1.24
%(Membrane) ^b	–	10.09	11.72	12.19	2.25	17.05	12.60
J (mol per 24 h) ^c	–	–	–	–	–	–	1.55
40% $CHCl_3$ + 60%DCM							
%(Receiving) ^a	–	–	–	–	–	–	1.41
%(Membrane) ^b	–	3.97	13.96	13.18	–	15.42	9.03
J (mol per 24 h) ^c	–	–	–	–	–	–	1.76
25% $CHCl_3$ + 75%DCM							
%(Receiving) ^a	–	–	–	–	–	–	1.57
%(Membrane) ^b	–	12.36	13.78	14.61	1.18	23.67	10.28
J (mol per 24 h) ^c	–	–	–	–	–	–	1.96
Pure DCM							
%(Receiving) ^a	–	–	–	–	–	–	1.79
%(Membrane) ^b	–	3.99	13.39	6.74	1.58	20.27	8.68
J (mol per 24 h) ^c	–	–	–	–	–	–	2.23

The average relative standard deviation for cations transport is obtained $\pm 0.02\%$

^a Percent of total metal cations in the receiving phase after 24 h

^b Percent of total metal cations in the membrane phase after 24 h

^c All values are $\times 10^{-7}$

^d The hyphenated symbols mean that the values are about zero

Table 4 Data for seven-metal ions competitive transport across CHCl_3 -NB binary systems as bulk membrane with NB18C6

Solvent	Cr(III)	Cu(II)	Co(II)	Ag(I)	Cd(II)	Zn(II)	Pb(II)
Pure CHCl_3							
%(Receiving) ^a	– ^d	–	–	–	–	–	0.83
%(Membrane) ^b	–	8.17	12.83	12.15	–	14.12	11.40
J (mol per 24 h) ^c	–	–	–	–	–	–	1.04
75% CHCl_3 + 25%NB							
%(Receiving) ^a	–	–	–	–	–	–	1.59
%(Membrane) ^b	–	13.24	13.94	50.09	12.95	39.02	10.54
J (mol per 24 h) ^c	–	–	–	–	–	–	1.98
60% CHCl_3 + 40%NB							
%(Receiving) ^a	–	–	–	–	–	–	1.71
%(Membrane) ^b	–	11.52	12.49	50.05	–	35.02	10.15
J (mol per 24 h) ^c	–	–	–	–	–	–	2.14
50% CHCl_3 + 50%NB							
%(Receiving) ^a	–	–	–	–	–	–	1.86
%(Membrane) ^b	–	9.45	12.49	49.34	8.14	40.78	10.76
J (mol per 24 h) ^c	–	–	–	–	–	–	2.33
40% CHCl_3 + 60%NB							
%(Receiving) ^a	–	–	–	–	–	–	3.12
%(Membrane) ^b	–	10.14	11.52	50.05	1.16	26.90	9.52
J (mol per 24 h) ^c	–	–	–	–	–	–	3.90
25% CHCl_3 + 75%NB							
%(Receiving) ^a	–	–	–	–	–	–	2.60
%(Membrane) ^b	–	15.23	16.74	46.55	4.11	29.52	11.81
J (mol per 24 h) ^c	–	–	–	–	–	–	3.24
Pure NB							
%(Receiving) ^a	–	–	–	–	–	–	1.30
%(Membrane) ^b	–	16.20	20.10	17.95	8.84	15.30	19.55
J (mol per 24 h) ^c	–	–	–	–	–	–	1.62

The average relative standard deviation for cations transport is obtained $\pm 0.02\%$

^a Percent of total metal cations in the receiving phase after 24 h

^b Percent of total metal cations in the membrane phase after 24 h

^c All values are $\times 10^{-7}$

^d The hyphenated symbols mean that the values are about zero

higher viscosity of chloroform than that of dichloromethane can result in a decrease in transport rate of the lead ion as the mole fraction of CHCl_3 increases in CHCl_3 -DCM binary solutions. A linear relationship is observed between the transport rate of Pb^{2+} metal cation with the composition of this binary mixture. This probably reveals that there is no significant interaction between the chloroform and dichloromethane molecules that could affect the chemical and physical properties of each of these organic solvents in their binary solutions.

Effect of surfactants on transport efficiency

Surfactant systems have been recognized as very useful agents for improving surface properties and development

new concepts in analytical chemistry. Surfactants, well known as wetting agents, lower the surface tension of a liquid, allow easier spreading, and reduce the interfacial tension between two liquids [45, 46]. Surfactants reduce the interfacial tension between organic solvents and water by being adsorbed at the liquid-liquid interface. They are coupling agents normally functioning at the interface between bulk materials (for example; organic solvents and water) such that what would not normally mix does so in the form of an emulsion or colloid. The hydrophobic non-polar end attaches to organic solvents while the hydrophilic end attaches to water [45–48]. In fact, they serve as a bridge between two immiscible solvents in liquid-liquid interface through which the transport and exchange of molecules and ions take place easily.

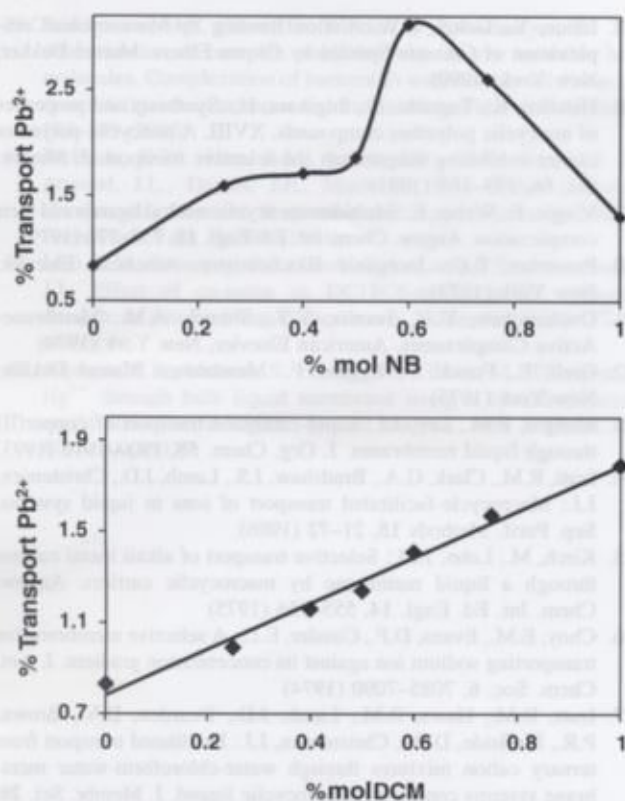


Fig. 3 The changes of Pb^{2+} ion transport with the composition of the $CHCl_3$ -NB and $CHCl_3$ -DCM binary systems. Source phase: pH 5.0 (CH_3COOH/CH_3COONa) containing metal ions at 0.01 M (10 mL). Membrane phase: contains NB18C6 (0.001 M) in $CHCl_3$ -NB and $CHCl_3$ -DCM binary solvents (50 mL). Receiving phase: pH 3.0 (NaOH/HCOOH) (30 mL), stirred for 24 h

The influence of the stearic acid, palmitic acid and oleic acid as surfactant in the membrane phase containing dichloromethane, chloroform, 1,2-dichloroethane and nitrobenzene on lead(II) cation transport by NB18C6 as carrier was also investigated. The results are summarized in Table 5. As is evident from this Table, in most cases, the efficiency of Pb^{2+} cation transport increases in the presence of fatty acids. This confirms the cooperative behaviour of two components as carriers.

Conclusion

The liquid membrane transport experiments of cobalt(II), copper(II), chromium(III), silver(I), cadmium(II), zinc(II) and lead(II) metal cations using NB18C6 and DA18C6 as ion carriers in various organic membranes showed that the rates of cation transport are strongly influenced by the nature of the ligand and also the organic solvents. NB18C6 showed a good selectivity for Pb^{2+} cation and the order of the transport ability of the ligand for this metal cation in different membrane systems was found to be: DCM > 1,2-DCE > NB > $CHCl_3$. While the use of DA18C6 as ion carrier in the organic membranes, resulted in no transport of these metal cations. A good selectivity was also observed for Pb^{2+} cation in the case of using NB18C6 as carrier. A linear behavior was observed between the transport rate of lead (II) cation and the composition of $CHCl_3$ -DCM membrane system, but a non-linear relationship was observed for the case of $CHCl_3$ -NB system.

Table 5 Effect of surfactants on lead ion transport across organic solvents system as bulk membrane with NB18C6

Solvent	Fatty acid	%(Receiving) ^a	%(Membrane) ^b	J (mol per 24 h) ^c
DCM	-	1.79	8.68	2.23
	Stearic acid	1.54	11.44	1.93
	Palmetic acid	1.74	12.23	2.17
	Oleic acid	1.37	9.39	1.72
$CHCl_3$	-	0.83	11.40	1.04
	Stearic acid	0.65	7.09	15.80
	Palmetic acid	0.76	0.95	4.74
	Oleic acid	1.78	12.82	2.23
NB	-	1.30	19.55	1.62
	Stearic acid	2.43	13.72	3.03
	Palmetic acid	3.05	15.93	3.81
	Oleic acid	2.99	11.88	3.74
1,2-DCE	-	1.13	7.03	1.42
	Stearic acid	1.39	14.96	1.74
	Palmetic acid	2.77	9.33	3.47
	Oleic acid	2.12	11.89	2.65

The average relative standard deviation for cations transport is obtained $\pm 0.03\%$

^a Percent of total metal cations in the receiving phase after 24 h

^b Percent of total metal cations in the membrane phase after 24 h

^c All values are $\times 10^{-7}$

The results obtained for competitive liquid membrane transport of the studied metals in the presence of stearic acid, palmitic acid and oleic acid as surfactant in different organic phases show that the transport rate of lead(II) cation increases in the presence of these fatty acids.

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