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Synthesis, Transport and Ionophore Properties of α,ω-Biphosphorylated Azapodands: V.[1] Acid–Base Properties of New Phosphorylated Azapodands and α,ω-Diamines and Their Participation in the Membrane Transport of I–III Groups Metal Ions

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Abstract—Acid–base properties of newly and previously synthesized phosphorylated azapodands and α,ω-diamines and their amine precursors were studied. We found that they differ in the same range as has been found previously for the other aminophosphoryl compounds. The investigation of the processes of passive membrane ion transport of a series of metals of I–III groups by these reactants showed with all diphosphoryl diamines higher values of the transfer flow of the ions Sc(III), Nd(III), and Sm(III), than the ions of alkali and alkaline earth metals. Under the conditions of active membrane transport the azapodand **IV** exhibits high efficiency in the ion transport of Sr(II) and Ba(II), while diphosphoryldiamine **III** exhibits effective transport of Nd(III) ions. The factors that determine the efficiency and selectivity of the membrane extraction of the I–III groups metal ions by these diphosphoryl diamines are discussed.

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Recently we showed a high efficiency of membrane extraction with phosphorylated aza- [1] and thiapodands [2] of substrates of different nature, including organic and inorganic acids and some metal ions. In this paper we present the results of a study of acid–base properties and the transport processes of the I–III groups metal ions through the impregnated liquid membranes using a number of transmembrane transporters, the phosphorylated azapodands and α,ω-diamines, both studied previously and first synthesized in this study.

In the recent years a high efficiency of aminophosphoryl compounds was found in the extraction, concentration, separation, and analysis of substrates of different nature, including ions of alkali and alkaline earth [1], noble [3–5], rare, and trace metals [6–9], mineral [10, 11] and organic acids [12]. This was confirmed also in the recent study of the extraction of lanthanides with bi- and polydentate aminophosphoryl compounds [13–15], liquid-liquid extraction of noble metals with diphosphorylamines and -diamines [4], as well as multibasic organic acids with bis(aminophosphorylmethyl)alkanes [16, 17]. Now we for the first time studied the processes of membrane transport of triply charged ions of rare and trace metals, like scandium, neodymium, and samarium, with bifunctional aminophosphoryl compounds, and compared their transport flows through the impregnated liquid membranes with the relevant characteristics of the transmembrane transport of alkali and alkaline earth metal ions in the same conditions.

An important requirement to the compounds used as industrial extractants, membrane transporters, and ionophores for electrochemical sensors, etc., is their high lipophilicity. We used α,ω-diphosphorylamines of the general formula **I**–**V**, and also taken for the comparison mono- **VI** and diphosphoryl monoamines **VII** with a lipophilic long-chain hydrocarbon groups with the nitrogen and phosphorus atoms as the potential coordination sites: $[R_2P(O)CH_2NH]_2Z$ (**I**–**V**), $R_2P(O)CH_2NHR$ (**VI**) and $[R_2P(O)CH_2]_2NR^1$(VII),

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[1] For communication IV, see [1].

Table 1. Dissociation constants of conjugate acids of aminophosphoryl compounds and their amine precursors

Comp. no.	pK_{a1}	pK_{a2}	Amine precursor	pK_{a1}	pK_{a2}	ΔpK_{a1}	ΔpK_{a2}
I	4.04	5.61	$NH_2(CH_2)_4NH_2$	8.28	9.85	4.24	4.24
II	5.38	5.70	$NH_2(CH_2)_6NH_2$	9.08	10.06	3.70	4.36
III	4.93	5.25	$NH_2CH_2CH(CH_3)(CH_2)_3NH_2$	8.85	9.74	3.92	4.49
IV	4.30	5.25	$NH_2(CH_2)_2O(CH_2)_2O(CH_2)_2NH_2$	8.20	8.98	3.90	3.73
V	5.17	5.79	$NH_2(CH_2)_3O(CH_2)_2O(CH_2)_3NH_2$	8.28	9.12	3.11	3.33
VI	5.23 [19]		$C_8H_{17}NH_2$	9.49		4.26	
VII	>2 [18]		$C_8H_{17}NH_2$	9.49		<7.5	

where R = C_6H_{13} (**I**, **II** and **VII**); R = R^1 = C_8H_{17} (**II**, **IV–VII**); Z = $(CH_2)_4$ (**I**), $(CH_2)_6$ (**II**), $CH_2CH(CH_3)(CH_2)_3$ (**III**), $(CH_2CH_2O)_2CH_2CH_2$ (**IV**), $(CH_2)_3O(CH_2)_2O(CH_2)_3$ (**V**), which we synthesized in the one-pot mode of the Kabachnik–Fields reaction from dialkylphosphinous acids with formaldehyde and the corresponding diamine, or, for analogs **VI** and **VII**, from monoamines.

To evaluate the characteristics of interphase distribution and to select complementary transporter-substrate pairs a very useful information can be obtained by analyzing the acid–base properties of the transporter reagents. In addition, the fact should be considered that the processing of a mineral raw material and the extraction of metal ions from it is carried out using aqueous solutions of mineral acids, so the basicity of diphosphoryldiamines used should be taken into account when analyzing the possibility of transfer from the aqueous phase of the mineral acid along with the metal ion [8, 9].

The dissociation constants of the conjugate acids of the diphosphoryldiamines **I** and **II**, aminophosphine oxide **VI**, and diphosphorylamine **VII** in the aqueous (50 vol %) 2-propanol medium were measured earlier [17, 18]. In the present study, we measured under the same conditions the pK_a values of diamine **III** and azapodands **IV** and **V**, as well as the corresponding amine precursors. As can be concluded from the results shown in Table 1, the influence of the acceptor phosphoryl group on the basicity of the investigated diphosphoryldiamines obeys the same laws that were found for all aminophosphoryl compounds: The change in pK_a values of amine-precursors as a result of their phosphorylation occurs within the same range that has been found in the study of acid–base properties of monobasic amines and their phosphorylated derivatives [18, 20]. Thus, the acceptor effect of methylenephosphoryl group reduces the basicity of amine centers on the average by 3–4.5 pK_a units, in the same range decreases the ΔpK_a of monoamine **VI**. It is indicative that there is no particular difference in ionization constants between the first and second stages, pK_{a1} and pK_{a2} on the one hand, and the corresponding values ΔpK_{a1} and ΔpK_{a2}. The most noticeable is the mutual influence of closely spaced aminophosphoryl groups in diphosphoryldiamine **I**, amounting to more than 1.5 units. This phenomenon, as well as a very strong influence of the two phosphorus-containing groups on the basicity of diphosphorylamine **VII**, was discussed in [17, 18]. In general, we can state that the mutual electronic influence of aminomethylphosphoryl groups in the molecules of potential membrane transporters described in this paper is not essential, and it can be assumed that, depending on the nature of the transported substrate, these compounds can act either as having two independent coordination sites or as bidentate ligands. In the latter case they like other phosphoryl podands [1] can also form chelates coordinating the metal ion by the oxygen atoms of the terminal aminomethylphosphoryl groups in the compounds **I–III**, and, moreover, through the donor-acceptor interaction with the metal ion also of the oxygen atoms of the polyester bridge in compounds **IV** and **V** forming pseudocavities of different size.

The high complexing power of the phosphine oxide and amino groups, and their high selectivity with respect to the ions of alkali and alkaline earth metals [21, 22] prompted us to study the processes of membrane transport of these substrates with the aminophosphoryl compounds considered in this paper, which combine just the structural fragments responsible for the complexation with metal ions. In addition, a goal of this work was the search for among the described

Table 2. Transfer flows (F) of metal nitrates with aminophosphoryl compounds

Comp. no.	$F\times10^5$, mol m^{-2} min^{-1}									
	Na(I)	K(I)	Cs(I)	Mg(II)	Ca(II)	Sr(II)	Ba(II)	Sc(III)	Nd(III)	Sm(III)
I	1.3	1.0	1.0	7.9	18	4.0	2.7	37	99	75
II	0.9	0.9	0.8	5.7	17	2.7	28	28	129	93
III	1.1	0.9	1.1	4.0	27	5.8	3.9	76	70	86
IV	2.3	1.3	1.6	18	47	16.3	63	56	64	80
V	1.3	2.4	1.9	38	3.9	3.9	2.1	66	66	64
VI	0.6	1.0	0.8	2.3	32	2.4	2.7	82	111	87
VII	0.9	0.6	0.3	2.1	7.4	2.2	1.7	70	88	81

aminophosphoryl compounds of effective and selective membrane extractants of rare and trace metals, of which we chose the triply charged ions of scandium, neodymium, and samarium. As the membrane solvent we used 1,2-dichlorobenzene, which readily dissolves the selected carriers. Note that in our preceding work [1], which describes the membrane extraction of the ions of the I and II groups metal with phosphorylazapodands, we used phenylcyclohexane as a membrane environment, in which, as it turned out, not all carriers described here are readily soluble. Transport flows of I–III groups metals are listed in Table 2.

Analyzing the experimental results, we can note a rather low efficiency of membrane extraction of alkali metal ions with the selected diphosphoryl diamines in the taken conditions. Also the rate of transport of the Mg(II), Sr(II) and Ba(II) ions is low, but azapodand **IV** shows more pronounced membrane extraction efficiency with respect to these ions. At the same time, we found a noticeable increase in the Ca(II) transport flow with all the used diamines. The expressed selectivity toward Ca(II) manifested by the carriers **III** and **VI** may be promising for the separation process of this ion from the ions of other alkali and alkaline earth metals.

We have repeatedly pointed out [1, 7, 17] that it is difficult to expect a sufficiently unambiguous dependence of the transfer efficiency on the structure of the carrier in the membrane extraction process, since the efficiency and selectivity of transmembrane transport are determined by a set of countervailing factors. However, the quite pronounced trend in the transport flow increase in these cases may be caused by the compliance of the atomic radius of the transported ion and the size of the pseudo-cavity formed by the carrier azapodand. We observed the same pattern earlier in the study of membrane transport properties of phosphorylated azapodands [1]. An indirect evidence of the probability of this phenomenon may be the very low transfer flows showed by phosphorylated monoamines **VI** and **VII**.

A completely different pattern is observed in the processes of membrane extraction of the triply charged metal ions Sc(III), Nd(III), and Sm(III). All the used aminophosphoryl compounds including diaminoalkanes **I–III**, polyesters **IV** and **V**, and monoamines **VI** and **VII** exhibit fairly high efficiency in the membrane transport of these ions, however not exhibiting any noticeable selectivity with respect to certain substrates. The high efficiency of transport of Nd(III) ion by diamine **II** might be attributed to matching the size of this ion and the transporter pseudo-cavity, or to advantagious entropy of the resulting chelate node, but the similar high transfer rate with amine **VI** suggests that these factors do not play a decisive role. Moreover, the azapodands **IV** and **V**, which are able to provide several donor sites at once for the formation of complexes of the *guest–host* type, exhibit a moderate efficiency in this series. This fact once again confirms the ambiguity of the influence of various factors, including structural ones, on the efficiency and selectivity of the membrane extraction.

As to diphosphinyldiamine **VII**, as follows from our earlier results [6, 7], it acts as a tridentate ligand in the complex formation with triply charged ions of scandium and iron, forming complexes of 2:1 composition. Since this transporter is comparable by efficiency with the other diamines, we can assume that other transport agents studied by us also are able to act as polydentate ligands, but a definite answer can be obtained only by the study of the structure of the complexes transported through the membrane.

Attention should be drawn to the fact that the high selectivity of diphosphorylamine **VII** established earlier [6, 7] with respect to Sc(III) ions, both in the liquid phase and in the membrane extraction, is not observed in the case of the series of triply charged cations. As was mentioned above, phenylcyclohexane was used previously as the membrane solvent. Obviously, the use of 1,2-dichlorobenzene leads to a leveling of the selectivity, and practically the rates of transport of the studied triply charged ions of rare-earth metals become equal, while the flow transport value increases several times in comparison with phenylcyclohexane [6]. The reason of such behavior of the Sc(III) ions at the replacement of the membrane solvent is difficult to interpret: it may be due to the change in the solubility of the metal complex in 1,2-dichlorobenzene, in the membrane phase viscosity as a result of complex formation, and to many other reasons. Nevertheless, it is necessary to point out that a decrease in the transporter concentration from 0.1 to 0.025 (Table 3) increases the transport flow of Sc(III), which can be interpreted in favor of reducing the membrane viscosity. Note the opposite trend with the doubly charged ions: on decreasing the azapodand **IV** concentration they are extracted much more slowly. Thus, at a concentration of 0.1 M the transport flow falls almost ten-fold. It can be assumed that at the substrate concentration of 0.1 M the membrane most likely does not reach saturation. In this regard, the unusual behavior of the ion Sc(III) clearly deserves a special study which we have not yet carried out.

c_{tr}	$F\times10^5$, mol m^{-2} min^{-1}				
	Mg(II)	Ca(II)	Sr(II)	Ba(II)	Sc(III)
0.1	18	47	16	63	56
0.025	1.7	11.2	5.2	16	67

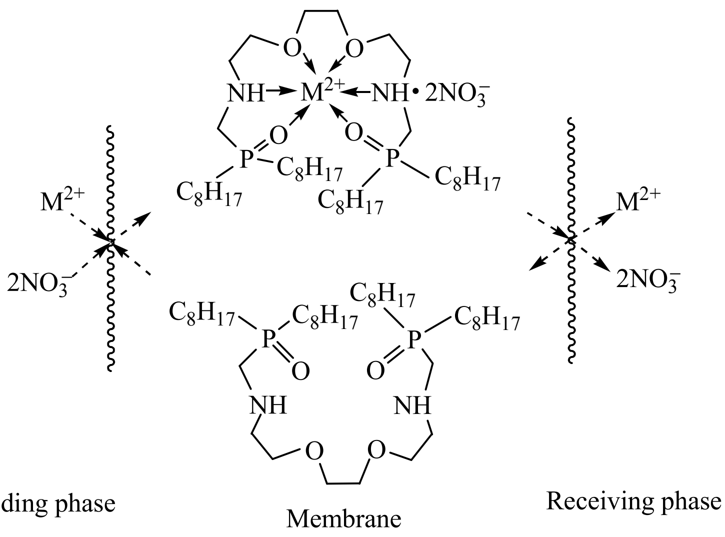
It is well known [23] that in the process of membrane extraction of metal ions the nature of the anion plays a certain role, which can affect the stability of the complex of the transferred metal salt with the reagent-carrier, in this case, obviously, of the *guest–host* complex or the corresponding chelate. In our selected conditions, we determined the transport flows of potassium iodide transport with all used aminophosphoryl compounds and found an increase in the efficiency of its transport on the average 1.5–2 times in comparison with potassium nitrate.

Thus, bisphosphoryldiamines **I–V** are shown to be effective membrane extractants for the triply charged ions Sc(III), Nd(III) and Sm(III). Among the metals of groups I and II, the highest rate of transport belongs to Ca(II) ion, which can be used to separate it from a number of accompanying ions of alkali and alkaline earth metals.

The above results on the membrane transport of metal ions were obtained under conditions of dialysis, that is, the substrate transfer from the solution with a higher concentration to a less concentrated solution. The *symport* mechanism realized in this case involves diffusion through the membrane in one direction of both the metal cations and anions. However, the membrane extraction as a technological process can be effective only when it possible to transfer a substrate against its concentration gradient (so-called active transport), which can be stimulated by the creation of an excess concentration of the anion in the feeding solution [23, 24].

Since the creation of innovative methods of extraction of the radioactive waste isotopes of heavy alkaline earth metals like barium, and particularly strontium, is of great practical importance, we investigated the process of membrane extraction under the active transport conditions of some metal nitrates of groups II and III. To implement the active transport of ions, that is, to complete the transfer of substrate from nitric acid medium of the feeding phase into the receiving one, is necessary to create a high concentration of nitrate ions in the feeding solution (symport) by adding sodium or potassium nitrate, since, as we showed above, the flows for the alkali metal cations are very small. We found that in the symport conditions, when 1,2-dichlorobenzene is used as a membrane solvent, the azapodand **IV** performs effective transport through the impregnated liquid membrane of the Ca(II), Ba(II), and Sr(II) nitrates, and bisphosphoryl diamine **I** is a transporter for Nd(III) ions.

The studied azapodands are electrically neutral ionophores, and membrane transport must be performed through formation of electrically neutral particles, therefore we can assume that the transport occurs by a mechanism shown below. The rate of ion transport should depend both on the carrier concentration in the organic and nitrate ions in the feeding aqueous phase. We studied the influence of these factors on the transport flows of Ca(II), Ba(II) and Sr(II) with the azapodand **IV**, by changing the concentration of potassium nitrate and aminophosphoryl carrier in a fairly wide range.



To study the effect of concentration of potassium nitrate on the rate of membrane transport, the inithial concentration of KNO_3 in the feeding phase was varied in the range 0.1–1 M, and the concentration of carrier in the membrane phase remained constant at 0.2 M. The flows of the Sr(II) ion transport with azapodand **IV** depending on the concentration of nitrate ions, listed as an example in Table 3, indicate the flow growing at the potassium nitrate concentration of 0.7 M, at which occurs the membrane saturation, then the flow is determined only by the diffusion rate and the rate of dissociation of the complex Sr(II) with the carrier at the membrane/receiving solution interface. A similar pattern was observed for the other metal cations of group II.

Another important factor in the effectiveness of active transport is the carrier concentration in the membrane phase. We measured the transport flow of Ba(II) with azapodand **IV** while varying the concentration of the carrier from 0.01 to 0.20 M. The dependence of the flow transport on the concentration of the ion transporter in the membrane phase shown in Fig. 1 suggests that with increasing carrier concentration in the membrane phase the transfer flow rate expectably increases, but a two-fold change in concentration of the carrier, from 0.1 to 0.2 M, affects the extraction of barium ions only insignificantly. Obviously, an almost complete saturation of the membrane phase is reached even at 0.1 M concentration of the extractant.

However, it should be noted that the interpretation of the effect of concentration on the transport of substrates is also a difficult task, because this interdependence is determined by many factors, often countervailing ones. On the one hand, increasing the carrier concentration should accelerate the complex formation and hence the transfer rate. At the same time, with increasing carrier concentration other important properties of the membrane liquid phase like viscosity and dielectric constant obviously change, probably increase. The increase in viscosity likely slows down the process. Finally, one can expect a reduction of the rate of complex re-extraction from the membrane phase at a high carrier concentration. It is clear that it is impossible to take into account all these factors compensating each other, especially on a quantitative level.

To evaluate the efficiency of the Ba(II) and Sr(II) membrane extraction, we operated with the values of the substrate flow transport (*F*), because the changes in their concentration in the feeding phase were not significant during the experiment. However, in the case of active transport of ions it is not always possible to use this characteristics since the concentration of the transported substrate can vary greatly within a relatively short time period. In this case, the transfer efficiency is commonly evaluated by the value of permeability (*P*), which is one of the important parameters of the membrane that determines the ability of the solute molecule to penetrate through the membrane [25]. Since the flow for Nd(III) ion transfer by diphosphoryldiamine **I** is sufficiently high (70.1×10^5 mol m^{-2} min^{-1}) it is logical to assume that at high concentrations of nitrate ion in the feeding phase the rate of metal transfer through the membrane per time unit will be high, and in this case to use the coefficient of permeability is most appropriate.

Table 3. Change in the transfer flow of $Sr(NO_3)_2$ depending on the concentration of KNO_3 in the feeding solution ($c_{0\ Sr(II)} = 1.25\times10^{-3}$ M)

KNO_3 concentration, M	$F\times10^5$ mol m^{-2} min^{-1}
0	68
0.1	112
0.2	149
0.4	193
0.6	250
0.7	295
0.8	211
1.0	211

In order to investigate the influence of the concentration of nitrate ion on the rate of Nd(III) membrane transport with carrier **II** we changed the concentration of nitrate ions in the feeding solution in the range from 0.05 to 2.0 M. The plots in Fig. 2 allow a suggestion that in this case the active transport is actually realized, since the concentration of neodymium in the receiving phase continues to increase after achieving equality with the concentration in the feeding phase (the point of intersection of the curves in Fig. 2).

Our experimental data make it possible to calculate the value of the permeability of the membrane according to the equation $\log c/c_0 = -SPt/V$, where c_0 and c are inithial and current concentrations of Nd(III) in the feeding solution, S is the membrane surface area, V is the volume of the feeding solution, P is the coefficient of permeability of the membrane. Figure 3 shows the dependence of the permeability P on the concentration of nitrate ions in the feeding solution. The nonmonotonic shape of the curve probably is associated with the formation of many forms of extractable complexes of Nd(III) and the possible change in the extraction mechanism. However, the understanding of the essence of the processes in this system requires a detailed study of the physicochemical parameters of the complex formation. The maximum reached permeability value is about 1.03×10^{-5} m s^{-1}.

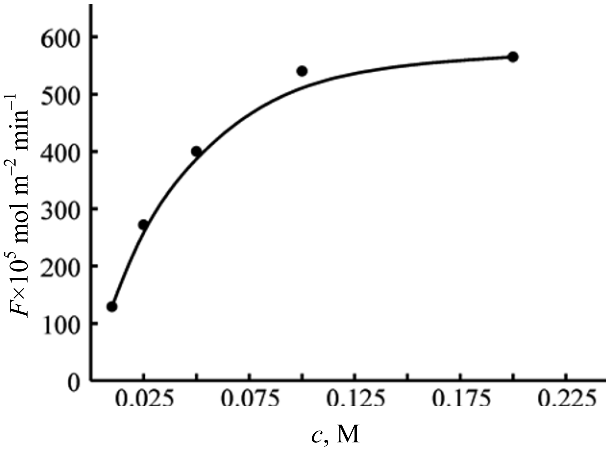


Fig. 1. The dependence of the transport flow of $Ba(NO_3)_2$ on the carrier **IV** concentration in the membrane phase.

As mentioned above, another important factor influencing the rate of membrane transport, along with the concentration of nitrate ions in the feeding solution, is the concentration of carrier in the membrane phase. We have studied the changes in the membrane permeability over time at a constant initial composition of the feeding solution. The membrane contained the transporter solutions in 1,2-dichlorobenzene of concentration in the range 0.025–0.30 M. The dependence of the effect of concentration of transporter **II** on the P value (Fig. 4) indicates that the permeability of the membrane increases with increasing carrier concentration to 0.20 M, and at the concentrations above 0.25 M begins to decrease, which is likely due to the increased viscosity of the membrane phase at the high concentration of the carrier. Thus, the optimal value of the carrier concentration in the membrane is equal to 0.2 M at which the maximum flow is observed.

We determined the maximum attainable membrane permeability in the extraction of the Nd(III) ion with the carrier **II** under the conditions of active transport: 1.14×10^{-5} m s^{-1} at the carrier concentration 0.2 M, nitrate ion concentration 1.48 M. Note that at the higher concentration of sodium nitrate, 0.25 M, the value of P was similar: 1.03×10^{-5} m s^{-1}, so there is no need to use a higher concentration of $NaNO_3$.

These experimental results allowed us the optimization of the conditions of membrane extraction of Sr(II) and Ba(II) ions with aminophosphoryl azapodand **VII** and Nd(III) ions with diphosphoryldiamine **II**, which obviously can be taken into account when planning the actual extraction technologies, concentrating and separation of the studied metals.

EXPERIMENTAL

NMR spectra were recorded on a Varian XL-300 instrument with an operating frequency 122.4 MHz (^{31}P, internal reference 85% phosphoric acid) and 300 MHz (^1H, solvent $CDCl_3$, internal reference TMS). In the syntheses the solvents of analytically pure and

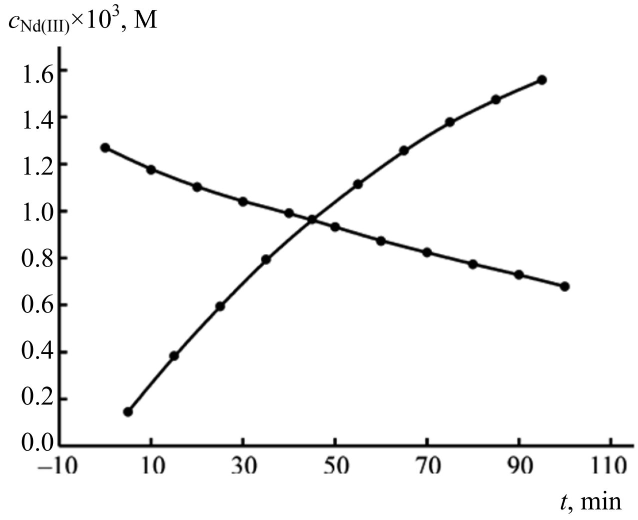


Fig. 2. The kinetics of ion transport of Nd(III): the content of the ion in the feeding and receiving solutions for membrane transport with diphosphoryldiamine **II**, $c_{0\ Nd(III)} = 1.27\times10^{-3}$ M, $c_{\mathbf{II}} = 0.1$ M, c(NaNO$_3$) = 0.25 M.

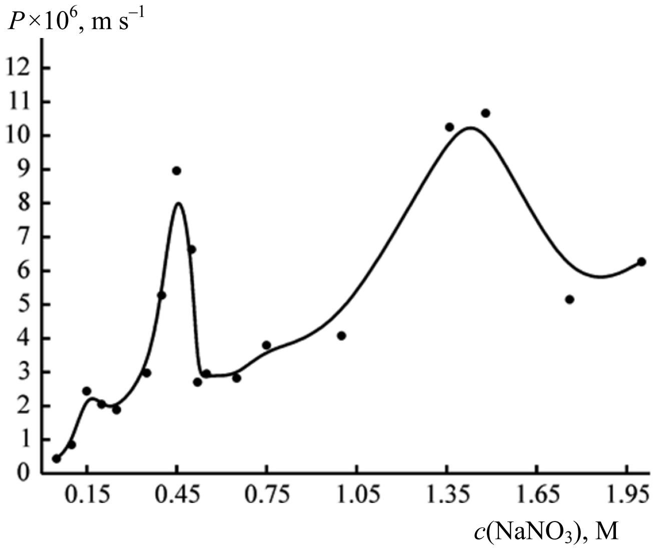


Fig. 3. Dependence of permeability coefficient of Nd ion on the NaNO$_3$ concentration, $c_{Nd(III)} = 1.27\times10^{-3}$ M, $c_{\mathbf{II}} =$ 0.1 M.

chemically pure grade were used, which, if necessary, were purified additionally by usual methods. The amines, diamines, and azapodands are of Acros Organics production. Other materials, if necessary, were synthesized by common methods from commercially available reagents.

For TLC Silufol UV 254 plates were used, eluent chloroform : acetone : methanol 5:8:1 by volume, development in iodine vapor followed by treatment with water.

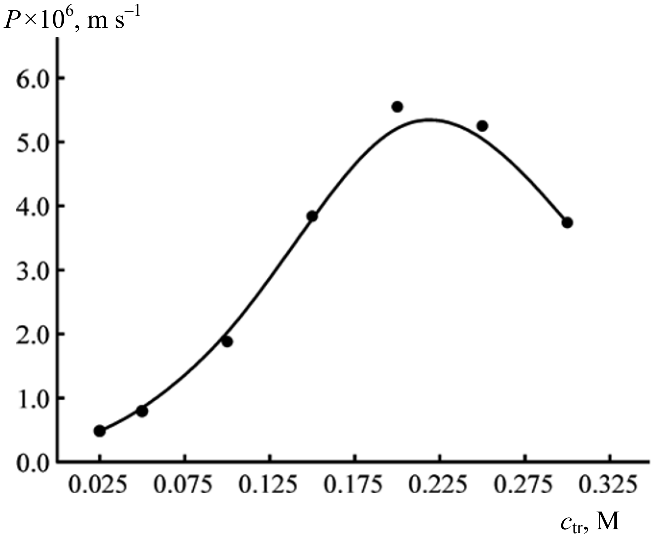


Fig. 4. Effect of carrier **II** concentration in 1,2-dichlorobenzene on the permeability of the membrane [c(NaNO$_3$) = 0.25 M].

Dissociation constants of the aminophosphoryl compounds and precursor amine was carried out by the methods in [26]. The methods to study membrane transport properties are described in [7]. The matrix for the liquid membrane was a membrane filter Vladipor MFFK-4 with a pore size 0.65 μm, as the membrane system were used solutions of the aminophosphoryl compounds in 1,2-dichlorobenzene, the receiving phase was twice distilled water. To create a gradient of concentration of nitrate ions, potassium or sodium nitrates were added to the feeding solution. The content of triply charged metal ions were determined on a KFK-3 photometer, content of alkaline-earth elements was measured using an atomic absorption spectrometer AAS 1N (Germany), the sodium ions content was measured on a flame photometer PFM U4.2.

Methods of synthesis and characterization of diphosphoryl diamines **I**, **III,** and aminophosphine oxide **VI** are given in [17], of diphosphoryl amine **VII** in [16], of azapodand **IV** in [27], diamine **III** and azapodand **V** were synthesized by the methods published in [17, 25], respectively.

***N,N'*-Bis(dioctylphosphorylmethyl)-1,10-diamino-4,7-dioxadecane (III)**. Yield 90%, mp 60°C, R_f 0.25. ^{1}H NMR spectrum (CDCl$_3$), δ, ppm: 2.91 d (P'CH$_2$N', $^2J_{PH}$ 7.2 Hz) , 2.89 d (PCH$_2$N, $^2J_{PH}$ 7.5 Hz), 2.66 t (NC$\underline{H}_2$CH$_2$, $^3J_{HH}$ 6.6 Hz), 2.59 d.d (NC$\underline{H}$'H''CH, $^3J_{HH}$ 11.4 Hz, $^2J_{HH}$ 6 Hz), 2.45 d.d (NCH'$\underline{H}$''CH, $^3J_{HH}$ 11.4 Hz, $^2J_{HH}$ 6 Hz), 0.91 t (CH$_3$, $^3J_{HH}$ 6.9 Hz), 0.93 d

($C\underline{H}_3CH$, ${}^3J_{HH}$ 6.3 Hz), 1.20–1.85 m [$(CH_2)_2$, $(CH_2)_7$]. ${}^{31}P$ NMR spectrum (chloroform, 122.4 MHz): δ_P 48.9 ppm.

***N,N'*-Bis(dioctylphosphorylmethyl)-1,10-diamino-4,7-dioxadecane (V).** Yield 79%, mp 55°C, R_f 0.10. IR spectrum, ν, cm^{-1}: NH (3180), P=O (1150), COC (1110). ${}^1H$ NMR spectrum ($CDCl_3$), δ, ppm: 2.92 d (PCH_2N, ${}^2J_{PH}$ 7.8 Hz), 2.78 t ($NC\underline{H}_2CH_2$, ${}^3J_{HH}$ 7.8 Hz), 0.92 t (CH_3, ${}^3J_{HH}$ 6.9 Hz), 3.59 s (OCH_2CH_2O), 3.56 t ($OC\underline{H}_2CH_2CH_2$, ${}^3J_{HH}$ 6.45 Hz), 1.15-1.85 m [$(CH_2)_7$, CH_2]. ${}^{31}P$ NMR spectrum (benzene), δ_P 43.9 ppm.

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