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Metal-Ion Recognition-Competitive Bulk Liquid Membrane Transport of Transition and Post-Transition Metal Cations Using a Thioether Donor Acyclic Ionophore[1]

G. H. Rounaghi, M. H. Arbab-Zavar, E. Fahmideh-Rad, and H. Sadeghian

Department of Chemistry, Faculty of Sciences, Ferdowsi University of Mashhad, Mashhad, Iran

e-mail: ghrounaghi@yahoo.com

Abstract—The competitive bulk liquid membrane transport of Cr^{3+}, Co^{2+}, Cu^{2+}, Zn^{2+}, Cd^{2+}, Ag^+ and Pb^{2+} metal cations with a new synthetic sulfur donor acyclic ligand (pseudo-cyclic ionophore), i.e. 1-(2-[(2-hydroxy-3-phenoxypropyl)sulfanyl]ethylsulfanyl)-3-phenoxy-2-propanol; $(C_{20}H_{26}O_4S_2)$, was examined using some organic solvents as membranes. The membrane solvents include: chloroform $(CHCl_3)$, 1,2-dichloroethane (1,2-DCE), dichloromethane (DCM), nitrobenzene (NB), chloroform-nitrobenzene $(CHCl_3$-NB) and chloroform-dichloromethane $(CHCl_3$-DCM) binary mixtures. The transport process was driven by a back flux of protons, maintained by the buffering the source and receiving phases with pH 5 and 3, respectively. The aqueous source phase consisted of a buffer solution (CH_3COOH/CH_3COONa) at pH = 5 and containing an equimolar mixture of these seven metal cations. The organic phase contained the acyclic ligand, as an ionophore and the receiving phase consisted of a buffer solution $(HCOOH/HCOONa)$ at pH = 3. For these systems that displayed transport behaviour, sole selectivity for Ag^+ cation was observed under the employed experimental conditions in this investigation. The amount of Ag^+ transported follows the trend: 1,2-DCE > $CHCl_3$ > DCM > NB in the bulk liquid membrane studies. The transport of the metal cations in $CHCl_3$−NB and $CHCl_3$-DCM binary solvents is sensitive to the solvent composition. The influence of the stearic acid, palmitic acid and oleic acid in the membrane phase on the ion transport was also investigated.

Acyclic polyether (podant) chemistry has received a great deal of attention for many years, and various types of compounds have been synthesized [1−3]. Selective transport of metal cations using acyclic poly-ethers (podants) has long been studied from the view-points of selective separation, recovery, volume reduc-tion, and selective instrumental sensor applied in most industrial fields [4−6]. Several studies have focused on determination of the selectivity and efficiency of podant-mediated extraction and transport of metal ions through an organic medium into an aqueous receiving phase [7]. In particular, selective separation of silver ion from industrial waste has been remarkably focused [8, 9]. Sulfur-containing podands were reported to show a selective complexation with silver ion over other metal ions [10].

In this study, the transport of Cr^{3+}, Co^{2+}, Cu^{2+}, Zn^{2+}, Cd^{2+}, Ag^+ and Pb^{2+} metal cations with pseudo-cyclic conformation of the organic ligand, 1-(2-[(2-hydroxy-3-phenoxypropyl)sulfanyl]ethylsulfanyl)-3-phenoxy-2-propanol, (Scheme I), as an ion carrier

was performed using chloroform $(CHCl_3)$, 1,2-dichlo-roethane (1,2-DCE), dichloromethane (DCM), nitrobenzene (NB), chloroform-nitrobenzene $(CHCl_3$-NB) and chloroform-dichloromethane $(CHCl_3$-DCM) binary mixtures as liquid membranes. The net result is the transport of Ag^+ cation from the aqueous source phase into the aqueous receiving phase across the bulk organic membrane phase. It is well known that sulfur ligands coordinate with transition metal cations as exclusive donor atoms. In this respect, macrocyclic and noncyclic thio compounds have attracted widespread attention owing to the unique properties of these compounds [11].
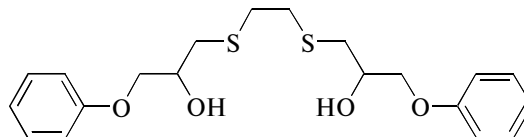
Scheme I. Structure of $C_{20}H_{26}O_4S_2$.

Compared with the solvent extraction, liquid membrane transport for the selective removal, con-centration or purification of given metal cations from
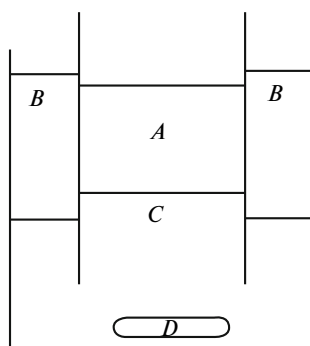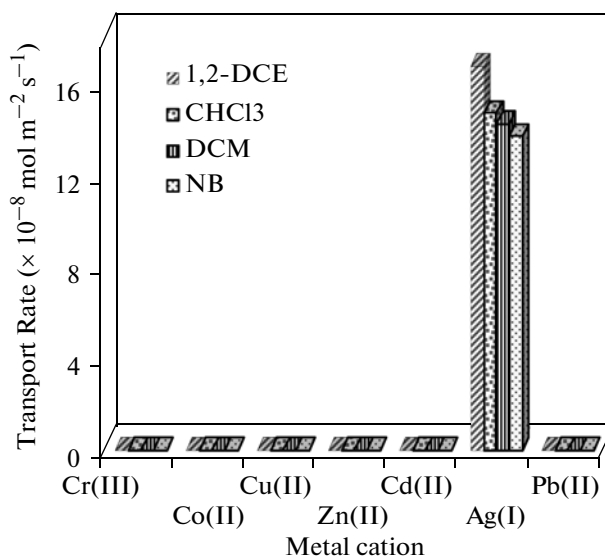
Fig. 1. Representation of the bulk type liquid membrane cell used: *A*, source phase; *B*, receiving phase; *C*, membrane phase; *D*, magnetic stirrer.

Fig. 2. Comparison of the results of metal ion transport (water/organic solvent/water) studies with $C_{20}H_{26}O_4S_2$. Source phase: pH = 5 (CH_3COOH/CH_3COONa) containing metal ions at 0.01 M (10 mL). Membrane phase: contains $C_{20}H_{26}O_4S_2$ (0.001 M), (50 mL). Receiving phase: pH = 3 (NaOH/HCOOH), (30 mL) stirred for 24 h at ambient temperature.

their mixtures have the advantage that the amount of organic solvents and metal ion complexing agents are markedly reduced. However, despite the biological and industrial importance of silver cation, information about its transport across liquid membranes, in comparison with other transition metal cations is sparse [12–14].

EXPERIMENTAL
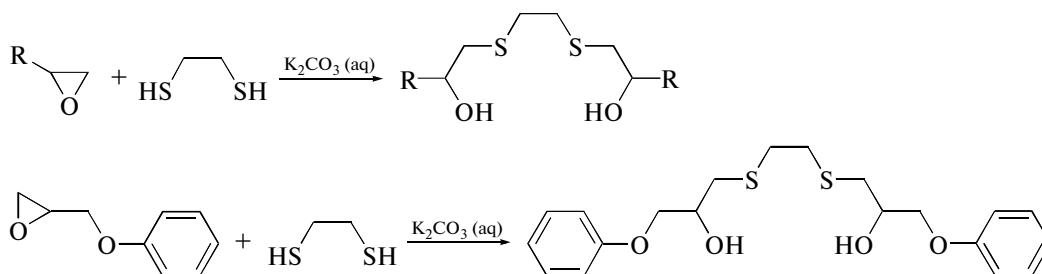
Reagents and Solvents

Chromium (III) nitrate (BDH), cobalt (II) nitrate (BDH), copper (II) nitrate (BDH), zink (II) nitrate (Merck), cadmium (II) nitrate (Riedel), silver (I) nitrate (Merck), lead (II) nitrate (BDH), sodium acetate (Riedel), sodium hydroxide (Riedel), stearic acid (BDH), palmitic acid (Riedel) and oleic acid (Merck) were used without further purification. Formic acid (Riedel), chloroform (BDH), 1,2-dichloroethane, dichloromethane, nitrobenzene, acetic acid and nitric acid, potassium carbonate, dimercaptoethane, epoxide, benzene, ethylacetate, silica gel 60 F_{254} (all from Merck) were used with the highest purity. All aqueous solutions were prepared using deionized double distilled water.

Synthesis of 1-(2-[(2-Hydroxy-3-phenoxypropyl) sulfanyl]-3-phenoxy-2-propanol

Synthetic route for the preparation of acyclic polyethers is described in Scheme II. The β,β'-dihydroxy-dithioethers were prepared by the action of two mole equivalents of epoxides with deporotonated dimercaptoethane which was formed by proton abstracting of carbonate anion under reflux condition and vigorous stirring. The method used here is a simple, efficient and environmentally friendly procedure with excellent yields, high regioselectivity and need not any organic solvents either for reaction medium or extracting the products. Therefore, the work follows the basic aims which are important to green chemistry [15].

Scheme II. Synthetic route for preparation of acyclic polyethers.

Table 1. Data for seven metal cations competitive transport across organic solvents as bulk liquid membrane with $C_{20}H_{26}O_4S_2$ as ligand

Solvent	Cr(III)	Co(II)	Cu(II)	Zn(II)	Cd(II)	Ag(I)	Pb(II)
CHCl₃							
% (Receiving)[a]	—[d]	—	—	—	—	6.05	—
% (membrane)[b]	—	8.32	—	—	3.03	13.42	6.01
J_M (mol m⁻² s⁻¹)[c]	—	—	—	—	—	14.68	—
1,2-DCE							
% (Receiving)[a]	—	—	—	—	—	6.90	—
% (membrane)[b]	2.95	4.20	—	—	—	23.47	4.61
J_M (mol m⁻² s⁻¹)[c]	—	—	—	—	—	16.74	—
DCM							
% (Receiving)[a]	—	—	—	—	—	5.86	—
% (membrane)[b]	—	3.21	6.10	—	—	22.42	7.45
J_M (mol m⁻² s⁻¹)[c]	—	—	—	—	—	14.20	—
NB							
% (Receiving)[a]	—	—	—	—	—	5.64	—
% (membrane)[b]	—	6.06	0.94	—	—	19.03	6.07
J_M (mol m⁻² s⁻¹)[c]	—	—	—	—	—	13.68	—

[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 flux values are ×10⁻⁸.

[d] The hyphenated symbols mean that the values are about zero or they are with high uncertainties.

General Procedure for Ring Opening of Epoxides with Dimercaptoethane

To a solution of potassium carbonate (50 g, 350 mmol) in water (65 mL) was added dimercaptoethane (13.5 mL, 160 mmol) followed by epoxide (300 mmol). The mixture was refluxed in oil bath while stirring vigorously. The completion of reaction was checked by TLC (silica gel 60 F_{254}, benzene-ethylacetate 50 : 50). After completion, the mixture was cooled and the precipitated products, were filtered, washed with water (3×50 mL) and dried in an oven at 50–55° for 4 h. White solid (Found: C, 61.13; H, 6.72; S, 16.07. $C_{20}H_{26}O_4S_2$ requires C, 60.88; H, 6.64; S, 16.25%); mp 79°C (from carbon tetrachloride); δ_H 2.39 (2H, br, 2 × OH), 2.71 (2H, dd, J 7.2 and 15.5, 2 × CH₂S), 2.79 (2H, dd, J 4.2 and 17.8, 2 × CH₂S), 2.85 (4H, s, SCH₂CH₂S), 4.04 (2H, dd, J 6.2 and 15.8, 2 × CH₂O), 4.12 (2H, m, 2 × CH), 4.15 (2H, dd, J 4.1 and 13.7, 2 × CH₂O), 6.84–7.38 (10 H, m, 2 × Ph); δ_C 33.10 (2 × t), 35.80 (2 × t), 69.91 (2 × t), 70.92 (2 × d), 114.90 (2 × d), 121.09 (d), 120.74 (2 × d), 159.23 (d); *m/z* EI 394 (M⁺), 287 (85%) $C_{13}H_{19}O_3S_2$, 243 (86) $C_{11}H_{15}O_2S_2$, 211 (90) $C_{11}H_{15}O_2S$, 75 (100) C_6H_5 [16].

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/ion meter using a combined glass electrode. A bulk type liquid membrane cell was used in all transport experiments.

Procedure

Bulk liquid membrane (BLM) transport measurements were performed at ambient temperature in a
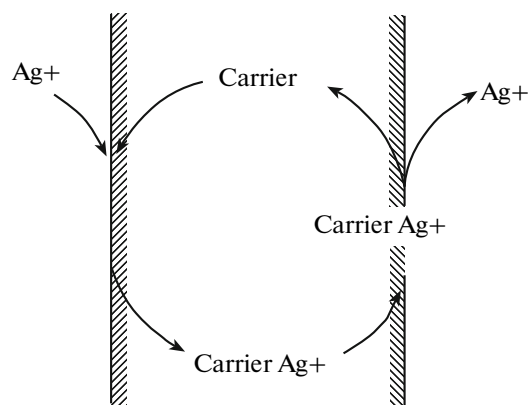
Fig. 3. Liquid membrane system for transport of Ag⁺ cation.

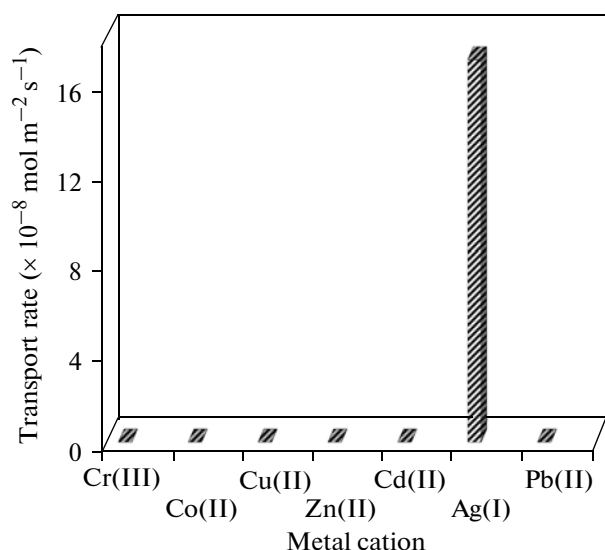**Fig. 4.** The results of metal ion transport (water/DCM/water) with $C_{20}H_{26}O_4S_2$. Source phase: pH = 5 (CH_3COOH/CH_3COONa) containing metal ions at 0.01 M (10 mL). Membrane phase: contains $C_{20}H_{26}O_4S_2$ (0.001 M), (50 mL). Receiving phase: pH = 3 (NaOH/HCOOH), (30 mL) stirred for 24 h at ambient temperature.

cylindrical glass cell (inside diameter 5 cm) holding a glass tube (inside diameter 2 cm), thus separating the two aqueous phases (Fig. 1). The aqueous source phase (10 mL) and receiving phase (30 mL) were separated by an organic phase (50 mL). The two aqueous i.e. source and receiving phases were floating on the organic membrane phase, respectively. The membrane phase was constantly stirred using a Teflon-coated magnetic bar at 20 rpm. The aqueous source phase consisted of a buffer solution (CH_3COOH/CH_3COONa) at pH = 5 containing an equimolar mixture of the metal cations (0.01 M). The organic phase (liquid membrane) contained the synthetic pseudo-cyclic (acyclic) ionophore (0.001 M) and the receiving phase consisted of a buffer solution (HCOOH/HCOONa) at pH = 3. The pH gradient was used in order to facilitate the transport of the metal ions across the organic membrane by counter transport of protons. The organic solvents: $CHCl_3$, 1,2-DCE, DCM, NB, $CHCl_3$-NB and $CHCl_3$-DMC binary mixtures were used as membrane phase.

All transport runs were terminated after 24 h and the samples were withdrawn from the receiving phase and analyzed for the amount of cation transported measurements using atomic absorption spectroscopy along with a series of standard solutions which were made similarly, in order to convert the atomic absorption signals to concentration units. Cation flux (J_M) values were calculated using the relation [17]:

$$J_M = \frac{C_{(receiving)}V}{At},$$

where $C_{(receiving)}$ is the concentration of the metal cation in the receiving phase, mol/L; V is the volume of the receiving phase, L; A is the effective area of membrane, m^2; and t is time, s.

The blank experiments were carried out for BLM transport studies for seven metal cation salts in which the membrane was devoid of carrier. No leakage of cations from source phase into the receiving phase was observed. All measurements were performed in triplicate to check the reproducibility.

RESULTS AND DISCUSSION

Effect of Solvent on Transport Efficiency of the Metal Cations

The ability of the solvent molecules to compete with the donor atoms of the ligand towards the coordination sites of cation is one of the factors that can thermodynamically influence the complexation process [18]. The data for competitive transport of Cr^{3+}, Co^{2+}, Cu^{2+}, Zn^{2+}, Cd^{2+}, Ag^+ and Pb^{2+} metal cations from an aqueous source phase through $CHCl_3$, 1,2-DCE, DCM and NB membranes containing synthetic ligand at ambient temperature is given in Table 1 and the graphical results are shown in Fig. 2.

The obtained results show that the ligand is a highly selective ionophore for Ag^+ cation and under the employed experimental conditions; the Ag^+ cation is transported from the source phase into the receiving phase. The liquid membrane used in this study, is shown schematically in Fig. 3. The movement of charged species through the hydrophobic liquid membrane is accomplished by the presence of a cooperative host composed of ligand. After complexation of the carrier with Ag^+ cation on the left side of the membrane, the complex diffuses down its concentration

Table 2. Some physicochemical properties of organic solvents used as liquid membranes [20]

Solvent	Structure	DN [a]	AN [b]	μ [c]	ε [d]	η [e]	d [f]
Chloroform	$CHCl_3$	4	23.1	1.35	4.8	0.58	1.479
1,2-dichloroethane	$ClCH_2CH_2Cl$	0	16.7	1.86	10.66	0.73	1.250
Dichloromethane	CH_2Cl_2	1	20.4	1.55	8.93	0.39	1.316
Nitrobenzene	$C_6H_5NO_2$	4.4	14.8	4.0	34.8	1.62	1.198

[a] Donor number; [b] Acceptor number ; [c] Dipole moment; [d] Dielectric constant ; [e] Viscosity ; [f] Density.

Table 3. Effect of surfactants on transport efficiency of the metal cations [a]

Membrane phase	Cr(III)	Co(II)	Cu(II)	Zn(II)	Cd(II)	Ag(I)	Pb(II)
CHCl$_3$	–[b]	–	–	–	–	6.05	–
CHCl$_3$ + stearic acid	–	–	–	–	–	7.12	–
CHCl$_3$ + palmitic acid	–	–	–	–	–	7.07	–
CHCl$_3$ + oleic acid	–	–	–	–	–	6.92	–
1,2-DCE	–	–	–	–	–	6.90	–
1,2-DCE + stearic acid	–	–	–	–	–	6.96	–
1,2-DCE + palmitic acid	–	–	–	–	–	9.16	–
1,2-DCE + oleic acid	6.72	6.46	6.56	6.74	6.59	9.01	7.24
DCM	–	–	–	–	–	5.86	–
DCM + stearic acid	–	–	–	–	–	7.49	–
DCM + palmitic acid	–	–	–	–	–	6.98	–
DCM + oleic acid	6.29	6.99	6.62	7.16	6.54	9.51	7.33
NB	–	–	–	–	–	5.64	–
NB + stearic acid	1.03	0.98	1.00	0.79	0.99	6.53	0.95
NB + palmitic acid	1.48	1.27	1.37	1.41	1.29	6.35	1.31
NB + oleic acid	5.41	4.21	4.29	4.38	4.28	8.12	4.45

[a] Data for percent of total metal cations in the receiving phase after 24 h.

[b] The hyphenated symbols mean that the values are about zero or they are with high uncertainties.

gradient. On the right side of the membrane, the metal cation would be released into the receiving phase under the pH gradient. At this stage, the free carrier diffuses back across the liquid membrane. The net result is the transport of Ag$^+$ cation from the aqueous source phase into the aqueous receiving phase across the bulk organic membrane phase.

According to Izatt and coworkers [19, 20], several parameters whose values depend on the membrane solvent can affect the transport rate of metal cations through bulk liquid membranes. These are the thickness of the unstirred boundary layers in the membrane (i.e., the diffusion path length), 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 ligand and 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 metal cations into the organic phase should also be affected by the dielectric constant of the organic solvent as membrane phase. The physical and chemical properties of solvents are closely related to their structures and play important roles in solute−solvent and solute−solute interactions in solutions.

As is seen from Fig. 2, the transport rate of Ag$^+$ cation by this ligand is varied in order: 1,2-DCE > CHCl$_3$ > DCM > NB. As is evident from Table 1, the selectivity of C$_{20}$H$_{26}$O$_4$S$_2$ for Cr^{3+}, Co^{2+}, Cu^{2+}, Zn^{2+}, Cd^{2+}, Ag$^+$ and Pb^{2+} metal cations does not depend on the identity of organic solvents which used as membrane phase in this study.

The results for competitive metal cation transport across 1,2-DCE as organic solvent are shown in Fig. 4. According to the physicochemical properties of the solvents, which are given in Table 2, this result may be attributed to the lower donor number (DN) of 1,2-DCE which leads to decreasing the competition between the solvent and the ligand molecules which results in increasing the stability of the complex formed between the silver cation and the ligand and, therefore, increasing the rate of cation transfer in this organic solvent compared to the other three organic solvents. Another possibility may be related to the higher dielectric constant and the dipole moment of 1,2-DCE ($\varepsilon = 10.66$, $\mu = 1.86$) than those of DCM ($\varepsilon = 8.93$, $\mu = 1.55$) and CHCl$_3$ ($\varepsilon = 4.8$, $\mu = 1.35$). The much higher dielectric constant and dipole moment of NB ($\varepsilon = 34.8$, $\mu = 4.0$), than those of 1,2-dichloroethane, dichloromethane and chloroform, can lead to destabilization of the ion pair in the organic phase leading to a decrease in the rate of transport of Ag$^+$ metal cation through nitrobenzene as liquid membrane phase.

Table 4. Data for seven metal cations competitive transport across $CHCl_3$-NB binary systems as bulk liquid membrane with $C_{20}H_{26}O_4S_2$ as ligand

Solvent	Cr(III)	Co(II)	Cu(II)	Zn(II)	Cd(II)	Ag(I)	Pb(II)
Pure $CHCl_3$							
% (Receiving)[a]	—[d]	—	—	—	—	6.05	—
% (membrane)[b]	—	8.32	—	—	3.03	13.42	6.01
J_M (mol m^{-2} s^{-1})[c]	—	—	—	—	—	14.68	—
75% $CHCl_3$ + 25% NB							
% (Receiving)[a]	0.84	0.77	0.76	1.10	0.94	4.78	0.74
% (membrane)[b]	—	—	—	—	—	63.38	—
J_M (mol m^{-2} s^{-1})[c]	2.03	1.88	1.85	2.66	2.27	11.65	1.80
60% $CHCl_3$ + 40% NB							
% (Receiving)[a]	—	—	—	—	—	4.36	—
% (membrane)[b]	9.62	0.73	4.04	—	—	60.62	3.59
J_M (mol m^{-2} s^{-1})[c]	—	—	—	—	—	10.56	—
50% $CHCl_3$ + 50% NB							
% (Receiving)[a]	—	—	—	—	—	3.55	—
% (membrane)[b]	18.89	1.40	0.21	—	—	38.42	4.83
J_M (mol m^{-2} s^{-1})[c]	—	—	—	—	—	8.61	—
40% $CHCl_3$ + 60% NB							
% (Receiving)[a]	—	—	—	—	—	5.99	—
% (membrane)[b]	—	4.22	2.54	—	3.92	21.33	4.75
J_M (mol m^{-2} s^{-1})[c]	—	—	—	—	—	14.53	—
25% $CHCl_3$ + 75% NB							
% (Receiving)[a]	—	—	—	—	—	3.95	—
% (membrane)[b]	2.88	5.56	—	—	1.64	45.28	5.53
J_M (mol m^{-2} s^{-1})[c]	—	—	—	—	—	9.59	—
Pure NB							
% (Receiving)[a]	—	—	—	—	—	5.64	—
% (membrane)[b]	—	6.06	0.94	—	—	19.03	6.07
J_M (mol m^{-2} s^{-1})[c]	—	—	—	—	—	13.68	—

[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 flux values are $\times 10^{-8}$.
[d] The hyphenated symbols mean that the values are about zero or they are with high uncertainties.

Effect of Ionophore Structure on Transport Efficiency of the Metal Cations

When a ligating agent complexes with a specific metal cation, the major factors which influence the stability constant of the resulting complex are the radius of the metal cation, the oxidation state and also the nature of the metal cation, the identity of the donor atoms of the ligand, the solvation effect, the anion effect, and the dipolar interaction between the organic ligand and the metal cation [9]. Ligands which are suitable as ion-carrier for Ag^+ cation in a liquid membrane system should fulfill certain conditions. They should be selective for Ag^+ over other metal cations; they should have rapid exchange kinetics, and should be sufficiently liphophilic to avoid leaching into the aqueous source and receiving phases. Complexing agents with soft coordination sites like sulfur atoms are known to generate a great affinity toward d^{10} transition metal cations such as Ag^+ [13, 21].

For competitive transport of the seven metal cations, we used a synthetic ionophore. The results showed that the transport of metal cations into the receiving phase was undetectable in absence of the ligand in the organic liquid membranes. The attach-

Table 5. Data for seven metal cations competitive transport across $CHCl_3$-DCM binary systems as bulk liquid membrane with $C_{20}H_{26}O_4S_2$ as ligand

Solvent	Cr(III)	Co(II)	Cu(II)	Zn(II)	Cd(II)	Ag(I)	Pb(II)
Pure $CHCl_3$							
% (Receiving)[a]	—[d]	—	—	—	—	6.05	—
% (membrane)[b]	—	8.32	—	—	3.03	13.42	6.01
J_M (mol m^{-2} s^{-1})[c]	—	—	—	—	—	14.68	—
75% $CHCl_3$ + 25% DCM							
% (Receiving)[a]	—	—	—	—	—	11.15	—
% (membrane)[b]	9.80	—	0.48	—	—	18.60	11.45
J_M (mol m^{-2} s^{-1})[c]	—	—	—	—	—	27.04	—
60% $CHCl_3$ + 40% DCM							
% (Receiving)[a]	—	—	—	—	—	10.29	—
% (membrane)[b]	7.15	—	—	—	—	13.32	4.58
J_M (mol m^{-2} s^{-1})[c]	—	—	—	—	—	23.96	—
50% $CHCl_3$ + 50% DCM							
% (Receiving)[a]	—	—	—	—	—	8.67	—
% (membrane)[b]	24.33	—	—	—	—	8.50	—
J_M (mol m^{-2} s^{-1})[c]	—	—	—	—	—	21.04	—
40% $CHCl_3$ + 60% DCM							
% (Receiving)[a]	—	—	—	—	—	12.29	—
% (membrane)[b]	22.76	—	2.10	—	—	23.72	0.53
J_M (mol m^{-2} s^{-1})[c]	—	—	—	—	—	29.81	—
25% $CHCl_3$ + 75% DCM							
% (Receiving)[a]	—	—	—	—	—	2.90	—
% (membrane)[b]	12.32	3.05	4.79	—	—	23.72	0.53
J_M (mol m^{-2} s^{-1})[c]	—	—	—	—	—	7.04	—
Pure DCM							
% (Receiving)[a]	—	—	—	—	—	5.86	—
% (membrane)[b]	—	3.21	6.10	—	—	22.72	7.45
J_M (mol m^{-2} s^{-1})[c]	—	—	—	—	—	14.20	—

[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 flux values are $\times 10^{-8}$.

[d] The hyphenated symbols mean that the values are about zero or they are with high uncertainties.

ment of two phenyl groups to ligand increases its lipophilicity, thus increasing its solubility and effectively trapping it in the organic phase into one or both of aqueous phases. The observed J_M values for Ag^+ transport (Table 1) with four organic solvents show that the ligand system preferentially transports the Ag^+ cation into the aqueous receiving phase. A strong interaction results between the soft Ag^+ cation (soft acid) and soft donating sulfur atoms of the carrier, therefore, this synthetic ligand acts as the most suitable carrier for the Ag^+ cation through the organic membrane. In addition, the interaction of Pi electron system present in aromatic rings with the silver cation may be effective on complexation process between this metal cation and the ligand. Therefore, the Ag^+ cation gets self encapsulated into the pseudo cavity and hence shows maximum transport efficiency.

Effect of Fatty Acids on Transport Efficiency of the Metal Cations

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 cation through the ligand membrane. A possible reason for this cooperative behavior would be existence of some proton
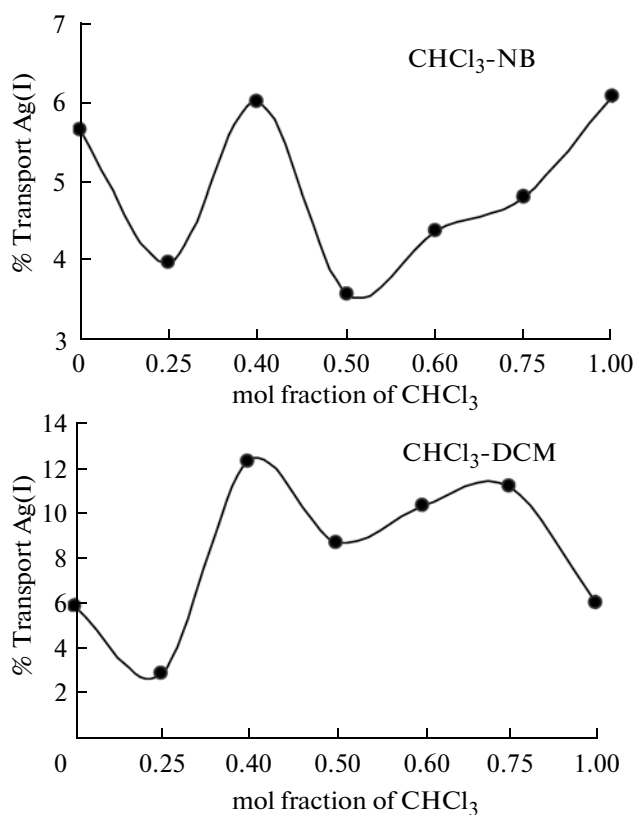
Fig. 5. Changes of Ag$^+$ cation transport with the composition of CHCl$_3$-NB and CHCl$_3$-DCM binary mixed solvents.

synthetic ligand in CHCl$_3$-NB and CHCl$_3$-DCM binary systems as membrane phase are shown in Tables 4 and 5. The graphical results for the transport of the metal cations in CHCl$_3$-NB and CHCl$_3$-DCM binary systems are shown in Fig. 5. As is obvious from these figures, the transport process for the Ag$^+$ metal cation is sensitive to the solvent composition and a non-linear relationship is observed for variation of the transport rate of this metal cation with the composition of the binary mixed solvent. This behaviour may be due to the interactions between chloroform and nitrobenzene molecules and also between chloroform and dichloromethane molecules in their binary solutions. It has been shown that in binary solutions of nitrobenzene and chloroform, the C−H vibration band in the Raman spectra shifts toward higher frequencies which has been explained by the formation of an intermolecular hydrogen bond between chloroform and nitrobenzene molecules in their binary solutions [23].These kinds of interactions will result in changing some of the chemical and physical properties of each of solvents such as acidity, basicity, polarity and relative permittivity which will affect the log K$_f$ value for formation of the cation-ligand complex in organic membrane phase and also changing the composition of the boundary layers, internal structure of the solvent mixtures, and, therefore, changing the desolvation of the aqueous metal species as the membrane phase is varied.

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 grater degree of lipophilicity to the ligand-metal ion complex, in order to facilitate the cation transport through the liquid membrane [22].

In another experiment, the competitive mixed metal ion transport processes (water/organic solvent/water) employed an organic phase containing known concentrations of the ionophore (10^{-3} M) and fatty acids (4×10^{-3} M) as surfactant. The results of the influence of the stearic acid, palmitic acid and also oleic acid as surfactants in the membrane phase on the cation transport are shown in Table 3. As is evident from this Table, the efficiency of Ag$^+$ ion transport increases in the presence of these fatty acids. It seems that both the acidity and lipophilicity of the fatty acids influence the transport efficiency of the Ag$^+$ cation through the membrane phase. As is obvious from these data, the cooperative behaviour in the presence of these long-chain hydrocarboxylic acids is increased.

Effect of Binary Mixed Solvent Membranes on Transport Efficiency of the Metal Cations

The data for competitive transport of Cr^{3+}, Co^{2+}, Cu^{2+}, Zn^{2+}, Cd^{2+}, Ag$^+$ and Pb^{2+} metal cations with the

CONCLUSIONS

The liquid membrane transport experiments of Cr^{3+}, Co^{2+}, Cu^{2+}, Zn^{2+}, Cd^{2+}, Ag$^+$ and Pb^{2+} metal cations using a new synthetic ligand, 1-(2-[(2-hydroxy-3-phenoxypropyl)sulfanyl]ethylsulfanyl)-3-phenoxy-2-propanol (C$_{20}$H$_{26}$O$_4$S$_2$), as an ion carrier in various organic membranes showed that the rates of cation transport are strongly influenced by the nature and composition of the membrane solvents. This synthetic ligand showed a good selectivity for Ag$^+$ cation rather than the other metal cations and the order of the transport ability of the ligand for this metal cation in different membrane systems was found to be: 1,2-DCE > CHCl$_3$ > DCM > 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 the Ag$^+$ cation is influenced by the composition of the mixed solvent and a non-linear behaviour was observed between the transport rate and the composition of membrane systems which was discussed in terms of solvent-solvent interactions. The experimental results obtained for competitive liquid membrane transport of the studied metal cations by this ligand showed that the transport efficiency increases in the presence of fatty acids in organic phase. The simplicity, low cost and high selectivity of the C$_{20}$H$_{26}$O$_4$S$_2$ ionophore for Ag$^+$ cation

transport obtained by the used liquid membrane systems, demonstrate their potential applicability for selective removal concentration or purification of silver cation from its mixtures with the other metal cations in solutions.

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