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Membrane Extraction of Metal Ions by Aminophosphoryl Reagents in the Active Transport Conditions

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Abstract—The process of membrane extraction of rare earth ions, Nd(III), Sc(III), and Sm(III), and also the accompanying them in the natural raw material ions Al(III) and Mg(II), by *N*,*N*-bis(dihexylphosphorylmethyl)-octylamine (BPA) was investigated under the conditions of active membrane transport, and its high efficiency and selectivity was demonstrated with respect to the two first rare earth metals. The influence of principal parameters of the three-phase extraction process, including the nitrate ion concentration, the releasing aqueous phase acidity, the extracting agent concentration in the membrane, and the nature of the membrane solvent, on the membrane permeability, characterizing the efficiency and selectivity of membrane transporters, was established. Comparison of the membrane permeability in the process of transmembrane transport of Nd(III) and Sc(III) with BPA and monophosphorylated amines showed a significant advantage of the biphosphorylated amine extractant.

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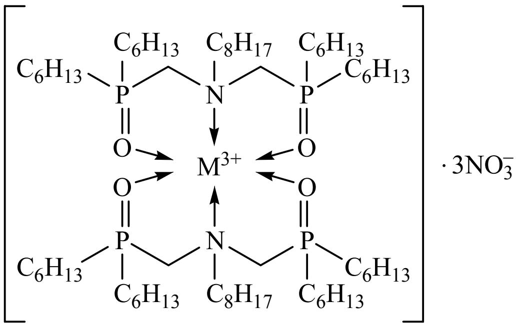
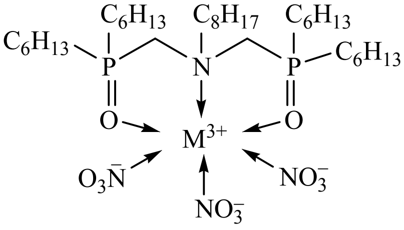
We have studied previously the processes of membrane extraction of ions of rare and trace metals, Sc(III), Gd(III), Sm(III), and Nd(III) by mono- and biphosphorylated amines in dialysis, i.e., transfer of the substrate through a liquid impregnated membrane from a solution of higher concentration in the solution of lower concentration. It was established that the rate of transmembrane transport of the Sc(III) ions by *N*,*N*-bis(dihexylphosphorylmethyl)octylamine is much higher than of the ions of rare-earth metals, aluminum, sodium, and potassium, so this carrier is efficient and selective membrane extractant for scandium [1]. A similar result we obtained in the study of solvent extraction processes by this aminophosphoryl extractant of Sc(III) ions from the media of the aqueous nitric and perchloric acids [2]. However, the efficiency of membrane extraction is determined also by the possibility of transfer of the substrate against its concentration gradient, that is, under conditions of the so-called *active* transport that is usually achieved by creating an excess of the anion in the releasing solution [3, 4]. At the extraction of the Sc(III) ion the process was carried out by adding an excess of sodium nitrate to the releasing aqueous phase in the process of transmembrane transport of scandium nitrate, with a solution of BPA in phenylcyclohexane as a carrier [1]. In this paper we present the results of the study of membrane extraction processes in the conditions of active transport by the indicated aminophosphoryl carrier of Nd(III), Sc(III), and Sm(III) ions, as well as the Al(III) and Mg(II) ions often accompanying them in the natural raw material. As a membrane solvent was selected commercially available 1,2-dichlorobenzene, the membrane was the commercially available film of a sintered P.T.F.E. fluoroplastic.

The results of earlier studies of the *N*,*N*-bis(dihexylphosphorylmethyl)octylamine extraction properties showed that at the solvent extraction of triply charged cations of rare and trace metals from nitric acid media two types of species can pass to the organic phase depending on the acidity of the aqueous phase and the concentration of nitrate ions in the organic phase [5]. At low acidity of the aqueous phase and low enough concentration of nitrate anions the ion associate A is formed, consisting of the metal cation coordinated with two molecules of reactant and three nitrate ions acting as counterions.

Increasing concentrations of nitrate ions leads to the displacement of one of BPA molecules from the coordination sphere with the formation of ternary complexes **B**.

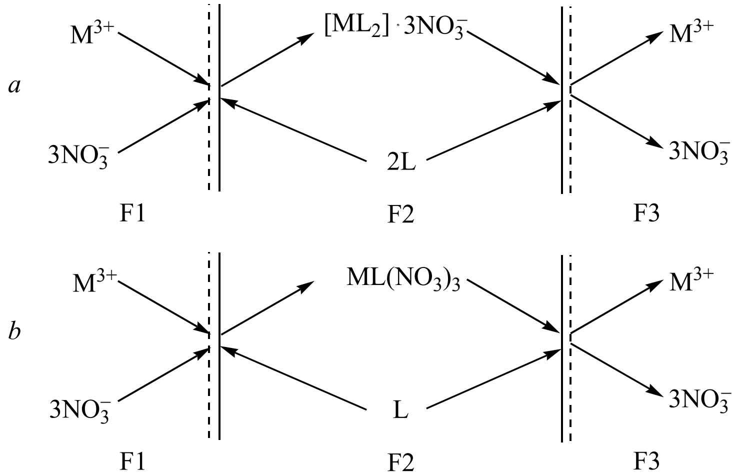


A



B

The membrane extraction with *N*,*N*-bis(dihexylphosphorylmethyl)octylamine can obviously be performed in accordance with two mechanisms of membrane transport (Fig. 1): In the membrane phase either homoligand complex **A** can be formed by the mechanism *a*, or alternative *b* mechanism is implemented leading to the formation of ternary complex **B**. However, in both cases the active transport could be carried out owing only to the concentration gradient of nitrate ion in the receiving and feeding solutions.



We determined the values of the permeability of the membrane [6] for BPA in the transport of ions Nd(III), Sc(III), Al(III), and Mg(II) (see below).

M^{z+}	Nd(III)	Sc(III)	Al(III)	Mg(II)
$c^0_{\mathrm{M}z+}$ 10^{-3}, M	1.24	2.40	6.24	100
$P\times10^6$, m s^{-1}	9.4	5.9	0.06	0.4

It is seen that the Nd(III) and Sc(III) ions are effectively extracted in these conditions, while for the ions Al(III) and Mg(II) only a very weak transport is observed: The membrane permeability for them is almost by one to two orders of magnitude lower, and Al(III) ions are not at all transferred in the selected conditions.

Thus, the *N*,*N*-bis(dihexylphosphorylmethyl)octylamine exhibits a pronounced selectivity with respect to Nd(III) and Sc(III) ions, which can be easily separated from the ions of magnesium and aluminum. In a special experiments we also showed that sodium ions are almost not transported across the membrane: in a blank experiment we could not fix by flame photometry any marked content of sodium at the analysis of samples of the feeding phase.

Figure 1 shows the change of Nd(III) concentration in the receiving and releasing phases in time, which positively confirms the implementation of active transport: The increase in the Nd(III) concentration in the receiving phase continues after equating it with the concentration in releasing phase (the point of intersection of the curves).

In the process of active transport its efficiency strongly depends on the concentration of nitrate ions. We investigated influence of this parameter on the rate

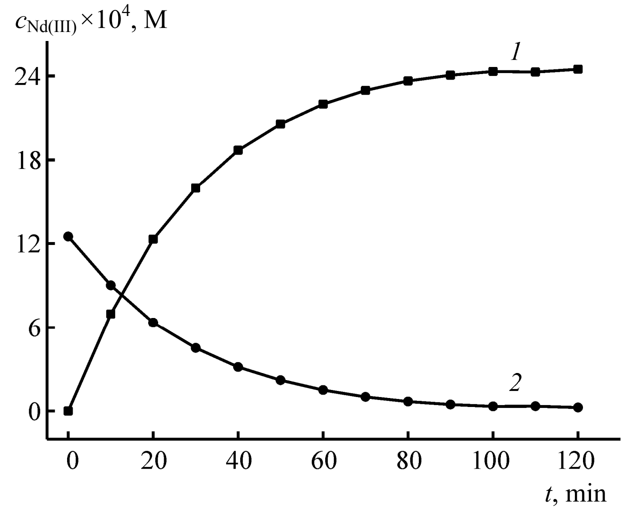


Fig. 1. The change in time of the concentration of Nd(III) in the receiving (*1*) and releasing (*2*) phases. Transporter *N*,*N*-bis(dihexylphosphorylmethyl)octylamine $V_{release}$ 50 ml, $V_{receive}$ 25 ml, $c^0_{Nd(III)}$ 1.25×10^{-3} M, $c^0_{Na(I)}$ 2 M, diaph-ragm P.T.F.E.; $c_{transporter}$ 0.2 M in 1,2-dichlorobenzene, measuring time 120 min, transporter *N*,*N*-bis(dihexyl-phosphorylmethyl)octylamine.

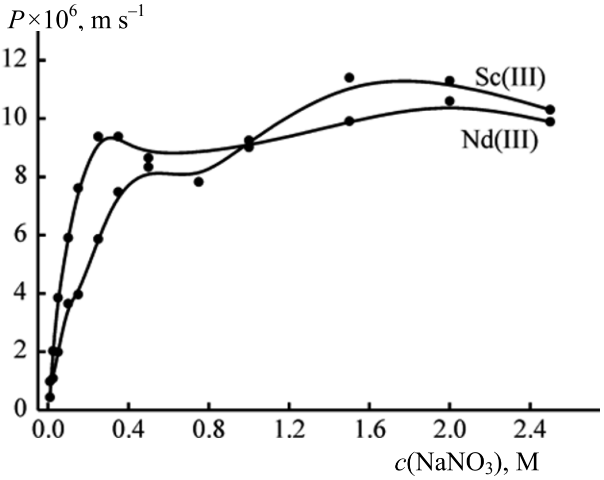


Fig. 2. Effect of the concentration of $NaNO_3$ in releasing solution on the extraction of Nd(III) and Sc(III); transporter *N*,*N*-bis(dihexylphosphorylmethyl)octylamine, $V_{release}$ 50 ml, $V_{receive}$ 25 ml, $c^0_{Nd(III)}$ 1.25×10^{-3} M, $c^0_{Sc(III)}$ 2.4×10^{-3} M, membrane P.T.F.E., $c_{transporter}$ 0.2 M in 1,2-dichlorobenzene, measuring time 110–150 min.

of membrane transport of Nd(III) ions by varying the concentration of nitrate ions in the releasing solution from 0.01 to 2.50 M at a constant concentration of *N*,*N*-bis(dihexylphosphorylmethyl)octylamine in the membrane. The changes in the substrate (metal ion) content in the releasing phase in time is described by Eq. (1) that includes the membrane permeability (*P*).

$$\log c/c_0 = -(S/V)Pt, \qquad (1)$$

where c_0 and c are initial and current concentrations of the solution releasing the metal ion, S is the membrane surface area, V is volume of the releasing solution. As evidence the obtained values of the membrane permeability towards the Nd(III) and Sc(III) ions (Fig. 2), the transfer rate increases to a certain limit with increasing concentration of sodium nitrate, but at concentrations of nitrate ions exceeding 0.25 M for Nd(III) and 0.5 M for Sc(III) the rate remained largely unchanged. We can assume that at high concentrations of sodium nitrate the membrane begins to act in a "saturation regime," when the rate of mass transfer is limited by the diffusion processes [7]. A small deflection of the plot in the range of concentrations of nitrate ion 0.35–1.5 M for Nd(III) and 5–1.5 M for Sc(III) is probably due to changes in the mechanism of extraction from the transfer of the homoligand **A** to the mixed-ligand **B** complexes.

Another important factor influencing the effecttiveness of active membrane transport is the concentration of carrier in the membrane phase. To assess the role of this parameter for the membrane extraction of Nd(III), we saturated the membrane with the solution of BPA in 1,2-dichlorobenzene of different concentrations in the range 0.01–0.20 M, while the initial composition of the releasing solution was left unchanged. Figure 4 shows the dependence of permeability on the concentration of BPA in the membrane phase: it increases with increasing concentration of the carrier up to 0.12 M. Further decrease of permeability is probably due to the increased viscosity of the membrane phase at high concentrations of the carrier, although we cannot exclude changes in the other characteristics of the membrane, for example, the dielectric constant of the medium.

The obtained result as well as our previous conclusions [8] showed that the characteristics of the impregnated liquid membrane are determined largely by the nature of the membrane solvent. Therefore, we evaluated its effect on the permeability of the membrane transport of Nd(III) ions [$c^0_{Nd(III)} = 1.25\times10^{-3}$ M] using for this purpose 0.1 M solution of *N*,*N*-bis(dihexylphosphorylmethyl)octylamine in *n*-dodecane, 5,8,11-trioxa-*n*-heptadecane, 1,2-dichlorobenzene, phenylcyclohexane, and kerosene at a concentration of nitrate ions in the releasing solution that provides maximum flow transfer [$c(NaNO_3)$ 2.0 M]. The results indicate a minor role of the solvent nature in the

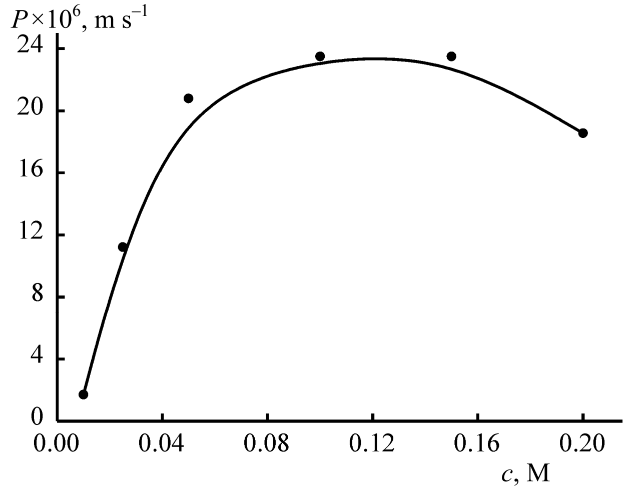


Fig. 3. The influence of concentration of *N*,*N*-bis(dihexylphosphorylmethyl)octylamine in 1,2-dichlorobenzene on the permeability (*P*) for the Nd(III) transfer process, V_{release} 50 ml, V_{receive} 25 ml, $c^0_{\mathrm{Nd(III)}}$ 1.25×10^{-3} M, $c^0_{\mathrm{Na(I)}}$ 0.25 M, measuring time 100 min.

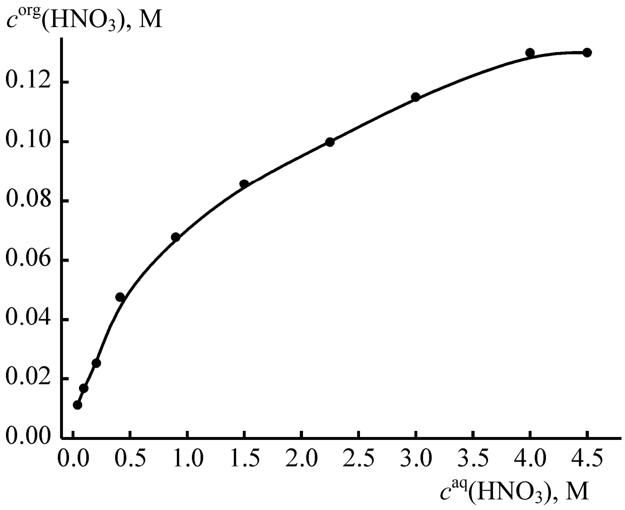


Fig. 4. Liquid–liquid extraction isotherm of nitric acid with 0.05 M solution of *N*,*N*-bis(dihexylphosphorylmethyl) octylamine in toluene.

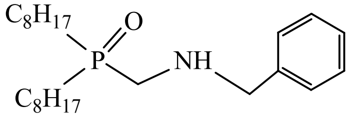
membrane extraction of this ion: the membrane permeability remains in the range $1.9–2.2\times10^{-5}$ mol s^{-1}.

The actual hydrometallurgical technology of extraction, concentration, and separation of metals involves the use of the methods of liquid or membrane extraction from acidic solutions of their salts. Thus, the ore of rare and trace metals as well as used fuel elements of nuclear reactors are dissolved in nitric acid [9]. Therefore, the influence of the acidity of the releasing solution on the efficiency and selectivity of the membrane extraction is one of the most important factors determining the use of three-phase extraction system for achieving the targets of the investigated processes. Effect of acidity of the releasing phase on the transfer rate of Nd(III) from nitrate media was tested using aqueous solutions of nitric acid of different concentrations. We found that the maximum permeability of the membrane $1.95–2.0\times10^{-5}$ mol s^{-1} is reached at the concentration of nitric acid in the releasing solution 0.025 mol l^{-1}, while further increase of acidity leads to a sharp decrease of this index: to 1.2×10^{-5} mol s^{-1} at 0.25 mol l^{-1} and almost three times, to 0.75×10^{-5} mol s^{-1} at 0.5 mol l^{-1}. This fact can be easily explained by the competing co-extraction of nitric acid. Isothermal liquid–liquid extraction of nitric acid by a solution of BPA in toluene (Fig. 5) also shows that with increase in the nitric acid concentration in the aqueous phase a nonmonotonic increase is observed in its concentration in the organic phase to some constant value, which is likely due to the formation of the H-complexes of different composition between the acid and the carrier. We have previously shown [10] that *N*,*N*-bis(dihexylphosphorylmethyl)octylamine is capable of extracting nitric acid to form the *N*,*N*-bis(dihexylphosphorylmethyl) octylamine–acid H-complexes of 1:1, 1:2, and 1:3 composition.

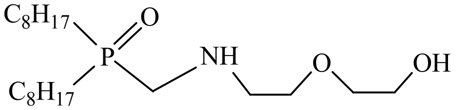
To establish the composition of the extracted complex, we have built a solvent extraction isotherm of Nd(III) by the *N*,*N*-bis(dihexylphosphorylmethyl)-octylamine solution (0.1 M) in 1,2-dichlorobenzene using a series of aqueous solutions with a constant concentration of sodium nitrate (0.2 M) and increasing concentrations of the extracted metal: 0.010, 0.025, 0.050, 0.100, and 0.200 M, the content of Nd(III) ion in the organic phase was 0.035, 0.075, 0.088, 0.074, and 0.114 M, respectively.

To establish the amount of Nd(III) passed into the organic phase, we extracted its 0.1 M solution with the carrier solution in 1.2-dichlorobenzene. The resulting isotherm (Fig. 6) reaches a limit at the concentration of Nd(III) close to 0.1 M, conclusively indicating that the membrane transport of Nd(III) ions proceeds through the formation of a complex **C** with a ratio of reagent: metal = 1:1.

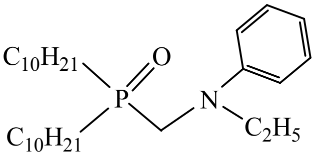
We compared the membrane transport properties of BPA with similar characteristics of the lipophilic aminomethylphosphine oxides **I–IV** with the substituents of different structure at the nitrogen atom (a slight difference in the length of the hydrocarbon residue at the phosphorus atom in the compound **III** did not affect appreciably the extraction ability of the aminophosphoryl reagents [1]). Selected carriers have more than 20 carbon atoms, and in accordance with our previous observations [11], their hydrophilic–lipophilic balance obeys the extraction processes:



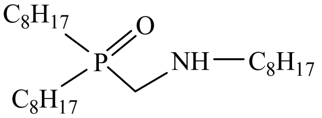
I



II



III



IV

The values of the permeability for the Nd(III) and Sc(III) ions of the membranes impregnated with these reagents listed in the Table 2 show that the most effective are the membranes of BPA, while the lowest rate of transfer shows benzylaminophosphine oxide (**IV**). However, it was difficult to find any marked dependence of the transfer efficiency on the electronic or steric nature of substituents at the coordination site, the nitrogen and phosphorus atoms, both for Nd(III) ad Sc(III) ions owing to the action of countervailing factors responsible for the transmembrane transport [12]. At the same time a clear trend in transfer efficiency is observed with both metals when *N*,*N*-bis-(dihexylphosphorylmethyl)octylamine is used as a transport agent.

Transporter		V	I	II	III	IV
$P\times10^6$, m s^{-1}	Nd(III)	17.4	1.1	7.9	6.6	5.7
	Sc(III)	13.5	0.03	11.2	9.9	3.6

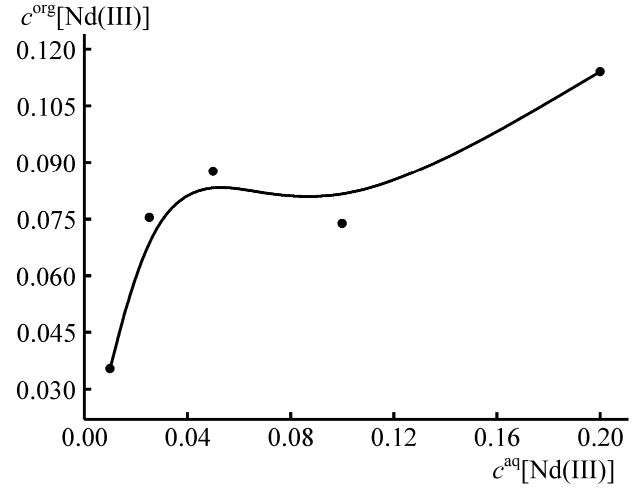


Fig. 5. Liquid extraction isotherm of Nd(III) with 0.1 M *N*,*N*-bis(dihexylphosphorylmethyl)octylamine solution in 1,2-dichlorobenzene.

We tried to evaluate the selectivity of the transport of this carrier in comparison with other above-mentioned carriers and plotted the kinetic data of Nd(III) extraction (Fig. 7). As seen, almost complete extraction of the metal occurs in 50 min after start of the experiment, indicating the high efficiency of the process of transfer by *N*,*N*-bis(dihexylphosphorylmethyl)octylamine, not attanrd at the use the studied aminophosphoryl reagents **I–IV**.

Similar plots were obtained also with Sc(III), but it is noteworthy that the selectivity of BPA was more pronounced in the transport of Nd(III) rather than Sc(III) ions; the values of permeability of the latter vary almost within the experimental error: 13.5×10^{-6} mol s^{-1} for the *N*,*N*-bis(dihexylphosphorylmethyl)-octylamine and 11.2×10^{-6} mol s^{-1} for the monophosphorylated amine (**III**).

Thus, we can state the high efficiency of *N*,*N*-bis-(dihexylphosphorylmethyl)octylamine for the membrane extraction of scandium and neodymium ions in the conditions of active transport, which makes it possible, moreover, to separate these metals from the co-ions of magnesium and aluminum. Comparison with the data on the membrane extraction using monophosphorylated amines with various substituents at the nitrogen atom confirms the advantage of BPA. The variation and the subsequent selection of conditions of the transmembrane transport such as the nature of the membrane carrier, concentration of nitrate ions, and acidity of the aqueous phase allowed us achieving a selective extraction of Nd(III) and Sc(III) ions. Thus, we have found the conditions for a very high permeability of membranes, up to 2.5×

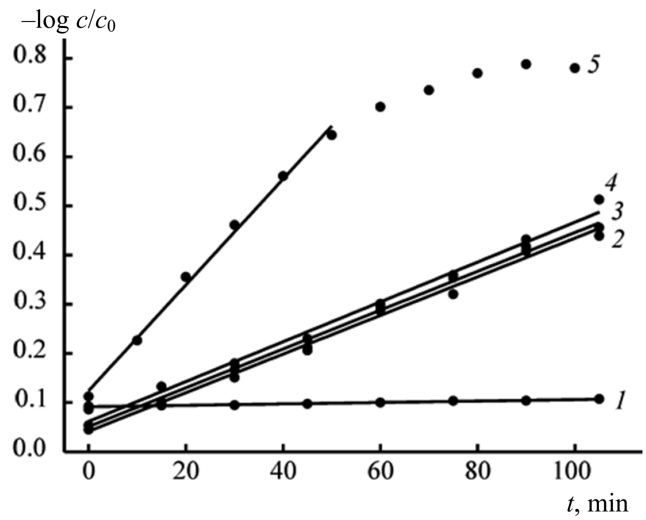


Fig. 6. Kinetic plots for the extraction of Nd(III) with the aminophosphoryl reagents **I–IV** and *N*,*N*-bis(dihexylphosphorylmethyl)octylamine (curves *1–5*, respectively).

10^{-5} mol s^{-1}. Note that the processes with the flow rate of transmembrane transport greater than 10^{-5} mol s^{-1} may be of interest [4] in developing the technology of extraction of metals in real hydrometallurgical processes.

EXPERIMENTAL

NMR spectra were recorded on a Varian XL-300 instrument with an operating frequency 122.4 MHz for the ^{31}P nuclei (external reference 85% phosphoric acid) and 300 MHz for the ^{1}H nuclei (solvent $CDCl_3$, external reference TMS). The IR spectra were obtained using a Bruker Tenson 27 Fourier transform infrared spectrometer. The melting point was determined on a Stuart melting point (SMP3) device or by TG and DSC analysis on a NETZSCH STA 449C instrument.

The content of the ions of rare-earth elements and aluminum were determined by photometric method on a KFK-3 spectrophotometer [15]. The content of magnesium ions in the samples was measured using an atomic absorption spectrometer AAS 1N (Germany), the content of sodium ions was measured by flame photometer PFM U4.2. Current pH was monitored using a pH-150MI pH-meter.

The membrane extraction was studied using a classical vertical cell with a movable cylinder. The receiving solution was placed to the inner glass with the impregnated liquid membrane as its bottom. The matrix was a membrane obtained by the longitudinal stretching of a band made of low-temperature sintered fluoroplastic (PTFE). The solvents in the membrane phase were either *n*-dodecane (99%), or 5,8,11-trioxaheptadecane, or 1,2-dichlorobenzene (chemically pure), or phenylcyclohexane (98%), or kerosene (TU 38.401-58 -10-01 rev.1-3).

For the syntheses solvents, salts and solid alkali of analytical grade and chemically pure grade were used, which, if necessary, were purified by known methods [13].

General method of the synthesis of α-aminomethylphosphine oxides by the Kabachnik-Fields reaction in a ternary system. In a three-neck flask of 100 ml equipped with a mechanical stirrer, reflux condenser, and Dean–Stark trap was placed 29.0 mmol of paraformaldehyde, 28.0 mmol of a dialkylphosphinous acid, 28.0 mmol of amine, 100 mg of *p*-toluenesulfonic acid, and 30 ml of anhydrous toluene (benzene) while using primary amines, or acetonitrile with secondary amines. The resulting mixture was stirred at the boiling point of the solvent for 3–5 h, and then the solvent was distilled off on a rotary evaporator. To remove traces of the catalyst the reaction mixture was treated with sodium carbonate. Liquid compounds were purified by the “oxalate” technique [14]. Crystalline compounds were recrystallized from ethyl acetate or petroleum ether. The resulting crystals were dried in a vacuum desiccator.

Amines used were of Acros Organics production. The remaining substances, if necessary, synthesized by usual methods from commercially available reagents.

(*N*-Benzylmethyl)dioctylphoshine oxide (I). White crystalline compound. Yield 94.0%, mp 49.8°C, R_f 0.57 (eluent acetone–chloroform–methanol, 5:8:1). ^{1}H NMR spectrum (δ, ppm, *J*, Hz): 0.88 two t (3H+3H, $(CH_3)_2$ in octyl, $^{3}J_{HH}$ 6.72), 1.26–1.76 m {14H+14H, $P[(CH_2)_7CH_3]_2$}, 2.84 d (2H, PCH_2N, $^{2}J_{PH}$ 8.08), 3.85 s (2H, NCH_2Ph), 7.36–7.31 m (5H, $NCH_2C_6\underline{H}_5$). ^{31}P NMR spectrum, δ_P 42.6 ppm (Toluene). IR spectrum (Vaseline oil, ν, cm^{-1}): 1150.49 (P=O); 1458.12, 1466.80 (Ph); 3272.09 (NH); Mass spectrum, *m*/*z*, $C_{24}H_{44}NOP$: found M = 394.1 ($[M+Na]^+$ = 416.1, $[M + K]^+$ = 432.1); calculated M = 393.6.

***N*-[(Dioctylphosphoryl)methyl]-2-(2-aminoethoxy)-ethanol (II).** Pale yellow oily liquid. Yield 73.0%, n_D^{20} 1.4771, mp (complex with oxalic acid) 162°C, R_f 0.28 (eluent: acetone–chloroform–methanol, 5:8:1). ^{1}H NMR spectrum (δ, ppm, *J*, Hz): 0.85 two t (3H+3H, $(CH_3)_2$ in octyl, $^{3}J_{HH}$ 6.66), 1.16–1.80 m {14H+14H,

$P[(C\underline{H}_2)_7CH_3]_2\}$, 2.62 br.s (1H, OH), 2.85 m (2H, $NC\underline{H}_2CH_2$, ${}^3J_{HH}$ 5.10), 2.90 d (2H, PCH_2N, ${}^2J_{PH}$ 7.78), 3.60–3.53, two overlapping multiplets (4H, CH_2OCH_2), 3.70–3.67 m (2H, CH_2OH). ${}^{31}P$ NMR spectrum, δ_P 47.5 ppm (Benzene), IR spectrum (thin film, ν, cm^{-1}): 1137.95 (P=O); 3076.34–3654.00 (NH, OH). Found, %: P 7.23. $C_{21}H_{41}NO_3P$. Calculated, %: P 6.92.

(*N*-Phenyl-*N*-ethylaminomethyl)didecylphosphine oxide (III). White powder. Yield 53.6%, mp 49.5°C, R_f 0.50 (eluent acetone–chloroform–methanol, 5:8:1) ${}^1H$ NMR spectrum (δ, ppm, *J*, Hz): 0.91 two t (3H+3H, $(CH_3)_2$ in decyl, ${}^3J_{HH}$ 6.66), 1.18–1.81 m {18H+18H, $P[(C\underline{H}_2)_9CH_3]_2\}$, 2.84 t (3H, $C\underline{H}_3CH_2N$, ${}^3J_{HH}$ 6.95), 3.00–2.93 overlapping d+q (2H+2H, PCH_2N and $NC\underline{H}_2CH_3$), 7.36–7.19 m (5H, NC_6H_5). ${}^{31}P$ NMR spectrum, δ_P 45.7 ppm (Benzene). IR spectrum (Vaseline oil, ν, cm^{-1}): 1148.56 (P=O), 1460.05, 1469.70 (Ph), 3272.09 (CH_{Ph}). Found, %: C 75.91, H 12.52 P 6.50. $C_{29}H_{54}NOP$. Calculated, %: C 75.11, H 11.74, P 6.68.

(*N*-Octylaminomethyl)dioctylphosphine oxide (IV). White crystalline compound. Yield 88.5 %, mp 45.5°C, R_f 0.50 (eluent acetone–chloroform–methanol, 5:8:1) ${}^1H$ NMR spectrum (δ, ppm, *J*, Hz): 0.92 three m (3H+6H, $(CH_3)_2$ in Oct–P, CH_3 in Oct–N, ${}^3J_{HH}$ 6.57), 1.21–1.88 m {12H+28H, $NCH_2(C\underline{H}_2)_6CH_3$, $P[(C\underline{H}_2)_7CH_3]_2\}$, 2.71 m (2H, $NC\underline{H}_2CH_2$, ${}^3J_{HH}$ 6.95), 2.94 d (2H, PCH_2N, ${}^2J_{PH}$ 7.73). ${}^{31}P$ NMR spectrum, δ_P 43.0 ppm (Toluene). IR spectrum (Vaseline oil, ν, cm^{-1}): 1148.56 (P=O), 3276.92 (NH). Found, %: N 3.32, P 7.41. $C_{25}H_{54}NOP$. Calculated, %: N 3.37, P 7.45.

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