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LETTERS TO THE EDITOR

# Synthesis, Transport, and Ionophore Properties of α,ω-Biphosphorylated Azapodands: VII.[1] Membrane Transport of Mineral Acids by Phosphorylated α,ω-Diamines and Azapodands

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Phosphorylated α,ω-diamines and azapodands were shown to be effective agents in the processes of liquid and membrane extraction of substrates of different nature, including the ions of alkali and alkaline earth, rare and trace metals, and mono- and polyhydric carboxylic acids [1-3]. It is known that extraction of metals from mining of raw materials is performed usually by transferring them into the aqueous phase in the form of salts of strong mineral acids, mostly nitric, hydrochloric, perchloric, sulfuric, and other acids. Therefore, information on the processes of extraction of inorganic acids by biphosphoryldiamide carriers is necessary rather than important: the optimization of metal extraction is not possible without this knowledge.

We have studied the processes of membrane transport of nitric, sulfuric, and phosphoric acids by the aminophosphoryl carriers **I–V** of the general formula $[R_2P(O)CH_2NH]_2Z$, where R = $C_6H_{13}$ (**III, IV**), $C_8H_{17}$ (**I, II, V**); Z = $(CH_2)_4$ (**IV**), $CH_2CH(CH_3)\cdot(CH_2)_3$ (**I**), $(CH_2)_6$ (**III**), $(CH_2CH_2O)_2CH_2CH_2$ (**II**), and $(CH_2)_3O(CH_2)_2O(CH_2)_3$ (**V**), often used in the Industrial extraction technologies, at a con-centration of the carriers in the membrane phase 0.1 M (**I–V**) and the acid concentration 0.1 M. The transport fluxes are given below.

| Transporter | **I** | **II** | **III** | **IV** | **V** |
|---|---|---|---|---|---|
| $HNO_3$ | 63 | 120 | 25 | 70 | 77 |
| $H_2SO_4$ | [a] | 18 | [a] | [a] | 15 |
| $H_3PO_4$ | 7 | 3 | 4 | 1 | 6 |

[a] The leakage of the membrane

We have previously shown [1] that the transfer of the selected by us acids of different strength by the aminophosphoryl reagents proceeds with the formation of the H-complexes O=PCH$_2$N···HA. The ease of their formation depends on the basicity of the amine site and the strength of the transferred acid. However, the analysis of migration flows of inorganic acids does not reveal the explicit dependence on the proton-acceptor basicity or the acid strength, which does not seem to us surprising, since the efficiency of membrane transport is determined by many, often widely differing structural and environmental factors [2].

For all the aminophosphoryl reagents the greatest efficiency of the transfer characteristic is typical for the transport of nitric acid, therewith the highest value of the flux shows the most lipophilic reagent, the diphosphoryldiamine **II**. The low efficiency of transport of phosphoric acid apparently rooted in the formation of H-complexes of different nature between the phosphorylamine and the acid molecules. If we assume that the complex structure includes one molecule of acid and amine, than the complex formed by the tribasic phosphoric acid contains unbound “excess” protons, which form in the releasing phase the intermolecular hydrogen bonds with water molecules, and with other (neighboring) phosphate anions. These selected carriers, obviously, do not provide the

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

trans-membrane transport of sulfuric acid as well: the use of its 0.1 M aqueous solution as a releasing phase results in the leakage of the membrane. Perhaps, this effect is associated with the formation of micelles at the interface membrane/releasing solution, which then form channels for passing water from the receiving phase. Thus, the highest transfer efficiency among all the studied inorganic acids is observed for nitric acid, often used in real hydrometallurgical technologies. This requires consideration at the implementation of the technology using aminophosphoryl extractants. Characteristics of the carriers and the membrane extraction technique are given in [1–3].

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## REFERENCES

1. Garifzyanov, A.R., Davletshin, R.R., Davletshina, N.V., Mustafina, L.K., and Cherkasov, R.A., *Zh. Obshch. Khim.*, 2013, vol. 83, no. 2, p. 206.
2. Cherkasov, R.A., Garifzyanov, A.R., Talan, A.S., Davletshin, R.R., and Kurnosova, N.V., *Zh. Obshch. Khim.*, 2009, vol. 79, no. 9, p. 1480.
3. Cherkasov, R.A., Vasil'ev, R.I., Garifzyanov, A.R., and Talan, A.S., *Zh. Obshch. Khim.*, 2008, vol. 78, no. 6, p. 940.