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Competitive Bulk Liquid Membrane Transport of Heavy Metal Cations Using the 18-Crown-6 Ligand as an Ionophore

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ABSTRACT: Competitive transport of Zn(II), Cd(II), Cr(III), Co(II), Ag(I), Pb(II), and Cu(II) cations from an aqueous source phase at pH 5 through bulk liquid membrane (BLM) containing 18-crown-6 (ion carrier), organic solvents chloroform, dichloromethane, 1,2-dichloroethane, and nitrobenzene, and chloroform–dichloromethane and chloroform–dichloroethane binary mixed solvents into an aqueous receiving phase at pH 3 has been investigated. The influence of the organic solvents and also the effect of some surfactants on the selectivity and transport efficiency of the metal cations through BLMs were studied. The obtained results show that the selectivity and the efficiency of transport for these heavy metal cations change with the nature of the organic solvents which were used as liquid membranes in these experiments. A good transport efficiency and high selectivity was observed for the Pb(II) cation under the experimental conditions in this investigation.

1. INTRODUCTION

Recently a remarkable increase in the applications of liquid membranes for separation processes has been found. A variety of chemical techniques have been employed for metal cation separations, including precipitation, ion exchange, liquid–liquid extraction (LLE), and solid phase extraction (SPE). Among these methods, LLE has been the most widely commercially for the recovery and purification of metal ions.[1] However, this methodology has drawbacks such as high consumption of organic reagents (normally high purity, potentially toxic, and expensive) and carriers, tedious and time-consuming procedures, frequently low enrichment factors, and the need of handling.[2] One serious limitation in traditional solvent extraction processes is the consumption of high purity solvents and carriers, especially in dilute solutions. To avoid some of these drawbacks, solid phase extraction (SPE) is increasingly used (i.e., a solid adsorbent or a bonded organic phase material is employed for analyte separation or preconcentration).[3] The SPE needs lower amounts of reagents than LLE, thus reducing the generation of toxic wastes. Besides, less manual work and cleaner conditions (avoiding sample contamination) are expected to enable better analyte-enrichment factors.[4] Nevertheless, SPE still involves some drawbacks (e.g., its limited capability to tune chemical conditions, possible low analyte recovery, or poor reproducibility).[5]

Membrane extraction, an improved version of solvent extraction, has found applications in the environmental sciences, in water pollution control, and in hydrometallurgical separation.[6,7] The attractive features of transport through membranes are their high selectivity, the simultaneous separation and preconcentration of elements, their simplicity, high transport efficiency, excellent selectivity, economic advantages, low operational costs, low energy consumption, and the fact that they can be used for a broad spectrum of elements by carefully selecting the carrier.[8]

A recent development in liquid membrane transport is the incorporation of selective carriers such as crown ethers within the liquid membrane phase.[9−13] Crown ethers have been studied extensively since their discovery nearly four decades ago.[14] Macrocyclic crown ethers form stable and selective complexes with metal cations and show characteristic cation transport and related functions.[15] Crown ethers as ion carriers have been used successfully for metal ion separation in solvent extraction, transport through liquid membranes, and ion-exchange systems.[16]

The separation and recovery of heavy metal cations from various sources are important from environmental aspects and economical and fundamental study viewpoints.[17] Since little attention has been paid to transport study of heavy and transition metal ions compared to alkali and alkaline earth metal cations, therefore, the information about the coordination behavior of crown ethers toward these metal cations and also their transport through liquid membranes is relatively scarce.[18]

Competitive bulk liquid membrane (BLM) investigations are very important because very often the results that can be achieved from a competitive system about the selective extraction of a cation over the others cannot be obtained from a single cation system,[19,20] and in environment extraction we often deal with numerous cations so we are interested in selective extracting one cation over the others. The goal of the present investigation is to study the effect of the nature of the cation and crown ether and especially the solvent properties on the liquid membrane transport. Here we report the results of liquid membrane transport of some of the heavy and transition metal cations using 18-crown-6 as an ion carrier in various organic liquid membranes.

2. REAGENTS AND SOLVENTS

18-Crown-6 (Merck), cobalt(II) nitrate (BDH), chromium(III) nitrate (BDH), copper(II) nitrate (BDH), zinc(II) nitrate (Merck), silver(I) nitrate (Merck), and cadmium(II) nitrate (Riedel), lead(II) nitrate (BDH), sodium acetate, sodium hydroxide, palmitic acid (all from Riedel), stearic acid (BDH), and oleic acid (Merck) were used without further purification. The solvents, chloroform (BDH), dichloromethane, 1,2-dichloroethane, and nitrobenzene, all from Merck with the highest purity, were used as liquid membranes.

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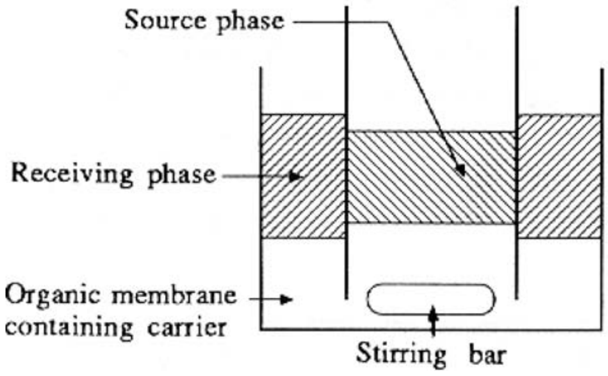

Figure 1. Liquid membrane cell.

Acetic acid (Merck), formic acid (Merck), and nitric acid (BDH) were used as received. All aqueous solutions were prepared using double-distilled deionized water.

3. PROCEDURE

The transport experiments employed standardized concentric cells in which the aqueous source phase (10 cm^3) and receiving phase (30 cm^3) were separated by an organic phase (50 cm^3). Details of the cell are shown in Figure 1. For each experiment, the organic phase (liquid membrane) was stirred at 20 rpm. The aqueous source phase consisted of a buffer solution at pH 4.9 ± 0.1 (6.95 cm^3 of 2 $mol \cdot dm^{-3}$ sodium acetate solution and 3.05 cm^3 of 2 $mol \cdot dm^{-3}$ acetic acid made up to 100 cm^{-3}) containing an equimolar mixture of the metal ions, each at the concentration of $1.0 \cdot 10^{-2}$ $mol \cdot dm^{-3}$. The organic phase contained the macrocycle at 10^{-3} $mol \cdot dm^{-3}$. The receiving phase consisted of a buffer solution at pH 3.0 ± 0.1 (56.6 cm^3 of 1 $mol \cdot dm^{-3}$ formic acid and 10 cm^3 of 1 $mol \cdot dm^{-3}$ sodium hydroxide) made up to 100 cm^{-3}.[21] All transport runs were terminated after 24 h, and atomic absorption spectrometry (AAS) was used to determine the amount of each metal ion transported over this period. Both source and receiving phases were analyzed (using a Shimadzo spectra AA-670 spectrometer) after each transport run. This also enabled the amount of the metal cations remaining in the membrane phase to be calculated. Reproducibility was confirmed to be 2 %. The transport results are quoted as the average values obtained from four experiments. In all cases, we used AAS for the measurement of the concentration of each metal cation in receiving and source phases. Because of its relatively low cost and high selectivity, AAS is generally the main instrument of analytical chemistry laboratories for the determination of heavy metal ion traces. This method is the most popular technique and has become established through its ability to provide very sensitive, accurate, precise determinations of trace and ultratrace elements and species in solid and liquid samples. These include high purity solutions, environmental materials, different types of water (rain, tap, river, sea, waste), biological and medical fluids (blood, serum, urine), and nuclear and radioactive waste solutions.

4. TRANSPORT MECHANISM

Transport of chemical species across liquid membranes occurs because of diffusivity and solubility differences between the aqueous and the membrane phases.

Ligands which form strong complexes lead to the recovery of the metal cation−guest complex:

$$M^+_{solv} + ligand_{solv} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} [M^+ligand]_{solv}$$

$$K_s = \frac{k_1}{k_{-1}} \tag{1}$$

Equation 1 defines the stability constant K_s for ligand−cation complexation. In most applications of solvent extraction, the cation is extracted from one liquid phase (aqueous source phase), transported through a hydrophobic membrane, and then deposited into an aqueous receiving phase.

This process demands that the cation carrier possess different properties in the different phases. In the source phase, binding should be strong and rapid, so both K_s and k_1 should be large. When passing through the hydrophobic membrane, the cation needs to remain bound strongly, so K_s must again be large. Finally the cation must be released into the receiving phase; therefore, K_s should now be small and k_{-1} large. In most cases, this presents a paradox and requires some compromise between host−guest binding strength and ligand dynamics.[22]

In transport systems, when the formation of a complex between the transported material and the carrier and dissociation of the complex are very fast and the stability constant of the complex in source−membrane interface and in membrane is large, mass transport of the complex in the membrane is the rate-determining step. Fick's first law is applied to quantify solute mass transport across liquid membranes, since the driving force for the transported species is considered a potential gradient through the different diffusional layers (aqueous and liquid membranes). Fick's law is expressed as:[23]

$$J_i = -D_i \cdot \frac{dC_i}{dx} \tag{2}$$

where J_i stands for the diffusive mass-transport flux of solute i, D_i for its diffusion coefficient, C_i for concentration, and x for the direction of diffusion. Another parameter used is the permeability coefficient, P, defined as:

$$P = D \cdot D_f \tag{3}$$

where D and D_f are the diffusion and distribution coefficients, respectively.

The carrier acts as an extractant agent favoring analyte transport from the feed solution to the stripping solution, due to its ability to complex with the analyte. The use of liquid membrane-dissolved carriers leads to higher mass fluxes, better selectivity, and higher preconcentration factors. Hence, carrying out an exhaustive study of the system becomes necessary to achieve these properties.

5. RESULTS AND DISCUSSION

To test the selectivity of the system under investigation, the transport of the seven metal cations was carried out by placing equimolar amounts of the cations in the source phase.

The results for competitive transport of the cations from a source phase at pH 4.9 through four liquid membranes: chloroform, dichloromethane, 1,2-dichloroethane, and nitrobenzene containing 18-crown-6 into the acidic receiving phase (pH 3) are listed in Table 1. The results obtained in the case of 1,

Table 1. Data for Competitive Transport of Seven Metal Cations across Bulk Chloroform, Dichloromethane, 1,2-Dichloroethane, and Nitrobenzene Membranes by 18-Crown-6 at 25 °C

membrane	Co^{2+}	Cr^{3+}	Cu^{2+}	Zn^{2+}	Ag^{+}	Cd^{2+}	Pb^{2}+
chloroform							
% (transport receiving)[a]	—	—	—	—	—	—	30.23
% (membrane)[b]	15.16	43.77	5.31	38.39	68.83	29.08	67.08
J (mol per 24 h)[c]	—	—	—	—	—	—	3.78
dichloromethane							
% (transport receiving)[a]	—	—	—	—	0.38	—	27.77
% (membrane)[b]	20.38	36.2	18.05	33.99	68.94	12.74	64.10
J (mol per 24 h)[c]	—	—	—	—	0.048	—	3.47
1,2-dichloroethane							
% (transport receiving)[a]	—	—	—	—	—	—	17.13
% (membrane)[b]	22.97	34.58	16.86	52.84	76.56	32.67	49.31
J (mol per 24 h)[c]	—	—	—	—	—	—	2.14
nitrobenzene							
% (transport receiving)[a]	—	—	—	—	—	—	3.00
% (membrane)[b]	20.38	30.26	14.87	42.16	66.91	12.08	23.07
J (mol per 24 h)[c]	—	—	—	—	—	—	0.37

[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 *J* values are ·10^{-6}.

Table 2. Data for Competitive Transport of Seven Metal Cations across Bulk Chloroform—1,2-Dichloroethane Binary Mixed Solvent Membranes by 18-Crown-6 at 25 °C

membrane	Co^{2+}	Cr^{3+}	Cu^{2+}	Zn^{2+}	Ag^{+}	Cd^{2+}	Pb^{2}+
pure $CHCl_3$							
% (transport receiving)[a]	—	—	—	—	—	—	30.23
% (membrane)[b]	15.16	43.77	5.31	38.39	68.83	29.08	67.08
J (mol per 24 h)[c]	—	—	—	—	—	—	3.78
75 % $CHCl_3$—25 % 1,2-DCE							
% (transport receiving)[a]	—	—	—	—	—	—	23.98
% (membrane)[b]	22.43	18.68	13.73	46.39	68.86	15.07	62.60
J (mol per 24 h)[c]	—	—	—	—	—	—	3.00
50 % $CHCl_3$—50 % 1,2-DCE							
% (transport receiving)[a]	—	—	—	—	—	—	26.21
% (membrane)[b]	15.24	17.84	12.64	60.33	67.62	19.52	66.91
J (mol per 24 h)[c]	—	—	—	—	—	—	3.28
25 % $CHCl_3$—75 % 1,2-DCE							
% (transport receiving)[a]	—	—	—	—	—	—	22.91
% (membrane)[b]	21.88	8.14	18.1	44.55	67.2	18.33	63.11
J (mol per 24 h)[c]	—	—	—	—	—	—	2.86
pure 1,2-DCE							
% (transport receiving)	—	—	—	—	—	—	17.13
% (membrane)[b]	22.97	34.58	16.86	52.84	76.56	32.67	49.31
J (mol per 24 h)[c]	—	—	—	—	—	—	2.14

[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 *J* values are ·10^{-6}.

Table 3. Data for Competitive Transport of Seven Metal Cations across Bulk Dichloromethane—1,2-Dichloroethane Binary Mixed Solvent Membranes by 18-Crown-6 at 25 °C

membrane	Co^{2+}	Cr^{3+}	Cu^{2+}	Zn^{2+}	Ag^{+}	Cd^{2+}	Pb^{2}+
pure DCM							
% (transport receiving)[a]	—	—	—	—	0.38	—	27.77
% (membrane)[b]	20.38	36.20	18.05	33.99	68.94	12.74	64.10
J (mol per 24 h)[c]	—	—	—	—	0.05	—	3.47
75 % DCM—25 % 1,2-DCE							
% (transport receiving)[a]	—	—	—	—	—	—	26.21
% (membrane)[b]	24.09	26.15	21.37	49.66	68.28	13.58	68.26
J (mol per 24 h)[c]	—	—	—	—	—	—	3.28
50 % DCM—50 % 1,2-DCE							
% (transport receiving)[a]	—	—	—	—	—	—	28.73
% (membrane)[b]	18.00	9.83	13.01	27.19	78.87	6.76	64.34
J (mol per 24 h)[c]	—	—	—	—	—	—	3.56
25 % DCM—75 % 1,2-DCE							
% (transport receiving)[a]	—	—	—	—	—	—	23.3
% (membrane)[b]	15.24	14.04	13.37	47.97	69.03	22.49	62.33
J (mol per 24 h)[c]	—	—	—	—	—	—	2.90
pure 1,2-DCE							
% (transport receiving)	—	—	—	—	—	—	17.13
% (membrane)[b]	22.97	34.58	16.86	52.84	76.56	32.67	49.31
J (mol per 24 h)[c]	—	—	—	—	—	—	2.14

[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 *J* values are ·10^{-6}.

2-dichloroethane—chloroform and 1,2-dichloroethane—dichloromethane binary mixtures containing 18-crown-6 as the membrane phase are listed in Tables 2 and 3, respectively. A pH gradient was utilized to facilitate the transport of the metal cations across the membrane by counter transport of protons. The results in the presence of surfactants in organic phase are listed in Table 4. The graphical results for competitive transport of metal cations across organic liquid membranes are shown in Figures 2 and 3. The change in transport rate of the Pb^{2+} cation versus the mole fraction of 1,2-dichloroethane in 1,2-dichloroethane—dichloromethane and 1,2-dichloroethane—chloroform binary solvents is shown in Figures 4 and 5, respectively.

5.1. Effect of Carrier Structure on the Cation Transport. The nature of a macrocyclic ionophore such as the ring size, the kind and number of donor atoms, and also the substituting groups present in the ring has an important effect on cation transport.[24] On the basis of the characteristics of the crown ethers, they can be used as carriers for both cationic and anionic forms of metal ions. For example, the complex which is formed between dicyclohexyl-18-crown-6 with potassium, [K-DCH18C6]$^+$, has been used for ion pair extraction of [$TlCl_4$]$^-$ through a BLM.[25] In such cases the selectivity of the system is not due to cavity size of crown ether, because the crown ethers display selectivity in complexation mainly based on cavity and ion size. But, in this work we used 18C6 as an ionophore for competitive BLM transport of some heavy metal cations.

However, dissolving a carrier into a liquid membrane may enhance the solute flux across it. The carrier acts as an extractant agent favoring analyte transport from the feed solution to the stripping solution, due to its ability to complex with the analyte. The use of liquid membrane-dissolved carriers leads to higher mass fluxes, better selectivity, and higher preconcentration factors. Hence, carrying out an exhaustive study of the system becomes necessary to achieve these properties.

Table 4. Effect of Surfactants on Lead(II) Cation Transport across Organic Solvent System as a Bulk Liquid Membrane with 18-Crown-6 as an Ionophore at 25 °C

membrane	fatty acid	% (receiving)[a]	% (membrane)[b]	J (mol per 24 h)[c]
DCM	–	27.77	64.10	3.47
	stearic acid	23.01	64.11	2.88
	palmetic acid	23.5	62.87	2.94
	oleic acid	27.77	63.19	3.47
$CHCl_3$	–	30.23	67.08	3.78
	stearic acid	29.12	69.35	3.64
	palmetic acid	30.68	67.54	3.83
	oleic acid	26.87	66.37	3.36
NB	–	3.00	23.07	0.37
	stearic acid	2.67	39.52	0.33
	palmetic acid	4.18	25.96	0.52
	oleic acid	3.93	21.63	0.49
DCE	–	17.13	49.31	2.14
	stearic acid	15.43	56.42	1.93
	palmetic acid	15.96	50.29	1.99
	oleic acid	13.32	41.12	1.66

[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 J values are $\cdot 10^{-6}$.

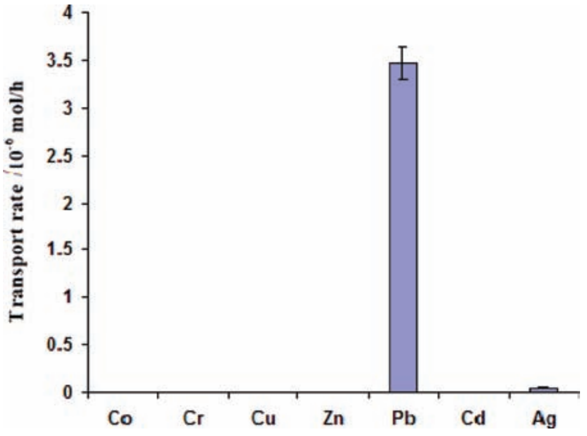

Figure 2. Results of metal ion transport (water/dichloromethane/water) studies for 18-crown-6. Source phase: pH 4.9 (CH_3COOH/CH_3COONa) containing metal ions at 0.01 M (10 mL). Membrane phase: contains ligand (0.001 M) (50 mL). Receiving phase: pH 3.0 (HCOOH/HCOONa; 30 mL), stirred for 24 h.

Under the usual conditions of transport, the concentration of carrier inside the membrane is extremely low compared with that of transported material outside the membrane. If the entrain of carrier becomes too high, the viscosity of the liquid membrane increases. This increase in viscosity leads to a lowering of diffusivity of the complex in the membrane and consequently lowers the transport rate of the species.

In this study, when no carrier is present in the membrane phase, the amount of cation transported through the membrane was below the detection limit.

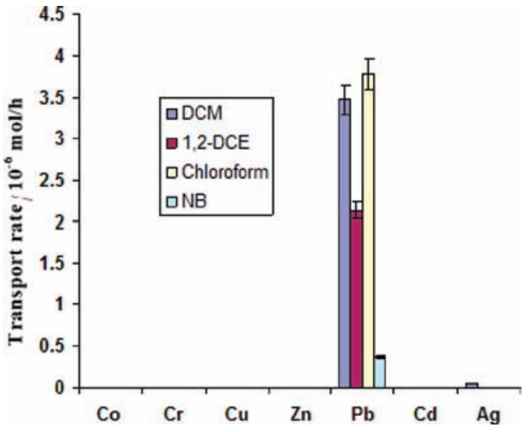

Figure 3. Comparison of the results of metal ion transport (water/organic solvent/water) studies for 18-crown-6. Source phase: pH 4.9 (CH_3COOH/CH_3COONa) containing metal ions at 0.01 M (10 mL). Membrane phase: contains ligand (0.001 M) (50 mL). Receiving phase: pH 3.0 (HCOOH/HCOONa; 30 mL), stirred for 24 h.

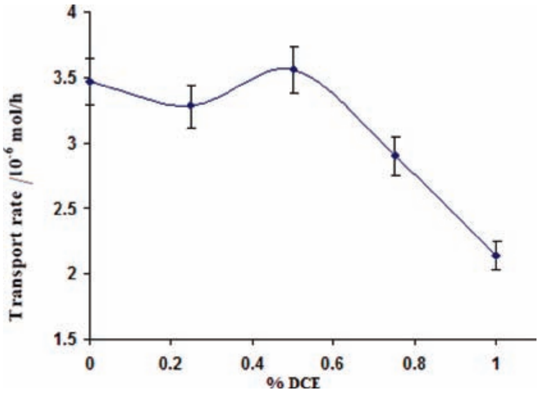

Figure 4. Changes of lead(II) ion transport with the composition of the 1,2-DCE–DCM binary systems. Source phase: pH 4.9 (CH_3COOH/CH_3COONa) containing metal ions at 0.01 M (10 mL). Membrane phase: contains 18-crown-6 (0.001 M) (50 mL) in 1,2-DCE–DCM binary solvents. Receiving phase: pH 3.0 (HCOOH/HCOONa; 30 mL), stirred for 24 h.

The selectivity of the 18-crown-6 was investigated in competition experiments with seven heavy and transition metal cations present in the source phase. The results obtained in this study show that 18-crown-6 system preferentially transports the Pb^{2+} cation among the other cations.

In a carrier transport membrane based on chemical interaction, it is very important to change the mechanism of chemical reaction for incorporation into the membrane and release to the outside of the membrane. At the source phase interface, there will be a competition between the crown ether molecule and seven metal cations. When the concentrations of the cations in the source phase are similar, the difference in transport of metal cations is attributed to the difference in complexation constant. While the Ag^+ cation can go to the membrane phase more easily than the five metal cations, it cannot transport as well as Pb^{2+} through the membrane into the receiving phase. The large difference in the fluxes of these two metal cations through the liquid membrane can be attributed to the difference in extraction equilibrium constant (K_{ex}). This is the product of the partition coefficient of the cation and the complexation constant.

The sizes of Zn^{2+} (r = 0.74 Å), Cd^{2+} (r = 0.97 Å), Cr^{3+} (r = 0.52 Å), Co^{2+} (r = 0.74 Å), and Cu^{2+} (r = 0.73 Å) are, to some

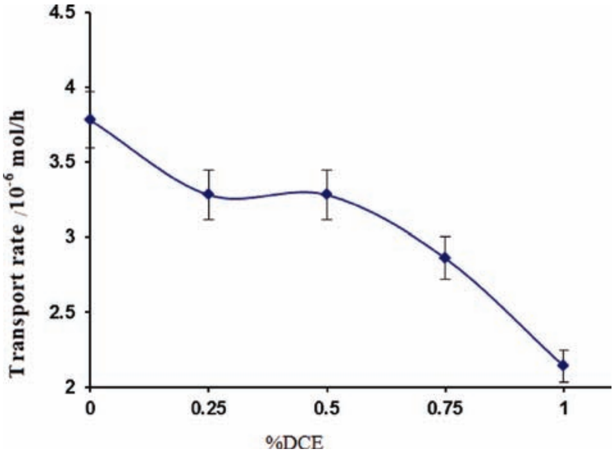

Figure 5. Changes of lead(II) ion transport with the composition of the 1,2-DCE–chloroform binary systems. Source phase: pH 4.9 (CH_3COOH/CH_3COONa) containing metal ions at 0.01 M (10 mL). Membrane phase: contains 18-crown-6 (0.001M) (50 mL) in 1,2-DCE–chloroform binary solvents. Receiving phase: pH 3.0 (HCOOH/HCOONa; 30 mL), stirred for 24 h.

extent, lower than the size of the Pb^{2+} (r = 1.18 Å) ion, and therefore, they cannot attain a convenient fit condition for the 18-crown-6 (r = 2.6 to 3.2 Å) cavity. Also the size of the Ag^+ cation (r = 1.26 Å) is to some extent bigger than the lead cation, but since the Pb^{2+} ion has a less soft character than Ag^+ ion, it seems that according to the hard and soft acid–base concept, it can form a more stable complex with oxygen donor atoms of 18-crown-6 as a hard base. Moreover, the Pb^{2+} ion bears a high charge density comparing to Ag^+ ion which results in a strong interaction with this ligand. Also strong solvation of the $[18C6\text{-}Ag]^+$ complex in membrane by organic solvents and also low diffiusion coefficient of this complex across the membrane phase and probably its unsuitable kinetic parameters may be effective on low transport rate of this metal cation to the receiving phase.

The highest extraction efficiency for the lead cation correspond to the strong complex formation with carrier and highest flux of $[18C6\text{-}Pb]^{2+}$ complex through the organic membrane; therefore, as shown in Table 3, a high selectivity is obtained for the Pb^{2+} cation in these experiments.

5.2. Effect of Solvent upon Fluxes and Selectivity in Bulk Liquid Membrane Transport. The selection of a suitable organic solvent in BLM is one of the most critical factors in membrane function, and its characteristics largely affect the extraction efficiency of membrane systems.

The solvent should be chosen in such a way that it must be immiscible with the aqueous phase and have low viscosity and volatility and, at the same time, it should provide a high distribution coefficient.[26,27] The performance of the various organic solvents including chloroform, dichloromethane, 1,2-dichloroethane, and nitrobenzene was examined in this investigation.

As is evident in Table 1, the order of the transport rate of Pb^{2+} metal cation through these organic solvents as BLM was found to be chloroform > dichloromethane > 1,2-dichloroethane > nitrobenzene.

One of the factors which affects the partitioning of the metal ions into the organic phase is the dielectric constant of the organic solvent.[28] As is evident in Table 1, a considerable separation of the Pb^{2+} metal cation occurs in chloroform, which may be due to the lower dielectric constant of chloroform (ε = 4.8) compared to dichloromethane (8.93), 1,2-dichloroethane (10.66), and nitrobenzene (34.8) which leads to stabilization of the ion pair in the organic phase leading to increase the rate of transport of Pb^{2+} metal cation through chloroform as the liquid membrane. It seems that the higher viscosity of nitrobenzene than those of chloroform, dichloromethane, and 1,2-dichloroethane decreases the rate of transport of Pb^{2+} metal cation through nitrobenzene as the liquid membrane.

5.3. Effect of Binary Mixed Solvent Membrane on the Transport Efficiency of the Metal Cations. The results of transport from a source phase containing seven metal cations through chloroform–1,2-dichloroethane and dichloromethane–1,2-dichloroethane binary mixtures containing the macrocyclic ligand are listed in Tables 2 and 3, respectively. As is evident in Table 2, the transport rate of Pb^{2+} cation increases as the concentration of chloroform is increased in chloroform–1,2-dichloroethane binary mixed solvent. This result may be due to the lower dielectric constant of chloroform and, therefore, formation of a stable ion pair and higher partitioning coefficient of the lead(II) cation into chloroform which leads to increase the transport of this metal cation through the liquid membrane.

The summarized data in Table 3 show that, as the mole fraction of 1,2-dichloroethane increases in dichloromethane–1,2-dichloroethane binary mixture, the transport rate of lead cation decreases; this behavior may be due to the higher dielectric constant of 1,2-dichloroethane rather than that of dichloromethane which leads to destabilization of the ion pair in the organic phase. In addition, the higher viscosity of 1,2-dichloroethane than that of dichloromethane may result in a decrease in the diffiusion of the lead(II) cation from the membrane phase into the receiving phase.

The change of transport rate of the Pb^{2+} cation versus the composition of dichloromethane–1,2-dichloroethane and 1,2-dichloroethane–chloroform binary solvent is shown in Figures 4 and 5, respectively. As is obvious from this figure, a nonlinear relationship is observed between the transport rate of this metal cation with the composition of this binary mixed solvent solution. This behavior may be due to some interactions between dichloromethane and 1,2-dichloroethane molecules which results in changing some of the chemical and physical properties of each solvent when they mix with one another.

5.4. Effect of Fatty Acids on Transport Efficiency of the Metal Cations. It is expected that the addition of a lipophilic counterion such as a fatty acid to the organic membrane phase can impart a greater degree of lipophilicity to the charged species and also removes the need for a simple counterion to cross the source phase/membrane interface on metal uptake.[29]

In this study we investigated the influence of three fatty acids (stearic acid, palmetic acid, oleic acid) as surfactant (0.004 M) in the membrane phase on the Pb^{2+} cation transport process. The results are given in Table 4. As is obvious from these data, the cooperative behavior in the presence of these long-chain hydrocarboxylic acids is decreased. This may be due to formation of hydrogen bonds between the donor atoms of the macrocyclic ligand and acidic proton of carboxylic acids in membrane phase which results in the formation of a weaker complex between Pb^{2+} and crown ether in the presence of these fatty acids, or it may be due to the formation of micelles of fatty acids in the membrane phase which trap the crown–cation complex.

6. CONCLUSION

The liquid membrane transport experiments of cobalt(II), chromium(III), copper(II), zinc(II), cadmium(II), silver(I), and lead(II) metal cations using 18-crown-6 as an ion carrier in various organic membranes showed that it is possible to separate the Pb^{2+} cation from the other metal ions by this macrocyclic ligand and the rate of transport of this heavy metal cation is strongly influenced by the nature of the membrane solvents. The transport rate of the Pb^{2+} cation is also influenced by the composition of the binary mixed solvent solutions, and a nonlinear behavior is observed between the transport rate and the composition of these membrane systems. The results obtained for competitive BLM transport of the studied metal cations show that the transport rate of the Pb^{2+} cation through organic membrane phases decreases in the presence of stearic acid, palmetic acid, and oleic acid as surfactant.

The simplicity, low cost, and high efficiency and selectivity for Pb^{2+} cation transport obtained by the studied liquid membrane systems demonstrate its potential applicability to selective removal, concentration, or purification of the lead(II) cation from other interfering cations present in solution.

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