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# Synthesis, Transport, and Ionophoric Properties of α,ω-Diphosphorylated Aza Podands: IV.[1] Induced Membrane Transport of Alkali and Alkaline-Earth Metal Ions

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**Abstract**—Membrane transport of alkali and alkaline-earth metal ions by polyether podands containing terminal α-(phosphinoylalkylamino) fragments is studied. Some features of the relationship between the structure of the polyether bridge and substituents at the phosphorus atom, on the one hand, and transport properties of the carrier, on the other, are revealed. Transport efficiency is found to tend to correlate with transported ion size and distance between carrier donor centers.

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In preceding communications [1–3] we have described the synthesis and study of ionophoric properties of bisphosphorylated azopodands whose polyether frame bears terminal α-phosphinoyl-alkylamino groups. In particular, we established the possibility of selective determination of alkali and alkaline-earth ions in low ($10^{-3}$–$10^{-5}$ M) concentrations, as well as of certain anions, using ion-selective electrodes containing podands or their metal complexes. Therewith, the electrodes were found to show the highest performance when the radius of the ion to be determined and the size of the potential pseudocavity formed by the podand molecule complement each other. The high complexing power of phosphinoyl and amino groups, as well as the significant selectivity toward metal ions shown by mono- [4] and bifunctional [5] systems as well as polyether systems containing such groups [2] allowed us to expect that the above organophosphorus azo podands would exhibit transport properties toward alkali and alkaline- earth metal ions. Earlier a high transport activity toward such ions found in oligodiamines, -amides, and -thioamides [6, 7] and polyoxyalkylene diphosphonates [8]. Moreover, in the preceding communication [1] we described the possibility of doping with the bis(phosphinoyl-methylamino) podand of copper- and mercury-sensitive electrodes which were applied for analytical purposes, in particular, for potentiometric and argentometric determination of iodide anions in various objects.

The transport through an impregnated membrane owes to the action of chemical potential gradient and follows a dialysis scheme. This process includes complex formation on the source phase–membrane phase interface, diffusion of the resulting complex inside the membrane phase, and re-extraction of the complex into the receiving phase. For the complex-forming agent to act as a neutral carrier of a substance through a liquid hydrophobic membrane, the structure and properties of the agent should fit certain requirements. First of all, the carrier should include polar and nonpolar fragments in a specific ratio, that is, it should possess a definite hydrophilic–lipophilic balance. Therewith, nonpolar groups retain the carrier and substrate within the membrane phase and preventing their washing out, and form a hydrophobic shell around the coordination sphere of the complex, providing an optimal solubility of the latter in the membrane phase. Furthermore, a high rate of complex formation and decomposition on phase interfaces should be provided. This is achieved by using carriers with optimal complexing properties and conformational flexibility. Note that if the complex formed by a carrier (e.g. crown ether) and a substrate is too strong,

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

**Table 1**. Membrane transport flows (Π, mol $mim^{-1}$ $m^{-2}$) of alkali and alkaline-earth metal perchlorates through an impregnated membrane. Carrier concentration in phenylcyclohexane 0.2 M, perchlorate concentration in the source phase 0.2 M

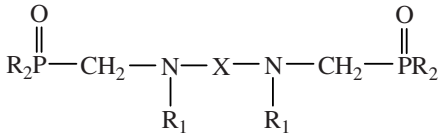
| Carrier | Π × $10^5$ | | | | |
|---|---|---|---|---|---|
| | $LiClO_4$ | $NaClO_4$ | $Mg(ClO_4)_2$ | $Ca(ClO_4)_2$ | $Ba(ClO_4)_2$ |
| **I** | 0.69 | 0.18 | 0.85 | 0.39 | 12 |
| **II** | 0.64 | 1.2 | 0.54 | 0.18 | 0.90 |
| **III** | 0.35 | 1.4 | 0.24 | 3.2 | 6.8 |
| **IV** | 11 | 7.8 | 21 | 34 | 18 |
| **V** | 12 | 6.0 | 19 | 28 | 18 |
| **VI** | <0.01 | <0.001 | <0.001 | <0.01 | <0.001 |

**Table 2**. Membrane transport flows (Π, mol $mim^{-1}$ $m^{-2}$) of alkali and alkaline-earth metal iodides through an impregnated membrane. Carrier concentration in phenylcyclohexane 0.2 M, iodide concentration in the source phase 0.2 M

| Carrier | Π × $10^5$ | | | |
|---|---|---|---|---|
| | LiI | NaI | KI | RbI |
| **I** | 1.1 | 0.66 | 0.37 | 1.3 |
| **II** | 1.1 | 1.0 | 0.23 | 0.72 |
| **III** | 1.3 | 1.5 | 0.42 | 3.4 |
| **IV** | 4.6 | 2.9 | 1.54 | 2.8 |
| **V** | 8.5 | 3.8 | 2.7 | 2.3 |
| **VI** | <0.001 | <0.001 | <0.001 | <0.001 |

no membrane transport may occur due to an insufficient exchange rate of the transported substance through phase interfaces. We presumed that the phosphorylated aza podands considered in this work fit all these requirements. The aza podands were synthesized using the Kabachnik–Fields reaction; their characteristics were given earlier [2].

In this publication we report on the results of investigation of the membrane transport properties of carriers possessing α-(phosphinoylmethylamino) fragments toward alkali and alkaline-earth metal perchlorates and iodides, and consider some of our revealed features of their structural effect on the efficiency of induced transport of metal ions. Aza podands **I–IV** differ from each other by the length of the hydrocarbon substituents at the phosphorus atom and, consequently, hydrophilic–lipophilic characteristics of the whole carrier. Furthermore, we varied the nature of the bridge between the terminal phosphinoylmethylamino fragments, taking into account that conformational flexibility of the carrier and presence (or absence) in it of donor atoms should define the structure of the potential pseudocavity and, therefore, complexing and, hence, carrier properties of the podand.



**I–VI**

X = $(CH_2CH_2O)_2CH_2CH_2$ (**I–IV**), $CH_2CH_2$ (**V**); R = *p*-Tol (**I**), Am (**II**), Oct (**III, V**), Dec (**IV, VI**); $R_1$ = Bu (**I–V**); $NR_1XNR_1$ = $NC_4H_8N$ (**VI**).

Considering interrelationships between the structure of aza podands and their carrier properties, one should not expect simple dependences. First of all, it should be taken into account that carrier efficiency depends on both the carrier–substrate binding rate and facility of re-extraction in the receiving phase. Besides, in polyfunctional complex-forming agents, including our studied aza podands, binding with the transported substance should not necessarily involve all coordination centers simultaneously, say, by steric reasons. Thus, with increasing length of the hydrocarbon substituents at the phosphorus or nitrogen atoms a moment may come when the coordination centers start to eclipse each other or changes in the liphophilic–hydrophilic balance occur, which are difficult to take into account.

Nevertheless, the flows of perchlorates and iodides, listed in Tables 1 and 2, allowed us to reveal certain correlations between this parameter and the structure of carriers **I–VI** for various cations.

Considering the phosphorylated 2,11-diaza-5,8-dioxadodecanes as analogs of oligoethers or glymes, one would expect the stability of the complexes to be highest in the case of $Li^+$ and then to fall down in the series of cations $Na^+$, $K^+$, $Rb^+$, and $Cs^+$ [8]. As noted earlier [9], the strongly donor phosphinoyl and amino groups should make complexes of the modified podands much more stable than those with glymes or oligoethers. The flows of $Li^+$ transport by the phosphorylated 2,11-diaza-5,8-dioxadodecanes fall slowly as the size and, consequently, lipophilicity of the substituents at the phosphorus atom increase the series of podands **I–III** (Table 1). However, further increase in the size of the lipophilic hydrocarbon groups at the phosphorus atom unexpectedly enhances

the flow of lithium transport by 2,11-diaza-5,8-dioxadodecane **IV**. This jump is hard to explain exclusively by the change in the electron density on the phosphoryl oxygen and/or on nitrogen, since, as we showed earlier [4], increasing length of the hydrocarbon group at the phosphorus or nitrogen atoms has almost no effect on the acid–base properties of aminophosphoryl compounds, and the efficiency of liquid extraction varies linearly with the hydrophilicity–liphophilicity of the hydrocarbon fragments. At the same time, our present results most likely suggest that the formation of these complexes is mostly contributed by the terminal α-phosphinoylmethylamino groups, rather than the donor oxygen atom of the polyether chain.

Comparison of the lithium perchlorate transport flows for structurally related compounds–phosphorylated 2,5-diazahexane (**V**) and polyether podands **I–III**, led us to conclude that the higher rate of membrane transport with carrier **V** may result from the fact that the coordination number of $Li^+$ (four) is equal to the number of donor atoms in the structure of 1,6-bis-(dioctylphosphinoyl)-2,5-dibutyl-2,5-diazahexane (**V**).

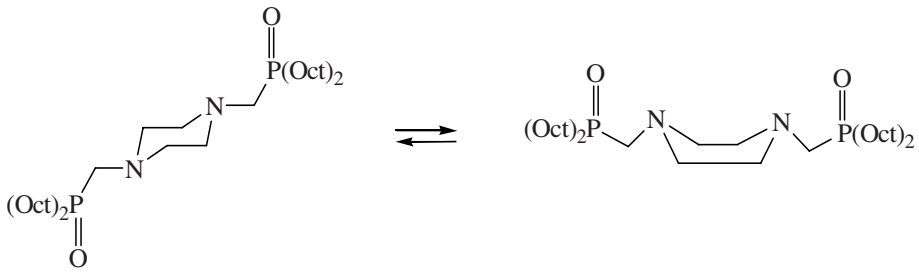
The data on the membrane transport of alkaline-earth metal perchlorates by phosphorylated 2,11-diaza-5,8-dioxadodecanes **I–III** allowed us to reveal some regularities associated with the structural features of the ligands. When carriers have relative small substituents at the phosphorus atom (pentyl or tolyl), the flow rate for alkaline-earth metal perchlorates fall in the sequence $Ba^{2+} > Mg^{2+} > Ca^2$. The higher flow rate in the case of barium perchlorate is probably explained by that the number of donor centers is complementary to the maximum coordination number of this cation, which favors effective coordination of the large-size $Ba^{2+}$ cation. The decrease in the flow rate for this cation as the size of the substituents grows increases in going from tolyl to pentyl and octyl is probably explained by steric hindrances to additional coordination of this cation by the donor phosphine oxide fragments. Nevertheless, in this case, too, we observe a sharply enhanced flow value with the most bulky and most lipophilic decyl analog **IV**. This fact provides further evidence for the above assumption on the possibility of compensation of substituent effects at probable coordination centers and its impact on transport properties of podands.

One more feature of the interrelationship between transport efficiency and carrier structure should be noted: Whereas the podand with pentyl substituent shows a maximum selectivity toward barium perchlorate as compared with calcium perchlorate (more than 4-fold), increase in the substituent size diminishes this difference, and aza podand **IV** preferably binds $Ca^+$.

The high rate of transport of a much smaller magnesium cation, comparable with the respective value for barium, is stipulated by the presence of amino groups in the structure of the ligands, which show a higher affinity to $Mg^+$ [10]. Note that while with phosphorylated aza podands with weakly lypophilic substituents at the phosphorus atom (tolyl or pentyl) the transport rate for alkaline-earth metal perchlorates falls in the sequence $Ba^{2+} > Mg^{2+} > Ca^2$, in the case of long-chain analog III another sequence occurs: $Ba^{2+} > Ca^{2+} > Mg^{2+}$. With even more lipophilic carrier with decyl substituents, the maximum flow rate is characteristic of calcium perchlorate; octyl-substituted podand **III** occupies an intermediate position in this series.

It can be concluded that increasing lipophilicity of substituents at the phosphorus atom is stronger and stronger masking involvement of donor centers of oxyethyl fragments of the phosphorylated 2,11-diaza-5,8-dioxadodecane chain in the formation of complexes with metal cations. Podands with bulky lipophilic substituents at the phosphorus atom, e.g, aza podand **IV**, in their complexing properties resemble polydentate analog **V** which has no donor oxyethyl oxygen atoms.

Enhancement of the conformational rigidity of podands by introducing in their structures poorly flexible fragments to reduce the number of possible conformations of the ligand is often used for enhancing the complexing power of podands, which thereby favor increased selectivity of complex formation [11]. Although in some cases the conformational rigidity of the frame hinders formation of a pseudocavity needed for effective complex formation with metal ions, this property of the carrier can nevertheless be a factor favoring optimal complex formation and endowing aza podands with appropriate ionophoric properties which can prove useful, for example, in the creation of ion-selective electrodes [1]. The extremely low flow rates of alkali and alkaline-earth metal perchlorates and iodides with the piperazine-containing podand as a neutral carrier can be explained by the low stability of the resulting complexes due, probably, to the specific steric structure of this carrier.



We suggest that effective carrier–substrate binding is only achievable in the *boat* conformation. The thermodynamic disadvantage of the *chair–boat* conformational transition in this case probably compels the ligand to behave like a monodentate one.

A picture similar to that described for perchlorates is observed with alkali metal iodides (Table 2). The transport rate tends to decrease in the series of cations $Li^+$, $Na^+$, and $K^+$ with all the phosphorylated 2,11-diaza-5,8-dioxadodecanes, and a certain burst of the flow rate is observed with $Rb^+$. However, while with ligands with low-lipophilicity substituents at the phosphorus atom **I** and **II** the flow rates for RbI are three times that for KI, with the most lipophilic aza podand **IV** having decyl groups at phosphorus this difference is insignificant. To compare, with aza podand **V** containing no donor oxyethyl oxygen atoms these values fall monotonically in the series $Li^+$, $Na^+$, $K^+$, $Rb^+$. This fact is most probably explained by the increasing atomic radii of the cations and, as a consequence, their less efficient binding of ligand donor groups.

Generally, our present results provide further one more example of the lack of simple correlations between the structure and membrane properties of phosphorylated aza podands [1–3], with is probably associated with the multitude of different factors responsible for transport of substrates of different nature. In particular, the trend in the hydrophilic and lipophilic properties of a carrier with changing length of the hydrocarbon substituent at the phosphorus atom is hard to account for. This also leads to changes in steric characteristics which can either facilitate or hinder access of the substrate to potential coordination centers, such as phosphoryl oxygen or amino nitrogen atoms. Furthermore, it is fairly difficult to assess whether internal basicity (coordination) centers, e.g. polyether oxygen atoms, are involved or not. Evidence for this statement is provided by the hardly explainable increase in the transport flow of metal ions in going from octyl- (**III**) to decyl-substituted aza podand **IV**. Nevertheless, the above-noted fact that the transport is favored when the size of the metal ion corresponds to the size of the potential pseudocavity formed by the podand allows targeted choice of substrate–carrier pairs for optimizing processes of membrane extraction of alkali and alkaline-earth metal ions.

## EXPERIMENTAL

Membrane transport of alkali and alkaline-earth metal ions was studied by the methodology described in [12]. The hydrophobic matrix for impregnated membranes was Vladipor MFFK-4 teflon filters with the pore diameter 0.6 μm.

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