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Membrane Transport of Inorganic Acids with α-Aminophosphoryl Compounds

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Abstract—Transport of some inorganic acids (HCl, HBr, $HClO_4$, HNO_3, H_2SO_4, and H_2PO_4) through hydrophobic impregnated membranes with aminophosphoryl compounds of the general formula $R^1{}_2P(O)CH_2 \cdot NR^2R^3$ [$R^1 = C_4H_9(C_2H_5)CHCH_2O$, $R^2 = C_4H_9$, $R^3 = C_8H_{17}$; $R^1 = R^3 = C_8H_{17}$, $R^2 = H$; $R^1 = C_{10}H_2$, $R^2 = R^3 = C_2H_5$; $R^1 = C_{10}H_{21}$, $R^2 + R^3 = (CH_2)_2O(CH_2)_2$; $R^1 = C_8H_{17}$, $R^2 = H$, R^3 = 2-quinolyl] and dodecylamine as carriers was studied. The membrane phases were solutions of the carriers in phenylcyclohexane and tridecane. General regularities that correlate the structure of an aminophosphoryl compounds to its transport properties toward inorganic acids were established. The largest flows are characteristic of perchloric, nitric, and hydrobromic acids.

The recent intense progress in the chemistry of separation and concentration of inorganic substrates by means of emulsion and impregnated membrane extraction is associated with the undoubted advantages this techniques offers in solving a variety of technological and ecological problems. These advantages include low material and energy consumption, expressed substrate and stereochemical selectivity, effectiveness, and high productivity. Successful use of membrane extraction depends, along with other factors, on correct choice of carriers that should selectively and reversibly bind target substrates. In the membrane transport of many metal ions, often employed are such known liquid extractants as higher amines and neutral organophosphorus compounds [1, 2]. In connection with that it seemed important to study the transport properties of α-aminophosphoryl compounds in which the amino and phosphoryl groups are present simultaneously and sometimes exhibit a synergetic effect. Due to the presence of two and, in certain cases, more basic functional groups, α-aminophosphoryl compounds are capable of multicenter binding substrates. We believe that they should act as carriers for electron-deficient substrates, such as protic acids, metal ions, and some other Lewis acids.

It was previously shown [3, 4] that α-aminophosphonates effectively extract noble metals from hydrochloric acid media. Moreover, they are capable of transporting hydrophilic organic compounds, viz. amino acids and hydroxycarboxylic acids, through hydrophobic membranes [5].

While studying processes of mass transport in membrane extraction one should take account of the possible transport, along with target components, of some other compounds present in the solution. Specifically, the technological solutions of hydrometallurgical processes often contain significant amounts of inorganic acids, which may significantly complicate the chemistry of processes on each side of the membrane. Moreover, in isolation of metal ions from highly dilute solutions, for example, in wastewater treatment by means of the membrane extraction by the antiport scheme, sulfuric acid receiving solutions are often used.

The aim of the present work was to study the membrane transport of inorganic acids, such as hydrochloric, sulfuric, hydrobromic, perchloric, phosphoric, and nitric, through liquid impregnated membranes containing solutions of α-aminophosphoryl compounds as the membrane phase.

Aminophosphonate **I** and aminophosphine oxides **II**–**V** were used as carriers. The latter compounds are hydrolytically and chemically more stable than aminophosphonates.

$$R^1_2P(O)CH_2NR^2R^3,$$
I–**V**

$R^1 = C_4H_9(C_2H_5)CHCH_2O$, $R^2 = C_4H_9$, $R^3 = C_8H_{17}$ (**I**); $R^1 = R^3 = C_8H_{17}$, $R^2 = H$ (**II**); $R^1 = C_{10}H_{21}$, $R^2 = R^3 = C_2H_5$ (**III**); $R^1 = C_{10}H_{21}$, $R^2 + R^3 = (CH_2)_2O(CH_2)_2$ (**IV**); $R^1 = C_8H_{17}$, $R^2 = H$, R^3 = NH-quinol-2-yl (**V**).

All the compounds studied contain the hydrophobic alkyl substituents, which excludes their washing out

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Flows of inorganic acids in various solvents[a]

Carrier	Membrane phase	$HClO_4$	HCl	H_2SO_4	J_3PO_4	HMr	HNO_3
I	Phenylcyclohexane	37	14	1.5	2.3	28	27
I	Tridecane	13	1.8	0.55	1.0	6.2	15
II	Phenylcyclohexane	26	2.7	3.0	5.0	30	40
III	"	3.1	1.0	3.8	4.0	19	17
III	Tridecane	7.1	2.6	3.0	1.1	5.6	15
VI	Phenylcyclohexane	4.8	4.0	4.0	4.7	4.1	29
V	"	9.9	6.8	1.2	9.4	11	21
VI	"	38	15	10	14	58	62
With no carrier	"	–	0.048	0.017	0.030	0.083	0.018
"	Tridecane	–	0.045	0.039	0.047	0.092	0.025

[a] Experimental conditions: temperature 25°C, carrier concentration in the membrane phase 0.2 M, acid concentration 0.2 M, flow is in $\times 10^{-5}$ mol m^{-2} s^{-1}.

of the membrane phase. To compare the transport properties of aminophosphoryl compounds and higher aliphatic amines, we have also studied the membrane transport of inorganic acids with didodecylamine (**VI**).

The membrane phase was a solution of an aminophosphoryl compound in tridecane and phenylcyclohexane. These solvents are sparingly soluble in water and have high boiling points, which is necessary for the impregnated membranes to be stable in time.

The table contains the flows measured on the membrane transport of inorganic acids with 0.2 M solutions of carriers in phenylcyclohexane and tridecane. All the compounds under study exhibit good transport properties toward inorganic acids. The flows are at least two orders of magnitude higher than those in blank experiments.

Analysis of the resulting data allows us to reveal some main peculiarities of the acid transport, associated with the nature of the acids. First of all it should be noted that the highest transport rates are characteristic of perchloric, nitric, and hydrobromic acids. Sulfuric, hydrochloric, and orthophosphoric acids are transported much slower. This regularity is characteristic of both aminophosphoryl compounds and didodecylamine.

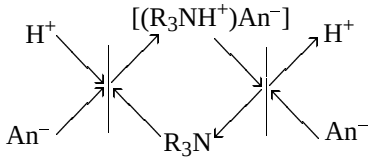
As the aminophosphoryl compounds are rather strong bases (their p*K* values in aqueous ethanol are 2.5–6.6 [6]), we can suggest that in transport properties they will be closer to higher amines than to neutral organophosphorus compounds that are much less basic. In this connection it is interesting to compare the rates of transmembrane transport of inorganic acids and their extractability with higher aliphatic amines.

It is known [7–9] that strong acids (HAn) are extracted with higher amines to form in the organic phase the corresponding alkylammonium salts.

$$H^+ + An^- + R_3N = [(R_3NH^+)An^-]_{(org)}.$$

Therewith, the extractability order of the inorganic acids $HClO_4 > HNO_3 > HBr > HCl > H_2SO_4$ parallels their proton affinity order and the order of the hydration enthalpies of their anions [10].

In the course of the membrane transport of inorganic acids the above-mentioned reaction proceeds on the interface between the feeding solution and the membrane phase, while the reverse process takes place on the opposite side of membrane.



The extractability and membrane transport rate orders coincide in cases where the limiting stage of the transport involves substrate transfer into the membrane phase. Hence, Chibizov [11] showed that the rates of transport of mineral acids through an impregnated membrane containing a 10^{-3} M solution of trioctylamine in toluene as the carrier decreases in the order $HClO_4 > HNO_3 > HBr > HCl > H_2SO_4$. However, the increase in the concentration of trioctylamine in the membrane to 10^{-1} M reverses this order: $HCl > HBr > HNO_3 > H_2SO_4 > HClO_4$. At the same time, the flow of nitric acid through the membrane decreases from 2.2×10^{-4} to 1.7×10^{-4} mol m^{-2} s^{-1}. According to [11], increase in amine concentration is accompanied by change of the limiting stage of

transmembrane transport, and H_2SO_4 is extracted as the hydrosulfate anion.

The results presented in the table show that, with aminophosphoryl compounds as the carriers, the extractability order depends on the structure of the carrier, as well as on the membrane solvent. In the case of aminophosphonate **I** and phenylcyclohexane as the membrane solvent, the transport rate decreases in the order $HClO_4 > HBr \approx HNO_3 > HCl > H_3PO_4 \approx H_2SO_4$. The same order is observed for the membrane phase consisting of a solution of didodecylamine in phenylcyclohexane. With phosphine oxides **II** and **III**, a slightly different order is observed: $HNO_3 \approx HBr > HClO_4 > HCl > H_3PO_4 \approx H_2SO_4$.

Carrier **IV** significantly differs by its behavior from the above-mentioned compounds. In this case, only nitric acid is transported at a high rate (2.9×10^{-4} mol m^{-2} min^{-1}). The transport rates of the other acids span the range $(4–5) \times 10^{-4}$ mol m^{-2} min^{-1}.

Carrier **V** much differs in structure from the other compounds, since it contains such an additional basic fragment as the quinoline ring. With this compound, the acid flows vary in the following order: $HNO_3 > HBr > HClO_4 \approx H_3PO_4 > HCl > H_2SO_4$.

Hence, the transport rate order coincides with the extractability order for aminophosphonate **I** and didodecylamine.

Aminophosphine oxides **II** and **III** which are more basic than compound **I** are worse carriers for perchloric acid than for hydrobromic and nitric acids. In view of the data in for mineral acids [11], we can suggest that the partial reversal of the transport rate order is associated with change of the limiting stage of the membrane transport.

Carrier **IV** which contains the weakly basic morpholine nitrogen atoms effectively transports nitric acid only. Here, probably, an H-complex rather than ion pair passes into the membrane phase.

Noteworthy is the high rate of transport of orthophosphoric acid with carrier **V**. As orthophosphoric acid is a relatively weak acid, this fact may be connected with formation in the membrane phase of a solvate in which orthophosphoric acid is bound with the carrier by three hydrogen bonds involving the phosphoryl group and the exo- and endocyclic nitrogen atoms.

With tridecane as the membrane solvent, perchloric acid is transported at a much lower rate both with aminophosphonates and with didocecylamine. This is evidently connected with the fact that the polar ionic associate is poorly solvates with the nonpolar hydrocarbon solvent. The transport rates of nitric and hydrobromic acids change to a lesser extent. The anions of these acids can form hydrogen bonds with the protonated form of the carrier, thus rendering the ionic associates less polar and ensuring their stronger solvation in tridecane.

Our present result demonstrate the utility of aminophosphoryl compounds in membrane technologies connected with transport of mineral acids. Like higher amines, aminophosphoryl compounds exhibit effective transport properties toward the substrates studied, and the alteration in the facility of transport of these or other acids depending on the structure of the carrier provides evidence to show that aminophosphoryl compounds are more selective than nonphosphorylated amines.

EXPERIMENTAL

The membrane transport study was carried out in a classical glass-in-glass cell [1, 2]. Vladipor MFFK-4 membrane filters (pore size 0.65 μm) were used as the matrix for impregnated liquid membranes. Phenylcyclohexane, tridecane, and 0.2 M solutions of carriers in these solvents were used as the organic membrane phase.

The measurements were carried out at 25°C, the volumes of the receiving and feeding solutions were 22 and 64 ml, respectively.

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REFERENCES

1. Ivakhno, S.Yu., Afanas'ev, A.V., and Yagodin, G.A., *Itogi Nauki Tekh., Ser. Neog. Khim.*, 1985, vol. 13.
2. Ivakhno, S.Yu. and Yurtov, E.V., *Itogi Nauki Tekh., Ser. Neorg. Khim.*, 1990, vol. 18.
3. Mikryukova, E.Yu., *Cand. Sci. (Chem.) Dissertation*, Kazan, 1991.
4. Garifzyanov, A.R., Mikrukova, E.Yu., and Toropova, V.F., *Zh. Obshch. Khim.*, 1991, vol. 61, no. 6, p. 1342.
5. Antipin, I.S., Stoikov, I.I., Garifzyanov, A.R., and Konovalov, A.I., *Zh. Obshch. Khim.*, 1996, vol. 66, no. 2, p. 391.

6. Zakharov, S.V., Nuryazdanova, G.Kh., Garifzyanov, A.R., and Cherkasov, R.A., *Zh. Obchch. Khim.*, 2004, vol. 74, no. 6, p. 946.

7. Ochkin, A.V. and Sergievskii, V.V., *Usp. Khim.*, 1989, vol. 58, no. 9, p. 1451.

8. Frolov, Yu.T. and Sergievskii, V.V., *Trudy Mosk. Khim.-Tekhnol. Inst. im. D.I.Mendeleeva*, 1966, vol. 51, p. 116.

9. Frolov, Yu.T. and Sergievskii, V.V., *Trudy Mosk. Khim.-Tekhnol. Inst. im. D.I.Mendeleeva*, 1963, vol. 43, p. 58.

10. Lur'e, Yu.Yu., *Spravochnik po analiticheskoi khimii* (Handbook of Analytical Chemistry), Moscow: Khimiya, 1989.

11. Chibizov, V.P., in *Sovremennye metody razdeleniya i opredeleniya radioaktivnykh elementov: Sbornik nauchnykh trudov* (Modern Methods of Separation and Determination of Radioactive Elements: Collected Scientific Papers), Moscow: Nauka, 1989, p. 128.