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Membrane Transport of Metal Ions with Lipophilic Aminomethylphosphine Oxides

**R. A. Cherkasov, A. R. Garifzyanov, R. R. Galeev,
N. V. Kurnosova, R. R. Davletshin, and S. V. Zakharov**

*Kazan (Volga Region) Federal University, Kremlyevskaya ul. 18, Kazan, Tatarstan, 420008 Russia
e-mail: rafael.cherkasov@ksu.ru*

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Abstract—The processes of membrane transport of ions of scandium(III), samarium(III), gadolinium(III), neodymium(III), aluminum(III), and a number of alkali and alkaline earth metals through liquid membrane impregnated with aminophosphoryl carriers of different structures were studied. Selectivity of bis (dialkylphosphinyl)amines towards scandium was found to be significantly higher than the selectivity of diphosphinylpiperazine and monophosphinylamine in particular. The dependence of transfer efficiency on the concentration of substrates and carriers was revealed. Optimal conditions for transporting rare and trace metal ions through the membrane were found, and the mechanism of transmembrane transport was discussed.

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Over the past two decades, a significant progress has been made in the field of membrane technologies, which are characterized by low power consumption, highly selective separation of gaseous and liquid substances and various substrates, in some cases by a possibility to solve complex environmental problems. The processes of separating substances with liquid membranes provides an efficient means for processing dilute solutions of complex composition, and can be best used for selective concentration of noble, rare, and trace metals. The high cost of these substrates is to some extent due to the complexity of their extraction, concentration, and separation from the technological solutions of low concentration. The basis for the development of new innovative technologies for extraction of these metals at present is based on the principles of transmembrane transport through liquid membranes using transporting substances of different chemical nature [1, 2].

The aim of this work was to study the transport properties of some lipophilic aminomethylphosphine oxides in the transport processes through impregnated liquid membranes of the ions Sc(III), Gd(III), Sm(III), Nd(III), and often of accompanying them in natural objects triply charged cation Al(III) and the ions of alkali and alkaline earth metals. Previously we used successfully the carriers of such structure in the processes of solvent extraction of noble metal ions [3, 4], Sc [5], as well as in membrane transport of organic and mineral acids [6, 7].

An experience gained so far in the use of organophosphorus compounds for the membrane transport of metal ions is fairly significant. Thus, neutral organyl phosphates, higher mono- and dialkyl phosphates, dialkyl alkylphosphonates, and dialkyl dithiophosphates proved themselves as efficient membrane transport extractants of ions Cr(III) [8], Ag(I) [9], Cu(II) [10], Zn(II) [11], and other metals, and in the separation of Co(II) and Ni(II) [12], the extraction and concentration of rare earth elements [13], the extraction of radionuclides from the wastes of the nuclear industry [14], the membrane extraction waste at the treatment of alkali and alkaline earth metals [15]. However, prior to our studies of the extraction and membrane transport properties of aminophosphoryl compounds [3–7], these efficient and selective complexing agents practically have not been used for extraction, separation, and concentration of metal ions. As we have shown, the especially promising for solving these problems are the aminophosphine oxides, characterized by high thermal and hydrolytic stability in strong acidic environments used as a rule in the processes of extraction of metal ions, e.g., in hydrometallurgical technologies. Recently we revealed high efficiency and selectivity of the solvent extraction of scandium [5] with bisphosphinoylamine (I), and for this reason we decided to investigate the processes of membrane extraction of ions of rare and trace elements using for the transport aminophosphine oxides **I–III** containing two lipophilic phosphinyl groups and, for comparison, their monophosphine oxide analog **IV**. To provide the desired hydrophilic–lipophilic balance (high coefficient of interphase distribution in the water–organic solvent system) we attached long-chain hydrocarbon substituents to the phosphorus and nitrogen atoms, the main working transport centers. Previously we found that lipophilic aminobisphosphine oxide were often proven to be effective extractants of Sc(III) in the solvent extraction from acidic nitrate and perchlorate media. In that case there was no noticeable transfer of the cations of alkali and alkaline earth metals and the ions Cu(II), Co(II) and Ni(II) into the organic phase, and In(III) and Ga(III) were extracted significantly worse than Sc(III) [5].

Bis(phosphinylmethyl)octylamines of general formula **I** and **II**, bis(didecylphosphinylmethyl)-piperazine (**III**), and *N,N*-dioctylaminodidecylmethyl-phosphine oxide (**IV**) were synthesized by the Kabachnik–Fields reaction in a one- and two-stage mode and purified in accordance with procedure in [7].

As a membrane solvent phenylcyclohexane was chosen having a high boiling point, which eliminates losses due to evaporation. In addition, we found that it dissolved well both the carrier and its complex with the transported substrate.

We studied the membrane transport of the selected metal ions through the impregnated liquid membrane, using bisphosphinylamine **I** at a concentration 0.1 M for the transport. As seen from Fig. 1, the plots of the concentration of the transported ion in the receiving phase versus the time show that the highest transfer rate is observed for the Sc(III) ions. Cations of rare earth elements are transferred at a much slower rate, and the minimal rate in the series of triply charged cations corresponds to the ion Al(III). The flux value of alkali and alkaline earth metals is even lower.

The data obtained are in good agreement with the results of solvent extraction of cations of these metals from nitric acid media [5]. This suggests that the Sc(III) cations form the same complexes with the transporting molecules in the membrane phase and in the solvent extraction process. Into the organic phase the Sc(III) complex with bisphosphinylamine (bfa) of 1:2 composition is transferred. All six coordination sites of Sc(III) are occupied by the donor nitrogen and phosphoryl oxygen atoms of the two phosphine oxide groups of the reagent. The positive charge is neutralized by three nitrate ions in the outer coordination sphere:

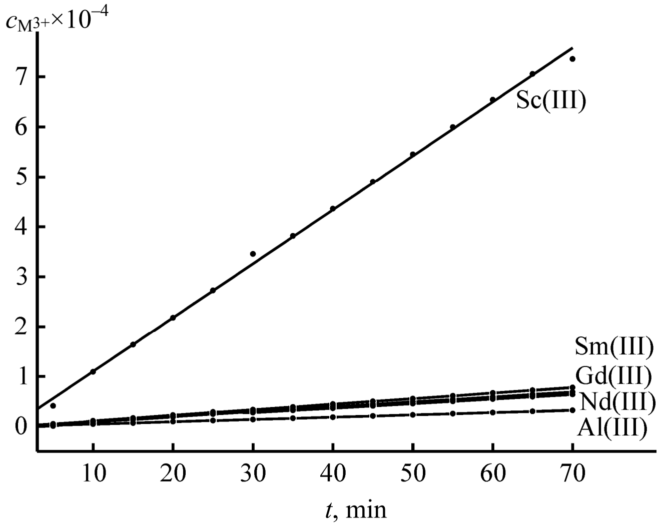
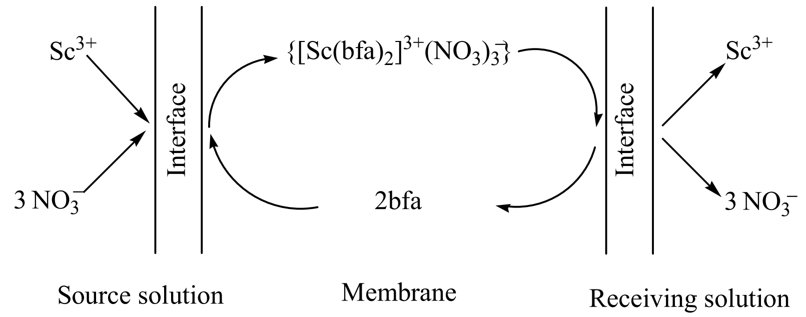


Fig. 1. Concentration dependence on time of the receiving solution for the membrane transport of Gd(III), Sc(III), Nd(III), Sm(III), and Al(III), carrier diphosphinylamine **I**.

$$Sc^{3+} + 2bfa_{org} + 3NO_3^- \rightarrow \{[Sc(bfa)_2]_3 + (NO_3)^{3-}\}_{org}.$$

The following mechanism of the co-directional transport (symport) seems to be the most probable: The scandium cation and nitrate anions are simultaneously transported with bisphosphinylamine from the source solution to the receiving one. At the source solution/membrane interface a lipophilic ion associate is formed, which diffuses into the membrane and is split at the membrane/receiving solution interface, therewith the Sc^{3+} and NO_3^- ions are transferred into the aqueous phase, while the highly lipophilic transporting molecules remains in the organic phase of the membrane. According to the published data [15], such a mechanism occurs in almost all cases of the membrane extraction of metal ions when a neutral carrier such as triorganyl phosphate or phosphine oxides is used.

Our results suggests that for the implementation of active transport of Sc(III) (that is, for the complete transfer of substrate from the source phase into the receiving one [16]) from nitric acid medium it is necessary to create a high concentration of nitrate ions in the source solution. For this purpose, to the source solution sodium or potassium nitrate can be added, since flux values for these cations are very low.



In accordance with the assumed mechanism, the transfer rate of ions Sc(III) should depend on the carrier concentration in the organic phase and the concentration of scandium cation and nitrate ions in the source phase. By an example of bisphosphinylamine **I** we studied the effect of these factors on the flux values of the ion transport of scandium, gadolinium, and aluminum, by changing the concentration of aminophosphinyl carrier in a fairly wide range (Table 1).

As seen, in all cases an increase in the concentration of carrier in the membrane phase leads to the increase in the rate of the metal ion transport. However, the extent of this effect is quite different for the selected metal ions: the rate is less for the Sc(III) ions than for Gd(III) and Al(III). The bilog plot log F vs. log C_{bfa} (F is flux, bfa means bisphospinylamine) has a slope 0.91 for Sc(III), 1.80 for Gd(III), and 2.57 for Al(III).

The interpretation of the concentration effect on the substrate transfer is a difficult task, because this interdependence is determined by many factors, often countervailing. On the one hand, increasing the carrier concentration should accelerate the complex formation and hence the transfer rate. At the same time, the increase in the carrier concentration obviously leads to the change of important properties of the membrane liquid phase such as viscosity and dielectric constant, which should be increasing, while, obviously, an increase in viscosity should slow down the process. Finally, at high concentrations of the carrier the lowering of the re-extraction rate of the complex from the membrane phase can be expected. It is clear that taking into account all the factors compensating each other on a quantitative level is practically impossible. However, the information about the extent of binding the substrate by the carrier in the membrane phase can provide some clarity in the description of the processes.

Table 1. Dependence of the metal ion flux value (F) on the carrier **I** concentration (c) in the membrane

c, M	$F\times10^{-5}$, mol m^{-2} min^{-1}		
	Sc(III)	Gd (III)	Al (III)
0.1	24.17	3.98	1.05
0.05	14.93	1.14	0.14
0.025	8.67	0.28	0.03
0.0125	3.55	0.10	[a]

[a] Concentration is below the sensitivity of the measurement method.

For this reason we decided to measure the concentration of metal in the membrane phase by weighing a certain area of the membrane impregnated with a solution of the carrier and contacted with 0.1 M scandium nitrate solution. Further, by X-ray fluorescence spectroscopy, we determined the content of Sc(III) in the membrane. We found that the molar ratio of bisphosphinylamine contained in the membrane to the amount of the Sc(III) transferred into the membrane is in strict conformity with the stoichiometric ratio, that is, the membrane is in the state of saturation [16]. This means that virtually the entire reactant located in the membrane phase is bound in a complex.

The data obtained allow us to conclude that, since the Sc(III) complexes are rather labile, the process of formation of a lipophilic complex with biphosphinylamine is relatively fast, and the transfer efficiency depends mainly on the diffusion and dissociation rates of the complex.

As mentioned above (see also [5]), the complex to be extracted is an ionic associate, consisting of a triply charged cation of large radius and three nitrate ions. Compounds of this type are prone to association in nonpolar media, and the resulting associates of this kind can greatly increase the viscosity of membrane phase and slow down the diffusion process. This situation is confirmed by the fact that the increase of the flux value of weakly extractable ions Gd(III) and Al(III) with increasing concentration of carrier occurs in a much greater extent than that of Sc(III).

Our results showed also that, as is evident from Table 2, with decreasing concentration of the carrier the selectivity of Sc(III) relative to Gd(III) and Al(III) increases.

To study the effect of substrate (scandium nitrate) concentration on the rate of membrane transport, we determined the magnitude of the transfer flux by the carrier **I** changing the substrate initial concentration in the source phase in the range 0.0055–0.0125 M, while the concentration of carrier in the membrane phase was maintained constant, equal to 0.1 M. We found that with increasing substrate concentration from 0.0055 M to 0.010 M the flux value ($F\times10^{-5}$, mol m^{-2} min^{-1}) increased more than threefold, from 5.83 to 19.91, while further increase in concentration did not cause a significant increase in the flux value: 24.2 (0.0125 M) and 25.6 (0.05 M).

These results agree well with the mechanism we assumed of extraction of scandium [5], according to which the constant of the extraction equilibrium at the source solution/membrane interface is expressed by Eq. (1).

$$K = \{[\mathrm{Sc(bfa)_2}]\cdot 3(\mathrm{NO_3^-})\}_{\mathrm{org}}/[\mathrm{Sc^{3+}}]\cdot[\mathrm{NO_3^-}]^3[\mathrm{bfa}_{2\mathrm{org}}]^2. \quad (1)$$

From Eq. (1) follows that the distribution coefficient of scandium ions D_{Sc} between the aqueous and membrane phases is defined by Eq. (2).

$$D_{\mathrm{Sc}} = K[\mathrm{NO_3^-}]^3[\mathrm{bfa}_{2\mathrm{org}}]^2. \quad (2)$$

From Eq. (2) follows that the D_{Sc} value is in a cubic dependence on the concentration of $\mathrm{NO_3^-}$ ions in the aqueous phase, which explains the increase in flux magnitude up to 0.05 M with an increase in the latter.

The reaching a limit is due to the fact that the reagent is bound completely to form complex with the substrate. Moreover, the dependence (2) suggests that the rate of transport of the substrate at the scandium nitrate concentration less than 10^{-3} M is influenced by the processes on both sides of the membrane and depends on the rate of diffusion through the membrane. At higher concentrations of $\mathrm{Sc(NO_3)_3}$ saturation of the membrane occurs, and the flux is determined by the rate of diffusion and dissociation of the Sc(III) complex with the carrier at the membrane/receiving solution interface.

Table 2. Transfer flux ratio of Sc(III) to Al(III) and Gd(III) at different concentrations (c) of carrier **I**

c, M	Sc/Gd	Sc/Al
0.100	6.1	23
0.0500	13	100
0.0250	31	250
0.0125	36	–

The membrane extraction process can be effective when the so-called active transport is possible, that is, the transfer of a substrate contrary to its concentration gradient. The above results on the membrane transport of metal ions were obtained under the conditions of dialysis, that is, the transfer of substrate from a solution with a higher concentration to a solution with lesser concentration. The symport mechanism realized in this case involves diffusion of the cations $\mathrm{Sc^{3+}}$ and anions $\mathrm{NO_3^-}$ through the membrane in the same direction, therefore the active transport of scandium can be stimulated in two ways: One is the creation of an excess concentration of nitrate ions in the source solution. In this case, the ions Sc(III) will be transferred due to the difference of chemical potentials of nitrate ions on opposite sides of the membrane. Another possibility is the introduction into the receiving phase of a reagent capable to form stable complex with the metal ion. We tried to apply the first method.

Preliminary, we found that the alkali metal nitrates practically are not transported through the membrane by bisphosphinylamines (Table 3), so we used the source solution containing scandium nitrate in an amount of 3.0×10^{-6} mol and potassium nitrate 1.8×10^{-3} mol. The obtained dependence of the Sc(III) concentration in the receiving and source phases is shown in Fig. 2.

The Sc(III) concentration in the receiving phase was measured by conductometry, in the source phase it was calculated according to Eq. (3).

$$c_{\mathrm{source}} = c_0 - (V_{\mathrm{receiving}}/V_{\mathrm{source}})c_{\mathrm{receiving}}, \quad (3)$$

where c_{source}, $c_{\mathrm{receiving}}$, and c_0 are current concentrations in the source and receiving phases, and the initial concentration of scandium ions, respectively. It was found experimentally that the transport of Sc(III) ions continues also when its the equilibrium concentrations in the source and receiving phases became equal (the

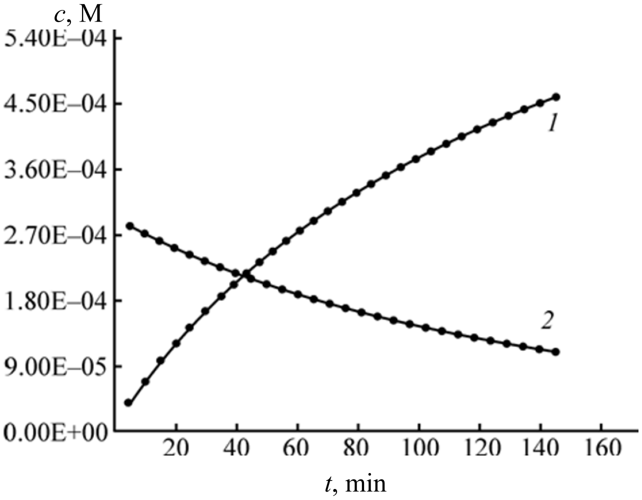


Fig. 2. Concentration dependence of Sc(III) (*1*) in the receiving and (*2*) source phases on time. The carrier **II**, $c_{\text{source}} = 5.4\times10^{-6}$ mol Sc(III), $V_{\text{receiving}} = 7.5$ ml $V_{\text{source}} = 18$ ml.

point of intersection of the curves in Fig. 2). Using this kinetic dependence, we determined the permeability coefficient of the membrane toward scandium [Eq. (4)].

$$\log (c/c_0) = -(Q/V)P_{\text{Sc}}T, \tag{4}$$

where c_0 and c are initial and current concentrations of scandium in the source solution, Q is the membrane surface area, V is the volume of source solution, P_{Sc} is the membrane permeability coefficient.

Table 3. Transfer flux (*F*) ratio of metal salts by carriers **I–IV**

Substrate	$c_{\text{substrate}}$, M	$F\times10^{-5}$, mol m^{-2} min^{-1}			
		I	II	III	IV
KNO_3	0.1	0.06	0.04	0.13	0.55
$NaNO_3$	0.1	0.26	0.21	0.33	
$Al(NO_3)_3$	0.05	1.85	2.42	1.42	2.56
	0.025	0.97	1.05	0.80	1.32
$Nd(NO_3)_3$	0.05	8.82	10.24	10.83	9.24
	0.025	1.99	2.99	1.85	2.84
$Gd(NO_3)_3$	0.05	15.07	9.81	5.83	3.98
	0.025	2.13	3.98	2.27	1.26
$Sm(NO_3)_3$	0.05	8.10	13.08	5.69	3.98
	0.025	2.42	3.70	2.13	1.26
$Sc(NO_3)_3$	0.05	25.03	23.89	15.36	7.82
	0.025	23.75	21.19	12.51	6.26
	0.0125	19.48	10.66	12.80	1.34

This relation implies that the slope (K) is equal to:

$$K = -(Q/V)P_{\text{Sc}}. \tag{5}$$

The permeability coefficient is defined as:

$$P_{\text{Sc}} = -(KV/Q). \tag{6}$$

The average estimated value of the membrane permeability using the carriers **I** and **II** is 2.47×10^{-6} m s^{-1}.

As mentioned above, we used as the carriers of the selected metal ions quite different by structure diphosphinylamines **I** and **II**, as well as diphosphinylpiperazine (**III**) and aminomethylphosphine oxide (**IV**) in order to compare the efficiency of membrane transport of metal ions with these organophosphorus reagents. The results shown in Table 3 indicate that diphosphinylamines **I** and **II**, which differ only in the length of hydrocarbon substituents at one of the phosphoryl centers (lipophilicity), transfers Sc(III) with approximately the same rate, while with two other carriers the flux is considerably less.

The minimal transfer rate is characteristic of monophosphorylated amine **IV**. The highest values of the flux in this series of compounds provide bisphosphinylamines **I** and **II**.

Thus, this study suggests that the membrane based on the studied aminophosphoryl compounds have a pronounced selectivity for scandium, except for the case of a derivative of piperazine, which at a concentration of 0.05 M carries the Nd(III) ions relatively better. The most effective as the carriers are compounds **I** and **II**. It is interesting to note that the compound **II** of the structure asymmetric due to the difference in the substituents at the phosphorus atom, is slightly inferior by the selectivity to its symmetric counterpart **I**. In all cases, the highest selectivity is reached at a concentration of carrier in the membrane phase 0.025 M. By creating an excess concentration of nitrate ions in the source solution we proved that scandium ions can be transported by active transport, which makes it possible to use these carriers in industrial processes.

EXPERIMENTAL

We used the scandium, gadolinium, neodymium, and aluminum nitrates and alkali and alkaline earth metal perchlorates of analytically pure grade. The method of study the membrane transport and the used installation were described in [17]. As a hydrophobic matrix for the impregnated membranes were used Vladipor MFFK-4 teflon filters with 0.6 μm pore diameter.

The metal ion concentrations were determined by X-ray fluorescence spectroscopy according to the methods described in [3]. Conductometric studies and potentiometric determination of acid-base properties were performed by the method described in [18].

Synthesis of the phosphinylamines **I–IV** is based on the Kabachnik–Fields reaction in accordance with the procedure described previously [7, 19], characteristics of diphosphinylamine **I** are given in [7], of bis(didecylphosphinoylmethyl)piperazine (**III**), in [20].

Dihexyldidecyldiphosphinyloctylamine (II). Yield 70%, thick oil, $R_f = 0.45$ (eluent acetone–chloroform–methanol, 5:8:1). IR spectrum (film), $\nu_{P=O}$ 1162 cm^{-1}. ^{1}H NMR spectrum ($CDCl_3$, 300 MHz) δ, ppm: 2.82 t (CH_2, $^3J_{PH} = 6.30$ Hz), 2.89 d [$(CH_2)_2$, $^2J_{PH} = 2.89$ Hz], 0.86–0.82 m [$(CH_3)_4$, $(CH_3)_4$, CH_3], 1.82–1.16 m [$(CH_2)_{20}$, $(CH_2)_{36}$, $(CH_2)_{14}$]. ^{31}P NMR spectrum: $\delta_P = 42.5$ ppm, broadened.

Didecyl-*N,N*-dioctylaminomethylphosphine oxide (IV) was obtained from didecylphosphinous acid, paraformaldehyde, and dioctylamine, yield 60%, mp 26.5°C; $R_f = 0.62$ (eluent acetone–chloroform–methanol, 5:8:1). IR spectrum (film): $\nu_{P=O}$ 1155 cm^{-1}. ^{1}H NMR spectrum ($CDCl_3$, 300 MHz), δ, ppm: 0.82 m [$(CH_3)_4$, $^3J_{PH} = 6.53$ Hz], 1.70–1.21 m, $(CH_2)_{32}$, 2.67 d (CH_2, $^2J_{PH} = 6.97$ Hz), 2.48–2.43 m, CH_2. ^{31}P NMR spectrum: $\delta_P = 45.9$ ppm.

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