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PHYSICAL CHEMISTRY OF SOLUTIONS

Studies on the Macrocycle Mediated Transport of Some Metal Cations Through a Bulk Liquid Membrane System Using Kryptofix 22[1]

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Abstract—Competitive transport experiments involving Fe^{+3}, Cr^{+3}, Ni^{+2}, Co^{+2}, Ca^{+2}, Mg^{+2} and K^+ metal cations from an aqueous source phase through some organic membranes into an aqueous receiving phase have been carried out using 4,13-diaza-18-crown-6 (kryptofix 22) as an ionophore present in the organic membrane phase. Fluxes and selectivities for competitive of the metal cations transport across bulk liquid membranes have been determined. A good selectivity was observed for K^+ cation by kryptofix 22 in 1,2-dichloroethane (1,2-DCE) membrane system. The sequence of selectivity for potassium ion in the organic solvents was found to be: 1,2-DCE > DCM (dichloromethane) >$CHCl_3$. The transport of K^+ cation was also studied in the DCM-1,2-DCE, $CHCl_3$-1,2-DCE and $CHCl_3$-DCM binary mixed solvents as membrane phase. A non-linear relationship was observed between the transport rate of K^+ ion and the composition of these binary mixed solvents. The amount of K^+ transported follows the trend: DCM-DCE > $CHCl_3$-DCE > $CHCl_3$-DCM in the bulk liquid membrane studies. Then, the selective transport of K^+ cation through a DCM-1,2-DCE bulk liquid membrane was studied by kryptofix 22 as an efficient carrier. The highest transport efficiency was obtained by investigating the influence of different parameters such as the concentration of kryptofix 22 in the membrane phase, pH of the source and the receiving phases and the equilibrium time of the transport process. Maximum transport value of 71.62 ± 1.61% was observed for K^+ ion after 4 hours, when its concentration was 4×10^{-3} M.

Keywords: Bulk liquid membrane transport, Kryptofix 22, Seven metal cations

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Usually in many analytical methods, the performing of a separation step is necessary during the analysis of analytical samples. Among various separation methods such as ion exchange, solvent extraction, selective chemical precipitation, etc. One interesting approach is based on the recognition, binding and release of specific solutes carried out by transport membranes, i.e. organic liquid in contact with two separated aqueous phases working under chemical gradient as the driving force. This technique has been widely used for carrier metal ion separations [1] and, to a lesser degree, for organic compounds separation [2].

The specific transport of metal ions through a membrane is widely known to play an essential role in biological processes [3]. Potassium is a very significant body mineral, important to both cellular and electrical function. It is one of the main blood minerals called "electrolytes" (the others are sodium and chloride ions), which means it carries a tiny electrical charge (potential). Along with sodium ion, it regulates the water balance and the acid-base balance in the blood and tissues. Potassium ion enters the cell more readily than does sodium ion and instigates the brief sodium-potassium exchange across the cell membranes.

A number of ionophores such as crown ethers, cryptands and podands are known which transport metal ions selectively across various liquid membrane configurations and widely applied in separation science and construction of ion selective electrodes [4].

The cryptand molecules are three dimensional analogues of crown ethers, but they are more selective and complex the guest ions more strongly. The resulting complexes are lipophilic. Many cryptands are commercially available under the trade name "Kryptofix". The three-dimensional interior cavity of a cryptand provides a binding site—or nook—for "guest" ions. The complexes which are formed between the cationic guests and the cryptands molecules are called cryptates. Cryptands form complexes with many "hard cations" including NH_4^+,lanthanides, alkali metals, and alkaline earth metal cations. In contrast to the typical crown ethers, cryptands bind

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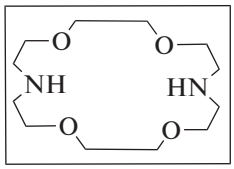
the guest ions by both nitrogen and oxygen donors. Their three-dimensional encapsulation mode, confers some size-selectivity. Cryptands as ion carriers have been used successfully for metal ion separation in transport through liquid membranes [5]. So we are interested in selective extracting one cation over the others. We report here the results of investigating of the selectivity of a macrocyclic ligand as carrier towards seven metal ions that are present together in solution at equimolar concentrations across bulk liquid membrane, i.e. competitive transport study of seven-metal cations membrane transport experiments involving Fe^{+3}, Cr^{+3}, Ni^{+2}, Co^{+2}, Ca^{+2}, Mg^{+2} and K^{+} metal cations with 4,13-diaza-18-crown-6 as a carrier, using dichloromethane (DCM), 1,2-dichloroethane (1,2-DCE) and chloroform ($CHCl_3$), as liquid membranes. Then the selective transport of potassium ions from aqueous solution phase with a defined pH into the receiving phase, was studied through a bulk liquid membrane containing 4,13-diaza-18-crown-6 (kryptofix 22) as a carrier. The experimental conditions were optimized with respect to the parameters influencing the efficiency of the transport of potassium ion such as the effect of concentration of the carrier in the membrane phase, as well as, the type of the membrane solvent used, the pH of the receiving and the source phases and also the equilibrium time for the transport process.

EXPERIMENTAL

Reagents and Solvents

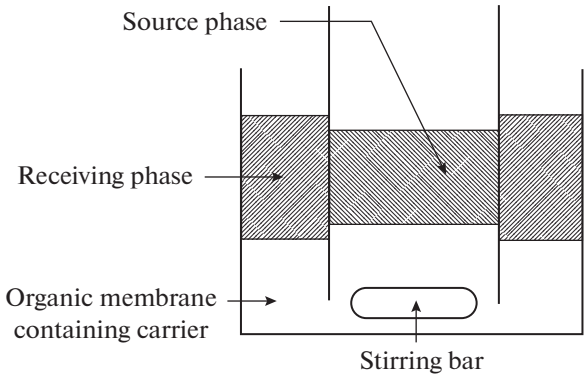
Kryptofix 22 (Merck) (Scheme 1), potassium nitrate (Merck), nickel(II) nitrate (BDH), magnesium nitrate (Riedel), iron(III) nitrate (Merck), calcium nitrate (BDH), cobalt(II) nitrate (BDH), chromium(III) nitrate (BDH), acetic acid, sodium acetate, formic acid and sodium hydroxide all purchased from Merck company and were used without further purification. Dichloromethane (DCM), 1,2-dichloroethane (1,2-DCE) and chloroform ($CHCl_3$) (all from Merck) were used with the highest purity. All aqueous solutions were prepared using double distilled deionized water.



Scheme 1. Structures of kryptofix 22.

Apparatus

The determination of the metal cations content in the aqueous receiving phase, was carried out by a Shimadzu AA-670 atomic absorption spectrometer (AAS) equipped with the hallow cathode lamps. The pH measurements were made with a Metrohm 827 pH-meter using a combined glass electrode. A bulk liquid membrane cell was used in all transport experiments (Scheme 2).



Scheme 2. Liquid membrane apparatus.

Procedure

Bulk liquid membrane (BLM) transport measurements were performed at ambient temperature in a cylindrical glass cell (inside diameter 5 cm) holding a glass tube (inside diameter 2 cm). The inner aqueous source phase contained a buffer solution of an equimolar mixture of seven metal cations involving Fe(III), Cr(III), Ni(II), Co(II), Ca(II), Mg(II) and K(I) for competitive experiments and potassium nitrate (10 mL, 5.0×10^{-4} M) for selective transport process of K^{+} ion. The transport process was maintained by the buffering the inner and outer i.e. source and receiving phases. The membrane phase (MP) contained 50 mL of 5×10^{-4} M kryptofix 22 as a carrier in organic solvent. The membrane phase was magnetically stirred by a Teflon-coated magnetic bar. 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. Determination of the potassium ion concentration in both aqueous phases was carried out by atomic absorption spectroscopy (AAS). The data points reported are the averages of at least three replicate measurements.

RESULTS AND DISCUSSION

Effect of Solvent Upon Fluxes and Selectivity

The effect of the nature of the organic phase was investigated, with dichloromethane, 1,2-dichloroethane and chloroform being screened as organic membranes. In summary, the characteristics of the membrane solvents are among the main factors in establishing the acceptable transport efficiency. The solvent should be chosen in such a way that it is immiscible with the aqueous phase, has low viscosity and volatility and at the same time it should render a high distribution coefficient [6].

Table 1. Data for seven-metal ions competitive transport across organic solvents as bulk membrane with kryptofix 22

Solvent	K(I)	Mg(II)	Ca(II)	Ni(II)	Co(II)	Cr(III)	Fe(III)
1,2-DCE							
% (Receiving)[a]	1.07	–	–	–	–	–	–
% (Membrane)[b]	2.24	–	30.48	–	–	–	9.05
J_M (mol per 24 h)[c]	13.40	–	–	–	–	–	–
DCM							
% (Receiving)[a]	1.02	–	–	–	–	–	–
% (Membrane)[b]	6.33	0.85	47.74	0.04	–	–	14.56
J_M (mol per 24 h)[c]	12.73	–	–	–	–	–	–
$CHCl_3$							
% (Receiving)[a]	0.95	–	–	–	–	–	–
% (Membrane)[b]	2.24	–	35.19	1.99	1.82	–	16.14
J_M (mol per 24 h)[c]	11.87	–	–	–	–	–	–

[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 $\times 10^8$.

The data for competitive transport of Fe^{+3}, Cr^{+3}, Ni^{+2}, Co^{+2}, Ca^{+2}, Mg^{+2} and K^+ metal cations from an aqueous source phase through DCM, 1,2-DCE and $CHCl_3$ membranes containing kryptofix 22 ligand at ambient temperature are given in Table 1. As is obvious from this Table, among the seven metal cations, only K^+ cation can be transported through bulk membranes which were used. Furthermore, 1,2-DCE has the best transport efficiency among the used bulk liquid membrane systems. These results can be explained by considering the physicochemical properties of organic solvents used as liquid membranes. The preference of 1,2-DCE in comparison with the other two solvents can be attributed to its higher dielectric constant and dipole moment and also the lower Donor Number of this solvent. It seems that because of the higher dielectric constant and dipole moment of 1,2-DCE, the ion-pair formation is weakened in this organic solvent and consequently, the cations are present as more ionic form in this solvent with respect to DCM and $CHCl_3$. Therefore, we may suggest that this factor can be an effective factor in the transport process of K^+ cation, which facilitates the transport of this metal cation through this membrane into the receiving phase. In addition, in a weak solvating solvent such as 1,2-DCE with a low donor number (DN = 0.0), the solvation of the metal cation and possibly of the ligand should be weaker than DCM with a bigger donor ability (DN = 1.0), therefore, the formed carrier-K^+ complex becomes more stabilized in this membrane system which results in an increase the efficiency of transport of K^+ ion from aqueous source phase into this membrane phase.

Effect of Ionophore Structure and its Concentration on Cation Transport Process

The transport and separating capabilities of the bulk liquid membranes are related to the chemical nature of the carrier. The selection of more efficient and selective carriers, represent a challenging task in this field of chemistry. Macrocycle carriers such as crown ethers (aza-crown ethers) have been used to transport the alkali metal [7, 8] and heavy metal cations through liquid membranes [9, 10]. On the basis of the characteristics of the cryptands, they can be used as carriers for transport of metal ions. For example, kryptofix 5 has been used for transport of Ag^+ cation [11].

In the present study, with no carrier in the organic membranes, no detectable transport of the studied metal ions from the source phase into the receiving phase was observed, therefore, a carrier of relatively lipophilic nature such as kryptofix 22 is necessary for the transport process of the metal cation in the bulk liquid membrane. The selectivity of the kryptofix 22 was investigated in competitive transport experiments with seven metal cations present in the source phase. The results obtained in this study show that kryptofix 22 system preferentially transports the K^+ cation among the other metal cations. The carrier used in this study has a similar structure to 18-crown-6 except the replacement of two oxygen atoms by nitrogen.

The observed J values (transport rate) for the transport of K^+ ion which are summarized in Table 1, show that kryptofix 22 forms a strong complex with K^+ cation and preferentially transports this metal cation into the aqueous receiving phase. Since the ionic size of K^+ cation (2.66 Å) is very close to the cavity size of

Table 2. Data for seven-metal ions competitive transport across DCM-1,2-DCE binary systems as bulk membrane with kryptofix 22

Solvent	K(I)	Mg(II)	Ca(II)	Ni(II)	Co(II)	Cr(III)	Fe(III)
1,2-DCE							
% (Receiving)[a]	1.07	–	–	–	–	–	–
% (Membrane)[b]	2.24	–	30.48	–	–	–	9.05
J_M (mol per 24 h)[c]	13.40	–	–	–	–	–	–
25% DCM + 75% (1,2-DCE)							
% (Receiving)[a]	1.97	–	–	–	–	–	–
% (Membrane)[b]	6.86	3.02	–	–	1.97	–	6.48
J_M (mol per 24 h)[c]	24.72	–	–	–	–	–	–
50% DCM + 50% (1,2-DCE)							
% (Receiving)[a]	1.51	–	–	–	–	–	–
% (Membrane)[b]	1.75	–	9.03	3.52	7.99	5.05	5.67
J_M (mol per 24 h)[c]	18.90	–	–	–	–	–	–
75% DCM + 25% (1,2-DCE)							
% (Receiving)[a]	1.22	–	–	–	–	–	–
% (Membrane)[b]	4.32	–	5.32	–	0.97	1.20	1.60
J_M (mol per 24 h)[c]	15.37	–	–	–	–	–	–
DCM							
% (Receiving)[a]	1.02	–	–	–	–	–	–
% (Membrane)[b]	6.33	0.85	47.74	0.04	–	–	14.56
J_M (mol per 24 h)[c]	12.73	–	–	–	–	–	–

[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 $\times 10^{-8}$.

18-crown-6 (2.6–3.2 Å), it forms the most stable complex.

Effect of Binary Mixed Solvents Upon Fluxes and Selectivity of Transport Process

The data obtained for competitive transport of Fe^{+3}, Cr^{+3}, Ni^{+2}, Co^{+2}, Ca^{+2}, Mg^{+2} and K^+ metal cations with kryptofix 22 in DCM-1,2-DCE, $CHCl_3$-1,2-DCE and $CHCl_3$-DCM binary solvent systems as membrane phase are shown in Tables 2–4 and the graphical results are shown in Figs. 1–3. As is evident from these data, the rate of transport of K^+ cation by this ligand in the binary mixed solvents is varied in order: DCM-1,2-DCE > $CHCl_3$-1,2-DCE > $CHCl_3$-DCM.

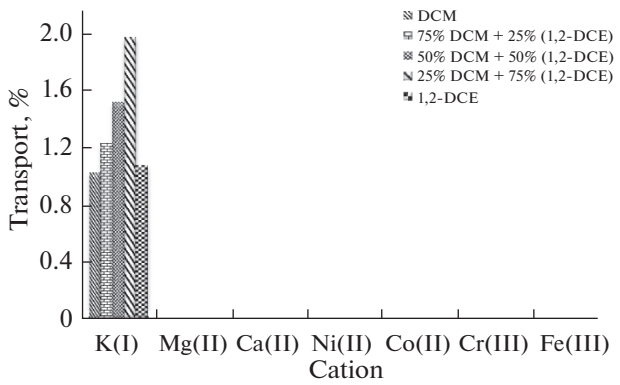


Fig. 1. Comparison of the results of metal ion transport (water/DCM-1,2-DCE/water) studies for kryptofix 22.

The graphical results for the transport of the metal cations in the binary solvent systems are shown in Figs. 4, 5. As is obvious from these Figures, the transport process for the K^+ 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 solvents. Some structural changes probably occur in the structure of the solvents when they mix with one another. These structural changes may result in changing the interactions of those solvents with the solutes and, therefore, the transport processes.

Effect of pH

The influence of pH of the source and receiving phases on the transport efficiency of K^+ ion was studied in the pH range 2–7 and it was found that maximum K^+ ion transport occurs at pH 4 for the source

Table 3. Data for seven-metal ions competitive transport across $CHCl_3$-1,2-DCE binary systems as bulk membrane with kryptofix 22

Solvent	K(I)	Mg(II)	Ca(II)	Ni(II)	Co(II)	Cr(III)	Fe(III)
1,2-DCE							
% (Receiving)[a]	1.07	–	–	–	–	–	–
% (Membrane)[b]	2.24	–	30.48	–	–	–	9.05
J_M (mol per 24 h)[c]	13.40	–	–	–	–	–	–
25% $CHCl_3$ + 75% (1,2-DCE)							
% (Receiving)[a]	1.48	0.29	–	0.14	0.02	–	0.03
% (Membrane)[b]	–	–	7.35	–	–	–	10.44
J_M (mol per 24 h)[c]	18.46	3.71	–	1.79	0.20	–	0.48
50% $CHCl_3$ + 50% (1,2-DCE)							
% (Receiving)[a]	0.75	–	–	–	–	–	–
% (Membrane)[b]	–	–	–	–	–	–	–
J_M (mol per 24 h)[c]	9.35	–	–	–	–	–	–
75% $CHCl_3$ + 25% (1,2-DCE)							
% (Receiving)[a]	1.04	0.09	–	–	–	–	–
% (Membrane)[b]	–	–	0.88	0.07	–	–	13.74
J_M (mol per 24 h)[c]	12.92	1.00	–	–	–	–	–
$CHCl_3$							
% (Receiving)[a]	0.95	–	–	–	–	–	–
% (Membrane)[b]	2.24	–	35.19	1.99	1.82	–	16.14
J_M (mol per 24 h)[c]	11.87	–	–	–	–	–	–

[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 $\times 10^{-8}$.

phase and pH 3 for the receiving phase (Figs. 6, 7). On either side of these two pH values there is a decrease in transport efficiency. This can be related to the fact that the process of transfer of potassium ions from the bulk membrane to the receiving phase is governed not only by diffusion process but also by the rate of chemical reaction between the carrier-K^+ complex and the hydrogen ions in the stripping phase.

Effect of Time Dependence of Potassium Ion Transport

We studied the time dependence of K^+ ion transport through the liquid membrane under optimal experimental conditions. It is obvious from Fig. 8 that

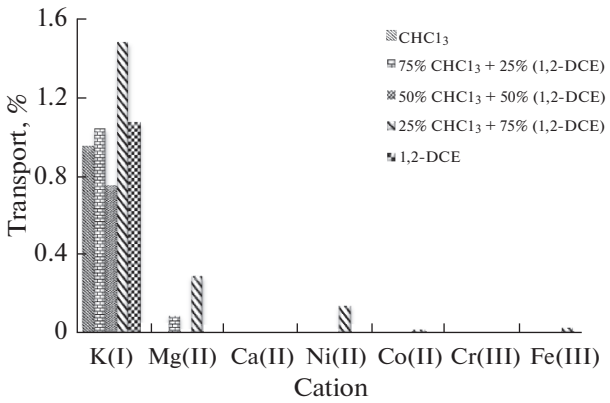


Fig. 2. Comparison of the results of metal ion transport (water/$CHCl_3$-1,2-DCE/water) studies for kryptofix 22.

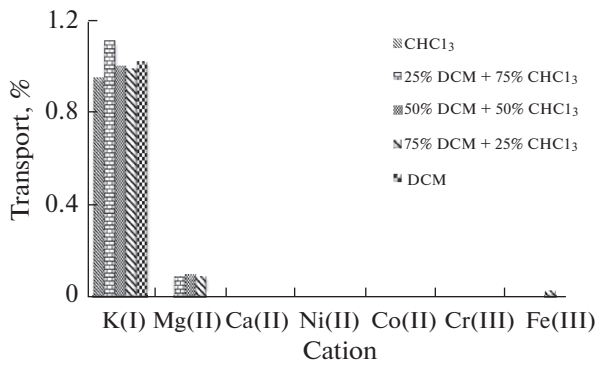


Fig. 3. Comparison of the results of metal ion transport (water/$CHCl_3$-DCM/water) studies for kryptofix 22.

Table 4. Data for seven-metal ions competitive transport across $CHCl_3$-DCM binary systems as bulk membrane with kryptofix 22

Solvent	K(I)	Mg(II)	Ca(II)	Ni(II)	Co(II)	Cr(III)	Fe(III)
DCM							
% (Receiving)[a]	1.02	–	–	–	–	–	–
% (Membrane)[b]	6.33	0.85	47.74	0.04	–	–	14.56
J_M (mol per 24 h)[c]	12.73	–	–	–	–	–	–
25% $CHCl_3$ + 75% DCM							
% (Receiving)[a]	0.99	0.09	–	–	–	–	0.03
% (Membrane)[b]	–	–	13.84	–	–	–	23.56
J_M (mol per 24 h)[c]	12.33	1.11	–	–	–	–	0.48
50% $CHCl_3$ + 50% DCM							
% (Receiving)[a]	1.00	0.10	–	–	–	–	–
% (Membrane)[b]	–	0.25	7.88	–	–	–	14.61
J_M (mol per 24 h)[c]	12.60	1.17	–	–	–	–	–
75% $CHCl_3$+25% DCM							
% (Receiving)[a]	1.11	0.09	–	–	–	–	–
% (Membrane)[b]	–	–	5.89	–	–	–	11.36
J_M (mol per 24 h)[c]	13.70	1.11	–	–	–	–	–
$CHCl_3$							
% (Receiving)[a]	0.95	–	–	–	–	–	–
% (Membrane)[b]	2.24	–	35.19	1.99	1.82	–	16.14
J_M (mol per 24 h)[c]	11.87	–	–	–	–	–	–

[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 $\times 10^{-8}$.

the efficiency of transport increases up to 4 hours, followed by a smooth increment. After 4 hours, 71.62% ± 1.15 of the K^+ cations were transported to the receiving phase and no major increment in transport efficiency was observed beyond this time.

Recommended Mechanism

The recommended mechanism for the transport of K^+ cation through bulk liquid membrane, is shown in Scheme 3. The movement of the charged species through the hydrophobic liquid membrane is accomplished by the presence of a cooperative host composed of kryptofix 22. After complexation of K^+ cation with the carrier on the source side of the membrane, the complex diffuses down its concentration gradient. As the pH of the receiving phase is lower than that of source phase, the concentration of K^+ ion increases in the receiving boundary phase of membrane due to a cation exchange process, i.e, replacement of the K^+ cation by the H^+ cation and permeation of (carrier H^+)

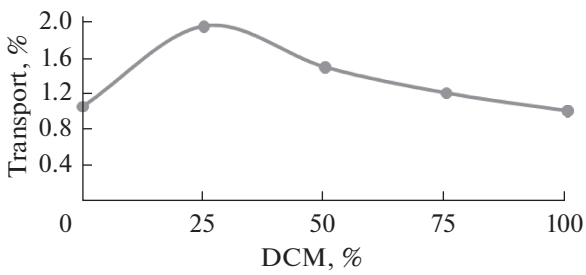


Fig. 4. The changes of K^+ ion transport with the composition of the DCM-1,2-DCE binary system.

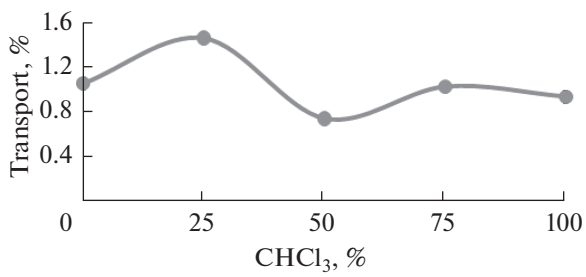


Fig. 5. The changes of K^+ ion transport with the composition of the $CHCl_3$-1,2-DCE binary system.

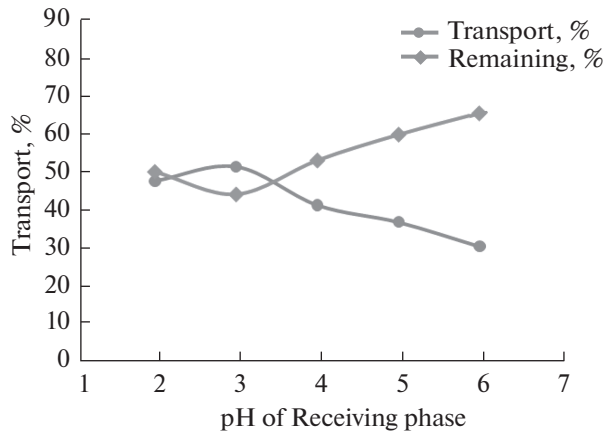


Fig. 6. Effect of pH in receiving phase on K^+ cation transport.

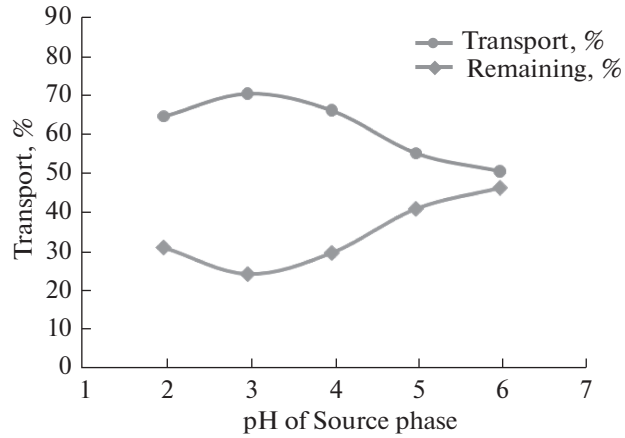
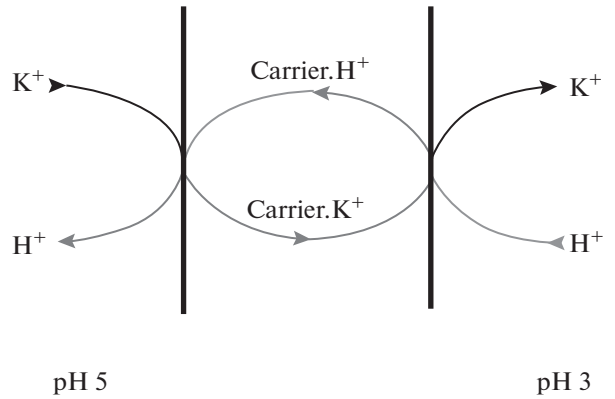


Fig. 7. Effect of pH in source phase on K^+ cation transport.

complex by back diffusion into the organic membrane. Then the free carrier diffuses back across the membrane and the cycle starts again. The net result is the transport of the metal cation from the source phase, on the left, to the receiving phase, on the right, across the liquid membrane.



Scheme 3. Schematic of potassium transport mechanism.

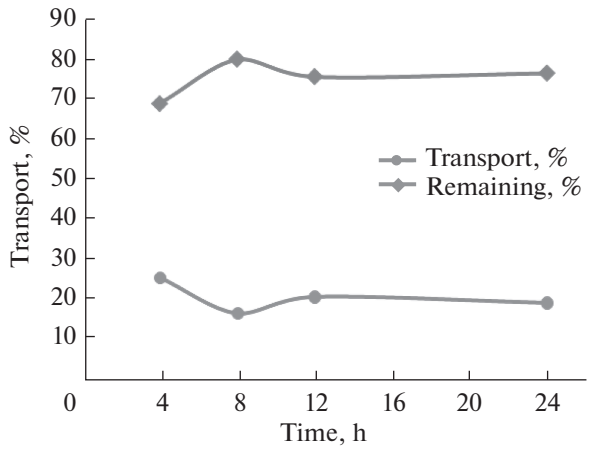


Fig. 8. Effect of time dependence of potassium ion transport.

CONCLUSION

Competitive metal ion transport experiments provide a means for documenting the selectivity in ion complex bonding. Competitive transport of Fe^{+3}, Cr^{+3}, Ni^{+2}, Co^{+2}, Ca^{+2}, Mg^{+2} and K^+ metal cations was studied from an aqueous source phase across DCM, 1,2-DCE and $CHCl_3$ bulk liquid membranes using kryptofix 22 as an ionophore into an aqueous receiving phase. The obtained results showed that the K^+ cation can be effectively separated and preconcentrated from water through a bulk liquid membrane containing kryptofix 22 in 1,2-DCE. The transport of K^+ cation was also studied in the DCM-1,2-DCE, $CHCl_3$-1,2-DCE and $CHCl_3$-DCM binary mixed solvents as membrane phase. The amount of K^+ transported follows the trend: DCM-DCE > $CHCl_3$-DCE > $CHCl_3$-DCM in the bulk liquid membrane studies. In the second part of this research, the selective transport of K^+ cation was studied using DCM-DCE bulk liquid membrane system. Under the optimized experimental conditions (kryptofix 22 concentration 4×10^{-3} M, process time 4 h, pH 4 for source phase and pH 3 for receiving phases), the maximum amount of transport of K^+ cation through DCM-DCE bulk liquid membrane was found to be ~71.6% ± 1.15. In conclusion, the results obtained in this study, show that the above bulk liquid membrane system containing kryptofix 22 as ion carrier is specific for the potassium ion and it can be a potential candidate for practical use in potassium separation, especially as it has the advantage of low solvent requirement, high precision, relatively high efficiency, selectivity, simplicity, and speed.

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