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Abstract

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HYDRATE-SOLVATE MECHANISM OF EXTRACTION

(Presented by Academician A. P. Vinogradov, 3 III 1962)

One of the most interesting and complex questions in the theory of extraction is the question of the mechanism of extraction of simple and complex metallohalide acids by oxygen-containing solvents. The aim of the investigations we have carried out is to elucidate this mechanism; in the present article, data on the hydration and solvation of the extracted compounds are briefly set forth. The principal object of study was the extraction of iron from chloride solutions. To solve the problem posed, the method of infrared spectroscopy was used; data obtained by other methods were also employed. Taken together, these results have made it possible, as we see it, to draw an unambiguous conclusion about the character of the hydration and solvation of the compounds.

Iron is extracted from hydrochloric-acid solutions by oxygen-containing solvents, apparently in the form of compounds of the general formula $HFeCl_4 \cdot nH_2O \cdot mS$, where S is a molecule of the organic solvent. In the work, the possibility of coordinative solvation of the anion $FeCl_4^-$ was studied and—what was the main task—the structure of the cationic part of the extracted compounds. Since it could be assumed that, in the case of strong acids, the structure of the cationic part should not depend significantly on the nature of the anion, from this point of view not only $HFeCl_4$ was studied, but also certain mineral acids—nitric, hydrochloric, and others. As solvents, chiefly complex esters were used, as well as ketones and simple ethers.

In the IR spectra of extracts containing iron, shifts of the band of the stretching vibrations of the carbonyl group of complex esters by 30–40 cm^{-1} were found in comparison with the spectra of pure solvents and the spectra of solutions of water in these solvents, where the formation of hydrogen bonds of the usual type is possible (Fig. 1). These shifts indicate binding of the solvent, i.e., its inclusion in the composition of the extracted compounds. The changes in the spectra of extracts containing iron do not differ in character from the changes observed in extracts containing only hydrochloric acid, and also in solutions of hydrochloric acid in organic solvents. In the spectra of extracts with iron there are no changes except for the noted shift of the $C=O$ group band and the associated shift of the $C-O$ bond band. In the spectra of solutions of $KFeCl_4$ in anhydrous organic solvents, no shift of the $C=O$ band is observed. These data show that the organic solvent and water do not attach to the anionic part of the extracted complex acid, i.e., to the anion $FeCl_4^-$; consequently, they can be located only in the cationic part. An essential conclusion that must be drawn is that in extracts the solvent is bound more strongly than simply with water through hydrogen bonds of the usual type.

It was also shown that water enters into the composition of the extracted compounds. The infrared spectrum of water in the frequency region of the stretching vibrations of the OH group reveals in the extracts a shift toward lower frequencies.

frequencies as compared with the spectra of solutions of water in the corresponding organic solvents, where the formation of ordinary hydrogen bonds is possible (Fig. 2). In a number of cases the absorption in the region of 3200 cm^{-1} increases, which may be ascribed to the appearance of strongly bound water. We emphasize that water, too, is bound more strongly in the extracts than in its solutions in organic solvents.

Fig. 1

Fig. 2

Fig. 1. Infrared absorption spectra in the region 1600–1800 cm^{-1}. 1—butyl acetate; 2—solution of water in butyl acetate; 3—extract containing Fe (solvent —butyl acetate, extraction was carried out from a LiCl solution); 4—the same, but from an HCl solution; 5—dibutyl ether; 6—extract containing Fe (solvent—dibutyl ether, extraction from HCl); 7—extract containing $HClO_4$ (dibutyl ether)

Fig. 2. Infrared absorption spectra in the region 3000–3600 cm^{-1}. 1—solution of water in butyl acetate; 2—extract containing Fe (solvent—butyl acetate, extraction from HCl solution); 3—extract containing Fe (solvent—dibutyl ether, extraction from HCl)

Having established that both the organic solvent and water are constituents of the extracted compounds (but not of the anionic part), we must "place" the proton, water, and the organic solvent in the cationic part. In the literature there are two hypotheses concerning the structure of the cationic part of the extracted strong acids. One of them, known as the oxonium mechanism ([1,2]), is based on the assumption that the acid proton attaches directly to the oxygen of the organic solvent, with formation of an oxonium cation. This hypothesis assumes that water does not participate in the extraction process and even hinders extraction. The second hypothesis, advanced in the literature ([3–6]), is based on the supposition that the acid proton attaches not to the oxygen of the organic solvent, but to the oxygen of water, with formation of a hydroxonium cation which, in turn, is hydrated by several water molecules. The organic solvent attaches to water molecules polarized in the field of the hydroxonium ion.

On the basis of the data presented above, it may be supposed that the organic solvent is bound to water molecules that are polarized in the field of a proton or hydroxonium ion. Indeed, if the water were not polarized, its bond with the solvent would not differ from that which occurs in solutions of water in the solvent, and the spectrum of the solvent would not differ in these cases. But in the present case water can be polarized only while in the field of a cation—the proton or hydroxonium ion. On the other hand, if the water were not bound to the proton or hydroxonium ion, its own spectrum would not show stronger binding than in the case of the same solutions of water in the solvent. But this is only a minimum of data.

If water attaches itself to the proton, then bands belonging to hydroxonium should be observed in the spectrum. It has been shown that hydroxonium is clearly manifested in a number of cases in the region 1600-1800 cm^{-1}. A well-defined band of the H_3O^+ ion is obtained when simple ethers are used as solvents, which in this region of the spectrum have only a weak overtone. Figure 1 shows the hydroxonium band in the spectrum of an extract of hydrochloric acid in dibutyl ether. In the case of esters, a broad band was observed in this region, which can be attributed to the sum of the band of the valence vibrations of the carbonyl and the band belonging to hydroxonium. Such bands were observed in extracts containing sulfuric acid (conditions were selected under which the extraction of H_2SO_4 into isoamyl acetate proved appreciable), and in extracts containing iron extracted from HCl solutions. In the extraction of iron from LiCl solutions the band attributed to hydroxonium is absent. In extracts with iron extracted by dibutyl ether, the hydroxonium band is very clearly manifested (Fig. 1).

These data, as well as certain others not mentioned here, lead to the conclusion that water plays an important role in the extraction of strong acids and make it possible to regard the principal interaction as the attachment of the acid proton to water with formation of the hydroxonium ion. The latter, in turn, is hydrated and solvated. The extracting compound may be represented schematically as:

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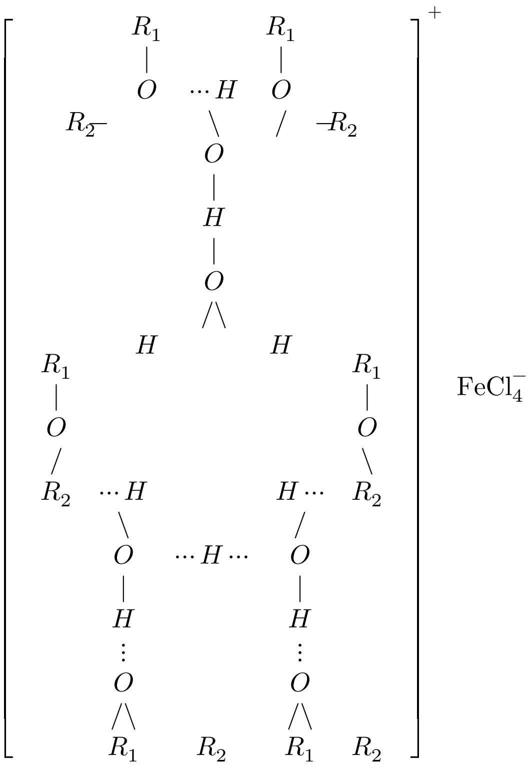

Part of the positions in the second solvation layer of hydroxonium may be occupied by water molecules; on the other hand, under certain conditions the organic solvent will be found in the first layer.

The basicity of the small and strongly polar water molecule is usually higher than the basicity of the molecules of oxygen-containing solvents used in extraction; therefore the proton binds preferentially with water. The hydroxonium thereby formed can readily be hydrated. It is a very convenient cation in this sense: in size it is analogous to the potassium ion, but differs from it in that its charge is concentrated at three points—on

hydrogen atoms, while the field symmetry of these cations is different. Therefore the bonds that the hydroxonium ion forms with water molecules are very strong. The complex $H_3O^+ \cdot 3H_2O$ is stable in aqueous solutions. In extraction from relatively dilute acid solutions, when there is no deficiency of water, this complex also passes into the organic phase, being solvated in the process by the organic solvent. In accordance with this, for extraction from dilute acid solutions one may expect hydration numbers of not less than 4. As the acid concentration in the aqueous phase increases, the activity of water decreases, and the degree of hydration of the proton also decreases. In this connection it should be expected that the hydration numbers of the strong acids being extracted should not be constant, but may decrease with increasing equilibrium concentration of the acid in the aqueous phase. At high acid concentrations the hydration number may even be equal to one, i.e., the hydroxonium ion remains unhydrated.

The mechanism under consideration provides that the solvation numbers may, of course, be greater than unity and may vary under the influence of various factors. Above all, the solvation numbers must be related to the hydration numbers; this is understandable: the fewer water molecules hydrate the hydroxonium ion, the fewer sites there are for attachment of the solvent. Therefore the solvation numbers may also, for example, decrease with increasing equilibrium concentration of the acid in the aqueous phase. The cationic part, in accordance with this mechanism, is a rather labile formation.

The available experimental data—both ours and those in the literature—are in good agreement with these ideas. This applies, for example, to data on hydration and solvation numbers. Information on the formation of two organic phases during extraction, and the data we obtained on changes in the spectra upon heating and prolonged standing of the extracts, correlate with the mechanism. Many other extraction data also find their explanation. The mechanism considered, which might be called, for example, the hydrate-solvate mechanism, applies to strong acids—both complex acids of the type $HFeCl_4$, $HGaCl_4$, and simple ones—HCl, $HClO_4$, etc. Acids of medium strength, for example nitric acid, behave somewhat differently.

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