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Liquid Extraction of Inorganic Acids with α-Aminophosphoryl Compounds

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Abstract—Liquid extraction of inorganic acids, such as hydrochloric, hydrobromic, hydroiodic, and nitric, with four α-aminophosphonates with different-size hydrocarbon substituents in the aminomethylphosphoryl skeleton was studied. The extraction effectiveness increases with increasing number of carbon atoms in the molecules of organophosphorus extractants, that is with increase in their lipophilicity, and is also affected by the hydration enthalpy of the inorganic acid anion. The extractive ability of phosphorylated amines is 3–4 orders of magnitude lower compared with corresponding amines, on account of the fact that the basicity of the former is decreased by the electron-acceptor phosphoryl group. The absence of satisfactory linear two- and three-parameter correlations between the extraction constants and the number of carbon atoms in and the basicity of phosphorylated amines is evidently connected with the disregard for other structural and medium factors that may influence the extraction coefficients.

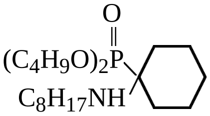
We previously found that α-aminophosphonates are capable of extracting ions of noble metals, such as gold, platinum, and palladium, as well as ions of other metals that accompany noble metals in natural and technological objects [1, 2]. Metal ions are most commonly extracted into organic phase from aqueous solutions of wide-range acidity, and the effectiveness of separation of extracted mixtures is much dependent on the ability of extractants to transport corresponding inorganic acids together with target substrates. The ability of α-aminophosphonates to transport inorganic acids through hydrophobic impregnated membranes we studied in one of our previous works [3].

$[C_4H_9CH(C_2H_5)CH_2O]_2P(O)C(CH_3)_2NHC_6H_{13}$

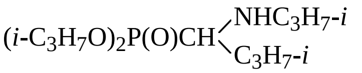
I

$[C_4H_9CH(C_2H_5)CH_2O]_2P(O)CH_2NHC_6H_{13}$

II



III



$(i\text{-}C_3H_7O)_2P(O)CH(NHC_3H_7\text{-}i)C_3H_7\text{-}i$

IV

In the present communication we report the results of investigation of the extraction of four monobasic inorganic acids (HA), viz. hydrochloric, hydrobromic, hydroiodic, and nitric, with four α-aminophosphonates **I**–**IV**. All the organophosphorus reagents belong to the type of phosphorylated secondary amines and, at the same time, significantly differ in structure. Compounds **I, II**, and **IV** contain linear hydrocarbon fragments, whereas **III**, cyclic. The hydrocarbon substituents on phosphorus, α-carbon, and nitrogen vary significantly in length. These extractants have much differnt lipophilicity. Among them the least lipophilic is phosphonate **IV** that contains four relatively hydrophilic isopropyl groups and should exhibit, in our opinion, the weakest extractive ability toward acids. The most lipophilic compound in this series is extractant **I**. It contains the longest hydrocarbon chains, and we expect it to be the best extractant for acids. The other two representatives of this series, compounds **II** and **III**, evidently present the intermediate case.

The extraction of acids with phosphorylated amines was studied by means of two-phase potentiometric titration of accurately weighed quantities of aminophosphonates in aqueous chloroform with an accurate concentration solution of the corresponding acid. The extraction coefficients were calculated by Gran's linearization of the titration curves, as we previously described for phase distribution of α-aminophosphonates [4]. The resulting log extraction constants are listed in the table.

Analysis of the experimental data (see table) reveals a well-defined tendency of the log extraction constants to increase as the lipophilicity of the aminophosphonate increases with increasing number of carbon atoms in its molecule (n_C). This tendency is characteristic of all the extracted acids and is evidently connected with the fact that the stability of

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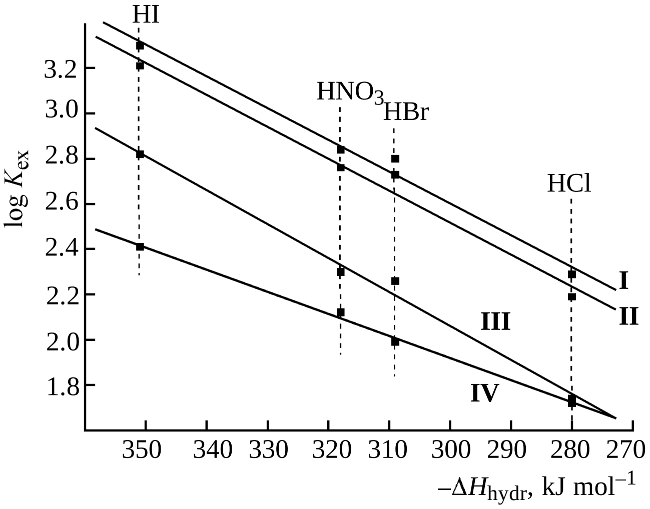
ionic associates increases with increasing lipophilicity (decreasing hydration energy) of their constituent ions. Evidence for this suggestion comes from published data which show that inorganic acids are better extracted with longer chain amines. Hence, for the extraction of hydrochloric acid with solutions of higher secondary aliphatic amines in carbon tetrachloride the following extraction constants were obtained ($K_{ex} \times 10^5$): 7.9 ($(C_6H_{13})_2NH$), 8.7 ($(C_7H_{15})_2NH$), 15.8 ($(C_8H_{17})_2NH$), and 17.2 ($(C_{10}H_{21})_2NH$) [5].

Comparing these values with our values for phosphorylated analogs of the above amines, for example, cyclohexylamine ($\log K_{ex}$ 5.90) and α-phosphorylated isopropylhexylamine **II** ($\log K_{ex}$ 2.29), we can see that introduction of the dialkoxyphosphoryl group decreases the extractive ability of secondary amines by more than 3 orders of magnitude. This is undoubtedly connected with the electron-acceptor effect of the phosphoryl group, that sharply decreases the basicity of the amine [6]. This electronic effect many times exceeds the effects of all other factors contributing into the extractive properties of the compounds in study. The effect of intrinsic structural factors in the aminophosphonate series on the facility of HCl extraction alters the log extraction constant by no more than 0.5 (see table).

As seen from the figure, with one and the same aminophosphonate, the log extraction constants ($\log K_{ex}$) of acids HA are linearly related to the hydration enthalpies of their anions A^- at 25°C and infinite dilution, equaling, kJ mol^{-1}, 280 for HCl, 309 for HBr, 351 for HI, and 318 for HNO_3 [7].

According to the experimental data, the facility of extraction of the acids decreases in the series HCl < HBr < HNO_3 < HJ and is determined by the proton affinities and hydration enthalpies of the corresponding anions. These results are in good agreement with published data for extraction of inorganic acids with higher aliphatic amines [8], which, in its turn, points to a common mechanism of acid extraction with amines and α-aminophosphoryl compounds. The slopes of the linear dependences of the log extraction constants ($\log K_{ex}$) of inorganic acids on the hydration enthalpy (ΔH_{hydr}) of the anions A^- of acids HA for compounds **I** and **II**, which are the most lipophilic of the aminophosphonates studied (see figure) are roughly equal to each other: The straight lines are almost parallel and are located much higher than the dependences for the other two extractants. From that it follows that it is the lipophilicity of the extractant that controls the effectiveness of acid extraction. At the same time, no satisfactory correlation between the acid–base properties of aminophosphonates and their extractive ability is observed (R < 0.94).



Dependence of the log extraction constants ($\log K_{ex}$) of inorganic acids with aminophosphonates **I**–**IV** on the hydration enthalpies (ΔH_{hydr}) of the anions A^- of acids HA.

Our attempts to establish a three-parameter correlation between the log extraction constant ($\log K_{ex}$), the number of carbon atoms in aminophosphonate (n_C), and the pK_a of the conjugate acid [6] by regression analysis failed. Here, too, the correlation coefficients with all the four acids were no higher than 0.91–0.96. Evidently, the extraction constants are affected, along with the above-considered hydrophilicity–lipophilicity balance in the molecules of aminophosphonates, their acid–base properties, and the hydration enthalpies of the anion A^-, by a number of other factors. Probably, they include solvation and

Log extraction constants ($\log K_{ex}$) of inorganic acids (HA) with aminophosphonates **I**–**IV** in aqueous chloroform

Comp. no.	n_C	pK_a [b]	$\log K_{ex}$			
			HCl	HBr	HI	HNO_3
I	25	4.97	2.29	2.80	3.30	2.84
II	23	5.06	2.19	2.73	3.21	2.76
III	22	4.67	1.74	2.26	2.82	2.30
IV	13	4.52	1.72	1.99	2.41	2.12

[a] Total concentration of the acid anion (C_{A^-}) in the aqueous phase 0.5 M. [b] Measured in a mixture of water (25 vol%) and 2-propanol (75 vol%).

steric interactions, that vary from one compound to another and accompany formation of aminophosphonate–acid associates, as well as intramolecular hydrogen bonding whose strength may also vary with molecular structure. However, no experimental evidence is available for quantitative assessment of the contribution of these “missing” factors, and, in view of the fact that fine details of the steric structure of the extractant molecules, for example, their conformational features, are difficult to take into account, more or less exact correlation between the extractive properties and the structure of the organophosphorus extractants studied seems quite an intricate problem. The same problems we faced in the attempted quantitative structure–basicity correlation for a wide range of aminophosphoryl compounds [6]. Nevertheless, we observe a well-defined tendency of the extractive ability of aminophosphonates toward inorganic acids to decrease with decreasing number of carbon atoms in, and, consequently, decreasing lipophilicity of the extractant molecules.

EXPERIMENTAL

The syntheses and characteristics of α-aminophosphonates **I**–**IV** are described in [6].

The extraction constants were determined by means of two-phase potentiometric titration with a glass indicator electrode. The cell was charged with 15 ml of a 0.05 M solution of aminophosphonate in chloroform and 10 ml of a solution of the background electrolyte (0.4 M solution of potassium salt of the corresponding acid). The mixture was magnetically stirred and titrated with a solution of the acid to be studied (concentration 0.1 M, ionic strength 0.4). During titration the ball of the indicator electrode was in the aqueous phase. Potential records were taken 5–7 min after addition of each successive portion of the titrant after phase equilibration; therewith, the magnetic stirrer was switched off. The resulting plots of the concentration of hydrogen ions in the solution on the titrant volume were subjected to Gran’s treatment. The extraction constants of inorganic acids with α-aminophosphonates are listed in the table.

ACKNOWLEDGMENTS

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