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

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Abstract   Competitive permeation of seven metal cations from an aqueous source phase containing equimolar concentrations of Co^{2+}, Fe^{3+}, Cd^{2+}, Cu^{2+}, Zn^{2+}, Ag^+ and 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-quino-lyl)-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 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 ($CHCl_3$), 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: DCM > $CHCl_3$ > 1,2-DCE > NB. The competitive transport of these seven metal cations was also studied in $CHCl_3$–NB and $CHCl_3$–DCM binary solvents as membrane phase. The results show that the transport rate of Ag^+ cation is sensitive to the solvent composition and a non-linear relationship was observed between the transport rate of Ag^+ and the composition of these binary mixed non-aqueous solvents. The influence of the stearic acid, 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-enrich-

ment 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 Wieczorek, 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 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 jewelery, 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 Co^{2+}, Fe^{3+}, Cd^{2+}, Cu^{2+}, Zn^{2+}, Ag^+ and 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 ($CHCl_3$), dichloromethane (DCM) and 1,2-dichloroethane (1,2-DCE) as liquid membrane. The effect of binary mixtures of chloroform-nitrobenzene ($CHCl_3$–NB) and chloroform–dichloromethane ($CHCl_3$–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 pur-

ity 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 pH measurements were made with a Metrohm 692 pH-meter using a combined glass electrode.

2.3. Procedure

The transport experiments employed a "concentric cell" in which the aqueous source phase (10 ml) and receiving phase (30 ml) were separated by an organic phase (50 ml) (Scheme 2). Details of the cell design have been reported elsewhere (Chia et al., 1993). The organic phase was magnetically stirred by a Teflon-coated magnetic bar at 20 rpm. The aqueous source consisted of a buffer solution ($CH_3COOH/CH_3COO-Na$) at pH 5 containing an equimolar mixture of metal cations (0.01 M). The organic phase contained Kryptofix5 (1.0×10^{-3} M) and the receiving phase consisted of a buffer solution (HCOOH/HCOONa) at pH 3. A pH gradient is used in order to facilitate the transport of the metal cations across the organic membrane by counter transport of protons. All transport runs were terminated after 24 h and atomic absorption spec-
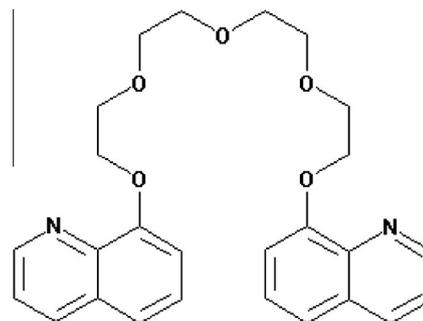
Scheme 1 Structure of 1,13-bis(8-quinolyl)-1,4,7,10,13-pentaoxatridecane (Kryptofix5).
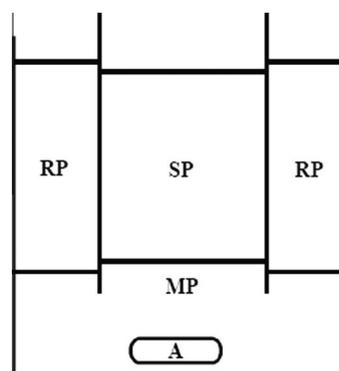
Scheme 2 Representation of the bulk type liquid membrane cell used: SP = source phase, RP = receiving phase, MP = membrane phase, A = magnetic stirrer.
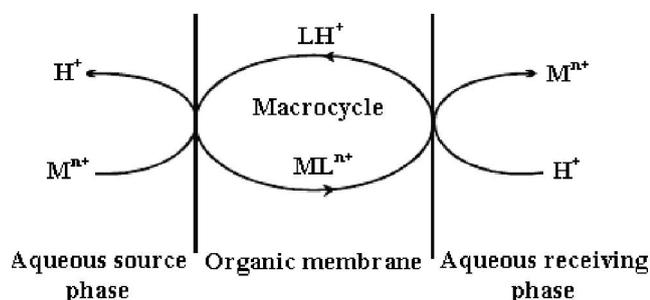
Scheme 3 Diagram illustrating the system used in the current study for the transport of a metal cation across a membrane phase.

troscopy was used to determine the amount of each of the metal cations. The metal ion transport arrangement used in this investigation is represented in Scheme 3.

3. Results and discussion

3.1. Effect of carrier on cation transport

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

The selectivity and fluxes of the metal cations are strongly influenced by the nature of the ligand. The observed J values (transport rate) for the transport of Ag^+ ion in Table 1 show that Kryptofix5 forms a strong complex with Ag^+ cation and preferentially transports this metal cation into the aqueous receiving phase. The attachment of phenyl groups to the ligand increases its lipophilicity, thus increasing its solubility and effectively trapping it in the organic phase into one or both of aqueous phases. In addition, the interaction of π-electron system present in aromatic rings with the silver (I) cation may be effective on complexation process between this metal

cation and the ligand (Rounaghi et al., 2006). Therefore, it seems that silver (I) cation gets self encapsulated by the ligand and hence shows maximum transport efficiency.

3.2. Effect of pure solvents on cation transport

According to Izatt and coworkers (McBride et al., 1984), several parameters whose values depend on the membrane solvent can affect the transport of the metal cations through liquid membranes. These include 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 the formation of the cation–ligand complex in the organic phase. Additional parameters are the partition coefficients of the ligand and the 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 partitioning of ions into the organic phase should also be affected by the dielectric constant of the medium (Izatt et al., 1986a,b).

The data for competitive transport of Co^{2+}, Fe^{3+}, Cd^{2+}, Cu^{2+}, Zn^{2+}, Ag^+ and Pb^{2+} metal cations from an aqueous source phase through NB, $CHCl_3$, DCM and 1,2-DCE membranes containing the ligand at ambient temperature are given in Table 1 and the graphical results are shown in Fig. 1. As is obvious from this figure, the sequence of transport rate for silver (I) cation in the organic solvents is: DCM > $CHCl_3$ > 1,2-DCE > NB. According to the physicochemical properties of the solvents, these results may be attributed to the lower viscosity of DCM ($\eta = 0.39$) which leads to increase of the rate of ion transfer in this organic solvent compared to the other three organic solvents. Moreover, the low donor number (DN) of dichloromethane (DN = 1) results in decreasing the competition between the solvent and the ligand molecules for the metal cation which leads to increase in the stability of the complex formed between the Ag^+ cation and the ligand

Table 1 Data for seven metal cations competitive transport across organic solvents as bulk liquid membrane with Kryptofix5.

Solvent	Co^{2+}	Fe^{3+}	Cd^{2+}	Cu^{2+}	Zn^{2+}	Ag^+	Pb^{2+}
NB							
% (Receiving)[a]	–[d]	0.03	–	–	0.01	3.56	–
% (Membrane)[b]	–	2.18	–	–	0.65	28.98	12.49
J (mol per 24 h)[c]	–	0.03	–	–	0.02	4.45	–
CHCl₃							
% (Receiving)[a]	–	0.19	–	–	0.03	8.16	0.11
% (Membrane)[b]	0.12	36.71	–	–	1.72	12.68	10.70
J (mol per 24 h)[c]	–	0.24	–	–	0.03	10.20	0.14
DCM							
% (Receiving)[a]	–	–	–	–	0.03	22.01	0.25
% (Membrane)[b]	–	38.48	–	–	1.05	36.94	4.05
J (mol per 24 h)[c]	–	–	–	–	0.04	27.51	0.32
1,2-DCE							
% (Receiving)[a]	–	–	–	–	–	4.37	–
% (Membrane)[b]	–	5.63	–	–	–	25.49	14.58
J (mol per 24 h)[c]	–	–	–	–	–	5.46	–

[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 or they are with high uncertainties.
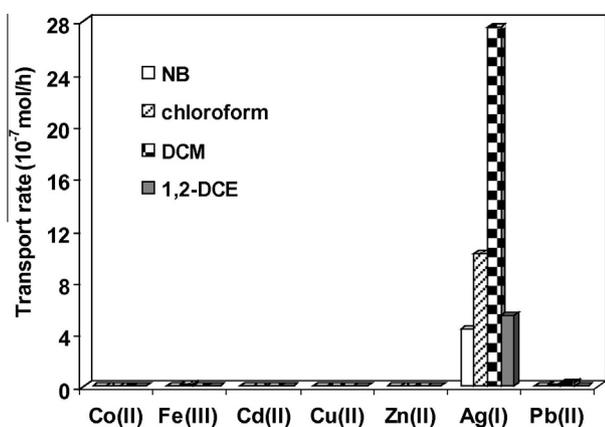
Figure 1 Comparison of the results of metal ions transport (water/organic solvent/water) studies for Kryptofix5. Source phase: pH 5 containing metal cations at 0.01M (10 ml). Membrane phase: contains the ligand (1.0×10^{-3} M) (50 ml). Receiving phase: pH 3 (30 ml), stirred for 24 h.

and, therefore, increasing the transport rate of this metal cation in this organic solvent.

The higher polarity of the solvent results in higher solubility of the complex in membrane phase and, therefore, the transport rate of the metal cation increases. Although the dipole moment of DCM ($\mu = 1.55$) is lower than those of 1,2-DCE ($\mu = 1.86$) and NB ($\mu = 4$) (Izutzu, 2002), but the transport rate for Ag^+ is larger in DCM with respect to the other solvents. The lower dielectric constant of DCM ($\varepsilon = 8.93$) than

those of 1,2-DCE ($\varepsilon = 10.66$) and NB ($\varepsilon = 34.80$), may aid the ion-pair formation in DCM which results in a better transfer rate in this membrane system.

3.3. Effect of binary mixed solvents on cation transport

The results of transport from a source phase containing seven metal cations through $CHCl_3$–NB and $CHCl_3$–DCM binary mixtures containing Kryptofix5 are listed in Tables 2 and 3, respectively. As is evident in these Tables, a good selectivity is observed for silver (I) cation among the seven metal cations. The changes of the transport of Ag^+ cation versus the composition of these binary mixed solvents are shown in Figs. 2 and 3, respectively. As is seen in Fig. 3, in $CHCl_3$–DCM binary solutions, the transport of Ag^+ metal cation increases as the mole fraction of DCM increases. This behavior may be attributed to the lower viscosity and donor number of dichloromethane rather than chloroform.

As is evident in these figures, the transport of Ag^+ cation is sensitive to the composition of $CHCl_3$–NB and $CHCl_3$–DCM binary solutions and a non-linear relationship is observed between the transport rate of this metal cation versus the composition of these binary mixed non-aqueous solvents. This behavior may be related to the interactions between chloroform and nitrobenzene molecules and also between chloroform and dichloromethane molecules in their binary systems which results 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 bound-

Table 2 Data for seven metal cations competitive transport across $CHCl_3$–NB binary systems as bulk liquid membrane with Kryptofix5.

Solvent	Co^{2+}	Fe^{3+}	Cd^{2+}	Cu^{2+}	Zn^{2+}	Ag^+	Pb^{2+}
Pure CHCl₃							
% (Receiving)[a]	–[d]	0.19	–	–	0.03	8.16	0.11
% (Membrane)[b]	0.12	36.17	–	–	1.72	12.68	10.70
J (mol per 24 h)[c]	–	0.24	–	–	0.03	10.20	0.14
75% CHCl₃ + 25% NB							
% (Receiving)[a]	–	–	–	0.01	0.04	9.57	0.13
% (Membrane)[b]	2.78	54.08	–	0.07	1.80	33.21	13.49
J (mol per 24 h)[c]	–	–	–	0.01	0.05	11.96	0.17
50% CHCl₃ + 50% NB							
(Receiving)[a]	–	–	–	–	0.04	4.43	–
% (Membrane)[b]	–	52.65	–	–	5.65	30.77	9.55
J (mol per 24 h)[c]	–	–	–	–	0.05	5.53	–
25% CHCl₃ + 75% NB%							
(Receiving)[a]	–	–	–	–	0.04	5.52	–
% (Membrane)[b]	–	50.69	–	0.79	2.07	26.28	7.86
J (mol per 24 h)[c]	–	–	–	–	0.05	6.91	–
Pure NB							
% (Receiving)[a]	–	0.03	–	–	0.01	3.56	–
% (Membrane)[b]	–	2.18	–	–	0.65	28.98	12.49
J (mol per 24 h)[c]	–	0.03	–	–	0.02	4.45	–

[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 or they are with high uncertainties.

Table 3 Data for seven metal cations competitive transport across CHCl$_3$–DCM binary systems as bulk liquid membrane with Kryptofix5.

Solvent	Co^{2+}	Fe^{3+}	Cd^{2+}	Cu^{2+}	Zn^{2+}	Ag$^+$	Pb^{2+}
Pure CHCl$_3$							
% (Receiving)[a]	–[d]	0.19	–	–	0.03	8.16	0.11
% (Membrane)[b]	0.12	36.71	–	–	1.72	12.68	10.70
J (mol per 24 h)[c]	–	0.24	–	–	0.03	10.20	0.14
75% CHCl$_3$ + 25% DCM							
% (Receiving)[a]	–	–	–	–	0.03	8.09	0.08
% (Membrane)[b]	–	49.06	–	–	4.97	24.08	9.56
J (mol per 24 h)[c]	–	–	–	–	0.04	10.11	0.10
50% CHCl$_3$ + 50%DCM							
(Receiving)[a]	–	–	–	–	0.06	11.95	0.36
% (Membrane)[b]	0.28	2.46	–	–	3.01	21.81	8.20
J (mol per 24 h)[c]		–			0.08	14.93	0.45
25% CHCl$_3$ + 75%DCM							
% (Receiving)[a]	–	–	–	–	0.06	12.48	0.19
% (Membrane)[b]	–	47.13	–	–	0.18	22.52	4.03
J (mol per 24 h)[c]	–	–	–	–	0.08	15.60	0.23
Pure DCM							
% (Receiving)[a]	–	–	–	–	0.03	22.01	0.25
% (Membrane)[b]	–	38.48	–	–	1.05	36.94	4.05
J (mol per 24 h)[c]	–	–	–	–	0.04	27.51	0.32

[a] Percent of total metal cations in the receiving phase after 24 h.
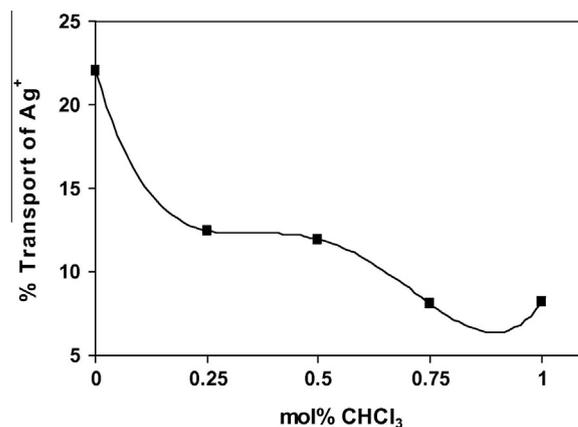[b] Percent of total metal cations in the membrane phase after 24 h.
[c] All values are ×10^{-7}.
[d] The hyphenated symbols mean that the values are about zero or they are with high uncertainties.
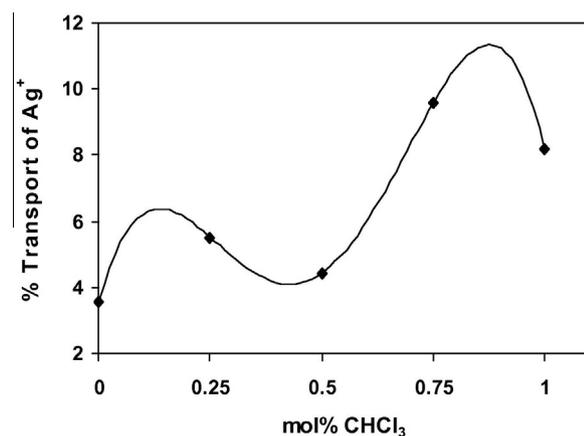
Figure 2 Changes of Ag$^+$ ion transport with the composition of the CHCl$_3$–NB binary system. Source phase: pH 5 containing metal ions at 0.01M (10 ml). Membrane phase: contains Kryptofix5 (1.0×10^{-3} M) in CHCl$_3$–NB binary solvents (50 ml). Receiving phase: pH 3 (30 ml), stirred for 24 h.

Figure 3 Changes of Ag$^+$ ion transport with the composition of the CHCl$_3$–DCM binary system. Source phase: pH 5 containing metal ions at 0.01M (10 ml). Membrane phase: contains Kryptofix5 (1.0×10^{-3} M) in CHCl$_3$–DCM binary solvents (50 ml). Receiving phase: pH 3 (30 ml), stirred for 24 h.

ary layers and also the partition coefficients of the ligand and the complex may change with the composition of the solvents (McBride et al., 1984). The interactions between some binary mixed solvents have been studied (Józwiak, 2004; Rounaghi et al., 2010, 2009). For example, the interaction between the chloroform and nitrobenzene molecules causes the formation of an intermolecular hydrogen bond (Tukhvatullin et al., 1991) in their binary solutions which will affect the log K_{f} values of the complexes in organic membrane phase and also

changing the composition of the boundary layers which results in the desolvation of the aqueous metal species as the membrane phase is varied.

3.4. Effect of surfactants on cation transport

Surfactant systems have been recognized as very useful alternatives for improving analytical methodologies and develop-

Table 4 Effect of surfactants on silver (I) ion transport across organic solvents as bulk liquid membrane with Kryptofix5.

Solvent	Fatty acid	% (Receiving)[a]	% (Membrane)[b]	J (mol per 24 h)[c]
NB	–	3.56	28.98	4.45
	Stearic acid	1.17	27.73	1.46
	Palmitic acid	3.00	26.10	3.75
	Oleic acid	3.54	23.64	4.43
$CHCl_3$	–	8.16	12.68	10.20
	Stearic acid	10.17	7.49	12.71
	Palmitic acid	10.44	10.78	13.05
	Oleic acid	12.41	23.75	15.51
DCM	–	22.01	36.94	27.51
	Stearic acid	13.72	21.06	17.08
	Palmitic acid	18.06	26.88	22.58
	Oleic acid	14.10	19.82	17.62
1,2-DCE	–	4.37	25.49	5.46
	Stearic acid	6.45	28.52	8.07
	Palmitic acid	6.06	30.56	7.58
	Oleic acid	7.31	30.72	9.14

[a] Percent of silver cation in the receiving phase after 24 h.
[b] Percent of silver cation in the membrane phase after 24 h.
[c] All values are $\times 10^{-7}$.

ment of new concepts in analytical chemistry (Hinze et al., 1984; Plizzetti and Pramauro, 1985). Addition of a long chain fatty acid, reduces the degree of carrier loss and also could have a cooperative effect in the uphill transport of the metal cation through the ligand membrane. A possible reason for this cooperative behavior would be existence of some proton donor–acceptor interaction between the lipophilic fatty acid (as proton donor) and the donor atoms of the ligand (as proton acceptor), which can impart a greater degree of lipophilicity to the ligand–metal ion complex, in order to facilitate the cation transport through the liquid membrane (Dadfarnia and Shamsipur, 1992).

The influence of the stearic acid, palmitic acid and oleic acid as surfactant (4.0×10^{-3} M) in the membrane phase containing known concentration of the carrier (1.0×10^{-3} M) and organic solvents (nitrobenzene, chloroform, dichloromethane and 1,2-dichloroethane) on the silver (I) ion transport was also investigated. The results are summarized in Table 4. As is evident from this table, the efficiency of Ag^+ ion transport increases in the presence of the surfactants in $CHCl_3$ and 1,2-DCE as liquid membranes. But, in the case of NB and DCM, the efficiency of Ag^+ ion transport decreases in the presence of the surfactants, therefore, the cooperative behavior in the presence of these long-chain hydrocarboxylic acids is decreased. This may be due to the formation of hydrogen bonds between the donor atoms of the ligand and the acidic proton of the carboxylic acids in these solvent systems which results in formation of a weaker complex between the Ag^+ ion and the ligand in the presence of these fatty acids. Another possibility is the formation of micelles of the fatty acids in the membrane phase which trap the ligand–cation complex and, therefore, the transport rate of Ag^+ ion decreases.

4. Conclusions

The liquid membrane transport experiments of Co^{2+}, Fe^{3+}, Cd^{2+}, Cu^{2+}, Zn^{2+}, Ag^+ and Pb^{2+} metal cations using 1,13-bis(8-quinolyl)-1,4,7,10,13-pentaoxatridecane (Kryptofix5) as ion carrier 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. The carrier showed a good selectivity for Ag^+ cation and the order of the transport ability of the ligand for this metal cation in different membrane systems was found to be: DCM > $CHCl_3$ > 1,2-DCE > NB. A good selectivity was also observed for Ag^+ cation in the case of using $CHCl_3$–NB and $CHCl_3$–DCM binary mixed solvents as membrane phase. The transport rate of Ag^+ is influenced by the composition of the mixed solvents and a non-linear behavior was observed between the transport rate and composition of the membrane system which was discussed in terms of solvent–solvent interactions. The results obtained for competitive liquid membrane transport of the studied metal cations in the presence of stearic acid, palmitic acid and oleic acid as surfactant in different organic phases show that the transport rate of silver (I) cation increases in the presence of these fatty acids in $CHCl_3$ and 1,2-DCE as liquid membranes and decreases in the presence of these fatty acids in NB and DCM liquid membranes.

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