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# HYDRATION AND SOLVATION OF ACIDS AND SALTS UNDERGOING EXTRACTION

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Recent experimental investigations of the mechanism of the extraction of iron from chloride solutions and also of some simple inorganic acids by oxygen-containing solvents[1-5,70-72] have led to conclusions extending insignificance beyond these systems. The results obtained, combined with existing data, gave an orderly picture of the mechanism of the extraction of simple and complex acids (partly in relation to the hydration and solvation of the compounds extracted). It has also been found that in several cases the extraction of salts, too, has much in common with that of acids. An attempt is made below to present this picture as a whole.

## 1. SOME EXPERIMENTAL DATA

It might be supposed that tervalent iron is extracted from hydrochloric-acid solutions by oxygen-containing solvents (ethers, esters, ketones, alcohols) in the form of compounds of general formula $HFeCl_4.nH_2O.mS$, where S represents a molecule of the organic solvent. Examination of the infra-red spectra of the iron compounds extracted from hydrochloric-acid solutions by esters (ethyl, butyl, and isopentyl acetates) has enabled several conclusions to be drawn concerning the character of the hydration and solvation of these compounds[1,3-5].

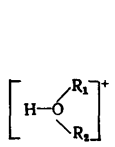
The extracts containing iron showed shifts in the band due to stretching vibrations of the C=O group of the esters by 30–40 $cm^{-1}$ compared with the spectra of the pure solvents and those of solutions of water in these solvents, where hydrogen bonds may be formed between the water and solvent molecules. These shifts indicate combination of the solvent, *i.e.* that it forms part of the extracted compounds.

The changes in the spectra of extracts containing iron do not differ in character from those observed in extracts containing hydrochloric acid alone, and also in solutions of hydrochloric acid in organic solvents. The spectra of extracts of iron show no changes other than the above shift in the C=O band and the associated shift in the C–O band. The spectra of solutions of $KFeCl_4$ in anhydrous organic solvents show no displacements of the C=O band. These

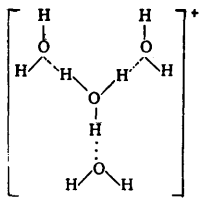
results indicate that the organic solvent, and probably water, do not add on to the anionic portion of the complex acid which is extracted, *i.e.* to the $FeCl_4^-$ ion; hence they can be located only in the cationic portion.

It has also been shown that the extracted compounds do contain water[1,4]. In the region of the OH-stretching vibrations, the infra-red spectrum of water in the extracts shows a displacement towards lower frequencies compared both with the spectra of gaseous or liquid water and with those of solutions of it in the corresponding organic solvents, where ordinary hydrogen bonds can be formed. It must be stressed that water is bound more strongly in the extracts than in solutions of it in the organic solvents.

Cole soon established that the compounds which are extracted contain both the organic solvent and water (but not in the anionic portion), and it was necessary to "stow" the proton, water, and organic solvent in the cationic portion. Two hypotheses exist in the literature concerning the structure of the cationic portion of extracted strong acids. One of them, known as the oxonium mechanism[6,7], is based on the assumption that the proton of the acid adds on directly to the oxygen atom of the organic solvent to form a "solvonium", or substituted oxonium cation (I). This hypothesis postulates that water does not take part in the process of extraction, that it even interferes with extraction, and that extraction can occur only from solutions of high hydrogen-ion concentration; it is also implied that only monosolvates should be extracted:



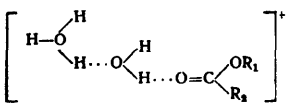
(I)



(II)

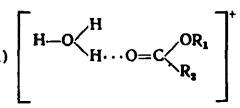
The second hypothesis[8-11] is based on the postulate that the proton of the acid adds on, not to the oxygen of the organic solvent, but to the oxygen atom of the water with the formation of a simple oxonium cation, which is in turn hydrated with three water molecules (II). The organic solvent adds on to the water molecules which are polarised in the field of the simple oxonium ion.

The above data suggest that the organic solvent is combined in the cationic portion of the extracted compounds with water molecules which are polarised in the field of the proton or the simple oxonium ion. Actually, if the water were not polarised, the changes in the spectrum of the solvent in the extract would not differ from those observed in solutions of water in the solvent and produced by an ordinary water–solvent hydrogen bond. On the other hand, the water can be polarised in this case only by being located in the field of the cation, proton, or simple oxonium. This hypothesis is supported by data on the change in spectrum of the water, which is greater than in hydrogen-bond formation with the solvent. In such a case it seems most natural to represent the cationic portion in the form $[H_2O^+ \ldots (H_2O)_{n-1} \ldots S_m]$ or (an individual fragment of this)



(III)

or (for $n = 1$)



(IV)

But this represents only the minimum data required. A further fact which probably indicates that the solvent is combined *via* water[4,5] is that the spectrum of a solution of anhydrous $FeCl_3$ in an anhydrous solvent contains a band due to a very strongly bound carbonyl group (displacement of 80 $cm^{-1}$). This indicates the direct addition of solvent to the iron, which is expected under these conditions. The spectrum of the hexahydrate of $FeCl_3$ in the solvent contains no bands due to the strongly bound C=O group, but there is a band due to more weakly combined carbonyl (displacement of 30–40 $cm^{-1}$). The coordination sphere of the iron is probably filled with water molecules, while molecules of the organic solvent add on to the water of hydration. The shifts in the C=O band are the same in this spectrum and in those of our extracts. Vdovenko and Suglobov[12] observed a similar shift in the C=O band of esters with the hydrates of uranyl nitrate, and with this system it was definitely proved that the link is effected *via* water. The nature of the cation binding the water obviously does not influence the solvent–water bond sufficiently for this to be noticeable in the spectrum.

But the most important result is that, if water is polarised in the field of the proton, the spectrum should contain bands due to strongly bound water, in other words oxonium bands[1,4]. If the simple oxonium ion appears in the spectrum, the problem is finally solved. In several experiments the presence of the simple oxonium ion is clearly revealed in the region of the O–H deformation vibrations. Thus an oxonium band has been found in the spectrum of an extract of sulphuric acid in isopentyl acetate (conditions were chosen such that the extraction of $H_2SO_4$ was considerable); the broad band observed represented the sum of a band due to carbonyl stretching vibrations and a band due to simple oxonium. In order to avoid such superimposition of bands, ethers were used, as they have only a weak overtone in this range. Distinct oxonium bands were obtained in the spectra of the extracts with perchloric acid and with iron[4].

Bands due to strongly bound water are observed also in the region of the O–H stretching vibrations. This is especially noticeable if, instead of extracts, solutions of the extracted substance are taken in the anhydrous solvent, to which known amounts of water are gradually added. Such experiments have been carried out with hydrochloric acid. Anhydrous pentyl acetate was saturated with dry hydrogen chloride, the quantity of which was determined by titration. The calculated quantity of water was added to the resulting solution. At a certain ratio of water and HCl, the spectrum contains only a band (3200 $cm^{-1}$) which can be assigned to strongly bound water.

These results lead to the conclusion that water plays an important part in the extraction of strong acids, and suggest that the main process is addition of the proton of the acid to water with formation of a simple oxonium ion. The latter is probably hydrated and solvated. We shall term this mechanism of extraction, involving the formation of a hydrated and solvated simple oxonium ion, the hydrate–solvate mechanism.

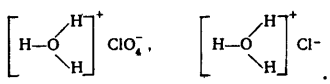
## 2. HYDRATION OF THE PROTON AND SOME CHARACTERISTICS OF THE MECHANISM OF THE EXTRACTION OF STRONG ACIDS

The above results enable us to regard the hypothesis of the addition of the proton to a water molecule as proved.

Let us examine the hydrate–solvate mechanism in greater detail.

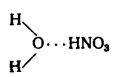
The oxygen atom in the small and strongly polarised water molecule is usually more basic than the active oxygen atoms in the solvents used for the extraction of acids. The high proton-acceptor capacity of water indicates that, in its presence, the proton should combine preferentially with water molecules and not with the organic solvent. This involves formation of a simple oxonium ion, a feature of which is the great strength of the O–H bonds. Actually, each O–H bond in the water molecule has an energy of about 110 kcal,[13] while the affinity of the proton for the water molecule is 180 kcal. Thus the total energy of formation of the $H_3O^+$ ion is 400 kcal. Since the O–H bonds in this ion are equivalent, each of them is associated with 133 kcal, a higher energy than in the water molecule. This great energy is responsible for the great stability of the $H_3O^+$ ion in solutions of strong acids. Such favourable conditions are not created by the addition of the proton to the oxygen atom of the organic solvent.

The $H_3O^+$ ion is more likely to be formed the stronger the acid (under otherwise identical conditions). Simple oxonium ions are formed, for example, by such acids as perchloric and hydrochloric:



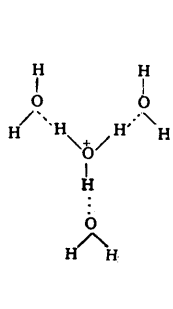
(V) (VI)

Nitric acid, which is of intermediate strength, shows less tendency to form $H_3O^+$ ions; it is characterised rather by hydrates in which the O–H bonds are not equivalent:

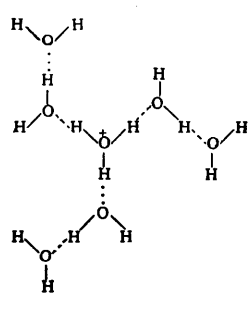


(VII)

In aqueous solution the simple oxonium ion is hydrated. Numerous data indicates that the hydration number of the proton is 4; Eigen *et al.*[14–17] supposed that the $H_3O^+$ ion forms the centre of three strongly bound water molecules, constituting by means of hydrogen bonds the pyramidal complex $H_9O_4^+$ (VIII). A few more weakly bound water molecules may be present in the outer hydration layer (IX):



(VIII)

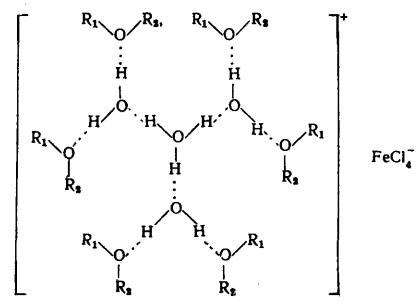


(IX)

The $H_3O^+$ ion differs from spherical monatomic ions, for example, the potassium ion, which is of the same size, in having three definite points for the addition of water molecules. The positive charge on the ion is concentrated at these points (hydrogen atoms); in spherical monatomic ions, however, the charge is uniformly distributed over the whole surface. The energy of hydration of simple oxonium is ~100 kcal mole$^{-1}$.[18,19] The complex consisting of four water molecules and one proton, *i.e.* $H_9O_4^+$, or $H_3O^+.3H_2O$, is stable in aqueous solution. In concentrated solutions even of strong acids the hydration number of the proton may be less than four; it is assumed, for example, that a change in concentration of sulphuric acid from 10 M to 20 M is accompanied by a change in hydration number from 4 to 2.[18]

It is further supposed that the proton is not fixed in the $H_3O^+$ ion, which constitutes the nucleus of the $H_9O_4^+$ complex, but migrates within this complex[9,15,18]; in time each of the four water molecules becomes the simple oxonium ion. The life of each $H_3O^+$ is of the order of $10^{-13}$ sec.

Since, as already noted, the ion usually interacts more strongly with water than with the organic solvent, it is more advantageous during extraction for the ion to pass into the organic phase together with its primary hydration shell, when the losses in energy of solvation will be a minimum[9]. In the organic phase the hydrated simple oxonium ion is solvated by molecules of the organic solvent, which add on to the water molecules by hydrogen-bond forces. Since each of the water molecules periodically becomes the oxonium ion, the organic solvent forms more stable bonds than in the water–organic solvent system. A structure of type (X) results:



(X)

This scheme is, of course, to a considerable extent arbitrary. Some of the sites in the second layer may be occupied also by water molecules; in systems in which there is a deficiency of water, solvent molecules may displace water also from the first layer ($n < 4$). The nature of the solvent plays an important part here, primarily its coordinating power, which is determined by the basicity and steric accessibility of the active oxygen atom. The degree of hydration or solvation depends on the degree of dissociation of the acid in the organic phase, which is determined both by the strength of the acid and by the nature of the organic phase (the dielectric constant).

The acidity of water in the equilibrium aqueous phase plays a great part. A hydration number of 4 (or above) may be optimum in relatively dilute solutions of strong acids. The activity of water diminishes with increase in concentration of the acid in the aqueous phase, and the degree of hydration of the proton should also decrease. It is therefore to be expected that the hydration numbers of the extracted compounds will not be constant, but may fall with rise in the equilibrium concentration of acid in the aqueous phase. At high acid concentrations the hydration

number may drop even to unity, *i.e.* unhydrated oxonium may remain. The mechanism under consideration envisages that the solvation numbers may, of course, be greater than unity and may vary under the influence of different factors. The solvation numbers should be linked firstly with the hydration numbers: it is probable that, the smaller the number of water molecules hydrating the oxonium, the fewer the sites for the addition of solvent. Therefore the solvation numbers also may, for example, diminish with increase in the equilibrium concentration of acid in the aqueous phase.

The above structure for the cationic portion indicates that solvation and hydration numbers are variable quantities, depending on many factors, while the cationic portion as a whole is a quite labile structure.

## 3. PUBLISHED DATA ON THE EXTRACTION OF STRONG ACIDS IN RELATION TO THE HYDRATE-SOLVATE MECHANISM

Experimental data on the extraction of strong acids agree well with the ideas reported above.

Let us examine published data on hydration and solvation numbers. We shall suppose that strong acids are extracted in the form of compounds of general formula $HA.nH_2O.mS$, where A is the anion of the acid, and S is a molecule of the oxygen-containing organic solvent.

Information in the literature indicates that the extraction of strong acids by oxygen-containing solvents is accompanied by combination of the acid molecule in the organic phase with a few molecules (more rarely with one molecule) of the organic solvent ($m \geq 1$). In several cases at least, the solvation number diminishes with rise in the equilibrium concentration of acid in the aqueous phase. In an absolute majority of cases the extraction of strong acids is accompanied by the withdrawal of water into the organic phase ($n > 0$), the number of moles of water per mole of acid in the equilibrium organic phase also diminishing with rise in the equilibrium concentration of acid in the aqueous phase.

Let us cite some examples. According to Siekierski and Gwozdz[11] the hydration number in the extraction of perchloric acid from dilute solutions with 100% tributyl phosphate (TBP) is 4. This gradually decreases with increasing concentration of $HClO_4$ in the aqueous phase. The solvation number also depends on the acid concentration (it is determined from the slope of the plot of the logarithm of the partition coefficient against the logarithm of the TBP concentration in the organic phase). At low $HClO_4$ concentrations the slope is about 3, and at higher concentrations it is unity. Similar results were obtained for the same system by Kertes and Kertes[20], who showed that, with rise in the concentration of $HClO_4$ in the initial and hence in the equilibrium aqueous phase, the solvation and hydration numbers diminish (they were determined by methods of physicochemical analysis using density, viscosity, volume changes, and electrical conductivity). Thus according to these results[20] the hydration number falls from 4 to 1. Similar results were obtained by Shevchenko *et al.*[21], according to whom the solvation number of $HClO_4$ in TBP diminishes with rise in concentration of acid in the aqueous phase (from 3.4 to 1 with a change in acid concentration from 0.1 M to 3 M). Analogous data on the solvation of perchloric acid in TBP were obtained by Fomin and Maiorova[22] ($m = 4$ and diminishes with rise in acid concentration).

Values of $n > 0$ and $m \geq 1$, and also a decrease in degree of hydration and solvation with increase in acid concentration, have been shown for the systems $HCl-TBP-H_2O$,[23] HCl–diisopropyl ether–$H_2O$,[24] and $HBr-TBP-H_2O$.[25] In the case of the strong complex acid $HFeCl_4$ and diisopropyl ether, the hydration number is also greater than zero and, according to Myers *et al.*[26], diminishes with rise in concentration of hydrochloric acid in the aqueous phase. A decrease in the solvation number in the $FeCl_3-HCl-TBP-H_2O$ system is probably indicated by the results of Specker and Cremer[27]: at hydrochloric acid concentrations in the aqueous phase of 4 M, 5 M, 7 M, and 9 M, the respective solvation numbers are 2.9, 2.4, 2.1, and 1.9.

Diamond and Tuck[8,9] pointed out the regular hydration number of 4 in the extraction of strong acids (simple oxonium hydrated with three water molecules). Actually, this number is frequently met; the results already quoted can be supplemented by data on a hydration number of 4.0–4.5 for $HClO_4$, HCl, and HBr in dibutyl Cellosolve, diisopropyl ketone, and TBP,[28] and for $HFeCl_4$ in diisopropyl ether[29-31,34]. However, it is essential to stress yet again the variability of the hydration number (as a more important fact), which is indicated in particular by the data cited here.

The labile character of the cationic portion of the extracted compounds is indicated also by other data, for example, the results of experiments[5] on the influence of several factors on the infra-red spectra of extracts with iron and hydrochloric acid. When extracts are heated or exposed to ultra-violet radiation, the spectra indicate a decreased degree of binding of the organic solvent, whereas the water is combined to a greater extent. This appears in diminished absorption in the band due to the combined C=O group, while the band due to free C=O becomes more intense; the bands assignable to free and combined water (the range of stretching vibrations) vary in corresponding fashion. With time, changes of a different type probably occur: the solvent is bound to a greater extent (the data for water do not enable a definite conclusion to be reached).

The instability of the cationic portion is indicated also by some data on the formation of three-phase systems. In several cases, especially when highly concentrated solutions of acids are used, the organic phase separates into two layers, one of which contains a greater proportion of the extracted substance.

Two organic phases are formed, for example, in the extraction of iron with diisopropyl ether[26,32-34]. The phases differ in the number of molecules of water per atom of iron, but are otherwise identical[33]. Laurene *et al.*[34] showed that it is the water which is the decisive factor in the formation of two ether phases; they regard the extraction system with two ether phases as analogous to the $HFeCl_4$–ether system, which contains insufficient water for a homogeneous solution to be formed. Two ether phases arise at high concentrations (above 8 M) of hydrochloric acid in the aqueous solution; under these conditions there is practically no longer any "free" water, the whole of the water being used up in the hydration of ions; the hydrochloric acid acts as a dehydrating agent. The degree of hydration of the proton is thus lowered, and different hydrates are formed, yielding the layers which separate out. According to these workers[34] two phases are formed also when sodium chloride is added to the isolated extract (diisopropyl ether–iron), the salt acting as a dehydrating agent.

In several cases three phases are formed also in the

extraction of simple acids. An example is the extraction of hydrochloric acid with undiluted TBP.[23] The homogeneous equilibrium extract, separated from the equilibrium aqueous layer, divides after several days into two layers. It was found that after some time dehydration occurs[35]: during extraction from 12.15 M HCl, the complex $HCl.3H_2O.TBP$ is first formed, and on standing $HCl.2H_2O.TBP$ appears. Three phases arise in the extraction of perchloric acid with solutions of TBP in "kerosene" (a mixture of saturated hydrocarbons of high boiling point, distilling over the range 182°–222°, $d^{25} = 0.743$).[36] The $HClO_4$ concentration used was 0.49 M, with a wide range of TBP concentrations; it is interesting that a third phase is not formed when benzene is used as diluent. Three phases have been observed in the $HNO_3$–TBP–$H_2O$ mepazine system[37]; in this case, however, other causes are probably operative. Formation of the anhydrous complex $3HNO_3.TBP$, soluble neither in the aqueous nor in the organic phase, plays a part here.

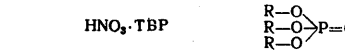
Let us now examine the dependence of extraction on the hydrogen-ion concentration. Since we are dealing with the extraction of acids, *i.e.* of extracted compounds containing the hydrogen ion, the partition coefficients should, in conformity with the law of mass action, increase with increasing concentration of hydrogen ions in the equilibrium aqueous phase. Monobasic acids are usually extracted, and hence there should be a linear relation, of unit slope, between $\log D$ (where $D$ is the partition coefficient) and $\log [H^+]$. Vdovenko and Krivokhatskii[38] showed, for example, that such a relation is observed in the extraction of iron from hydrochloric-acid solutions with diisobutyl sulphide, and Horrocks and Voigt[39] found a similar relation in the extraction of thallium(III) with diisopropyl ether. The second factor of significance here is the decrease in activity of the water with increasing equilibrium concentration of acid in the aqueous phase (caused by combination of the water with protons). In the case of complex acids, the decrease in activity of the water favours in particular the formation of extractable complex anions, for example $FeCl_4^-$. This fact definitely tends to increase the partition coefficients.

There are no grounds for ascribing the fact that extraction depends on the hydrogen-ion concentration to increasing stability of substituted oxonium cations. It is assumed that the latter should be stable only in solutions of very high hydrogen-ion concentration, whereas extraction of acids takes place quite often also from weakly acidic solutions. This does not contradict the two factors noted above, but is inconsistent with the substituted oxonium mechanism. Tervalent thallium, for example, is extracted by ethers from hydrochloric-acid solutions at HCl concentrations below 1 M. With complex acids in general, the position of the ascending portion of the extraction curve is determined to a considerable extent not only (or even, perhaps, not so much) by the hydrogen-ion concentration but also by conditions favouring the formation of a complex anion (stability constant, concentration of ligand, nature of solvent). The chloro-complexes of thallium or gold are probably extracted at lower HCl concentrations than, for example, the gallium or iron complexes, primarily because their chloro-complexes of the type $MCl_4^-$ are considerably more stable. Incidentally, if the formation of substituted oxonium compounds did play a decisive part, stronger acids should, under otherwise identical conditions, be extracted better, as Grinberg and Lozhkina[40] noted. However, this is not altogether so.

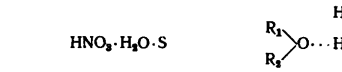
This mechanism explains the insolubility of anhydrous $HFeCl_4$ in anhydrous ethers, a fact established by Laurene *et al.*[34] and confirmed by Fomin and Morgunov[41] (dissolution occurs only after the addition of about five molecules of water per atom of iron). $HFeCl_4$ dissolves in anhydrous ketones[42]; in spite of this, the extraction of $HFeCl_4$ by ketones involves the participation of water.

## 4. EXTRACTION OF ACIDS OF MODERATE STRENGTH

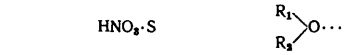
Acids of moderate strength do not always form the simple oxonium ion even in the aqueous phase, and the probability of this ion existing in the organic phase is still smaller. Water is linked to such acids by the hydrogen bonds, and some solvents readily displace this water† (especially under conditions such that the activity of water in the system is low). For example, nitric acid is extracted, by such an exceptionally basic solvent as tributyl phosphate, in the form of anhydrous solvates even at low acid concentrations (at any rate if addition takes place *via* the phosphoryl oxygen atom of the TBP). There is a vast literature on this question (see for example Tuck[43] and Alcock *et al.*[44]). Less basic solvents may not displace the water, and hydrated solvates are then extracted. The extractable compounds formed with nitric acid can be represented by the formulae (XI)–(XIII)

$HNO_3 \cdot TBP$ 

(XI)

$HNO_3 \cdot H_2O \cdot S$ 

(XII)

$HNO_3 \cdot S$ 

(XIII)

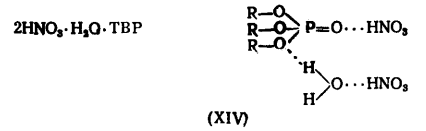
Let us cite some examples. According to Fomin and Maslova[45,46] nitric acid is extracted (at not very high concentrations) in the form of hydrated and partly as anhydrous solvates in the cases of ethyl propyl, dipropyl, and dibutyl ethers. The concentration of the anhydrous solvates becomes appreciable only at concentrations above 6 M and above 4 M with the ethyl propyl and dipropyl ethers respectively; in the case of dibutyl ether, both solvates are already extracted simultaneously at low $HNO_3$ concentrations. The complexes always contain at most one molecule of ether and of water. A decrease in degree of hydration with increase in acid concentration can be understood from all that has been said above. Similar data have been obtained for the $HNO_3$–$H_2O$–dibutyl ether system by Vdovenko *et al.*[47,48]. They showed in particular that the degree of hydration of nitric acid in the ether phase is 0.6 molecule of water per molecule of $HNO_3$ over the concentration range 0–1.5 m $HNO_3$ and 0.15 molecule in the range 3–6 m. Fractional values of the hydration number indicate the simultaneous extraction of anhydrous solvate and monohydrate.

Vdovenko and Alekseeva[49] showed that the degree of hydration of nitric acid in the phase formed by the dibutyl ether of diethylene glycol (dibutyl Carbitol) is 1.75 at low $HNO_3$ concentrations (up to 1.5 M), and that it depends on the concentration of $HNO_3$ in the aqueous phase. Tuck[50] found that nitric acid is extracted by the dibutyl ether of ethylene glycol (dibutyl Cellosolve) as a monohydrate (probably up to 7 M $HNO_3$ in the equilibrium aqueous phase). He

† See Tuck and Diamond[28].

suggested that a complex of the type (XII), produced by hydrogen bond formation, is formed between the acid hydrate and the solvent.

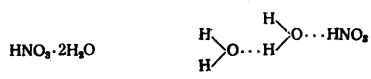
It is interesting that, although nitric acid adds not only to the phosphoryl oxygen atom of tributyl phosphate but also to the considerably less basic ester oxygen, these additional acid molecules probably add *via* water. This occurs at sufficiently high concentrations of nitric acid in the equilibrium organic phase, only after the phosphoryl oxygen atoms of the TBP molecule have been completely saturated‡. The complexes which are thus formed may be represented by the following formula:



(XIV)

Polish workers[37] have found that the TBP molecule may add up to four molecules of $HNO_3$ (all the oxygen atoms being occupied). A similar phenomenon probably occurs also with other solvents.

It is obvious that no hydrates of nitric acid exist (in the extracts) which could contain more than one molecule of water. This can be readily explained by the weak bond between water and the acid: the only water molecule which can add to the hydrogen atom of the acid is feebly polarised, and is unable to form stable bonds with other water molecules. But even if one of them is formed (formula XV), such compounds can hardly be extracted, since they cannot be stably solvated by the organic solvent. Actually, the water molecules in the second hydration layer should be practically unpolarised, and here, of course, there is no migration of the proton, because the proton as such is absent:



(XV)

Strong acids may sometimes occur under conditions such that they will behave like acids of intermediate strength. Hydrochloric acid, for example, can probably be extracted as an anhydrous solvate from highly concentrated solutions with not very basic solvents of comparatively low dielectric constant. This occurs in the case of dibutyl ether[42,52]. However, it is rare with strong acids.

The direct bonding of the organic solvent to the hydrogen atom of the acid, which is achieved in a small number of anhydrous solvates, is readily seen to have little in common with the formation of a substituted oxonium cation. Actually, we cannot speak here of the addition of a proton, which is essentially absent in this case; compounds of molecular type are formed.

Summing up, we must note that, in the vast majority of cases, the extraction of acids is accompanied by that of water. This water is simultaneously combined with the cation (proton or simple oxonium) and molecules of the organic solvent. The latter are located in a layer which is more remote from the cation than are the water molecules. Thus the decisive factor involving the organic solvent is its interaction with the hydrogen atom of the water of hydration.

‡ There is also another explanation for this phenomenon (see Pushlenkov *et al.*[51]).

Comparatively rarely, the solvent adds to the hydrogen atom of the acid. This occurs when the acid is feebly dissociated in the organic phase (weak acids or an organic phase of low dielectric constant) and/or when the activity of water is very low, for example, as a result of combination with ions present in the system. Molecular compounds in which the bonds are of the hydrogen type are then formed.

## 5. METHOD OF DETERMINING SOLVATION NUMBER FROM DISTRIBUTION DATA

A method often used to determine the solvation number of extracted compounds is based on a study of the dependence of partition coefficients on the concentration of active solvent in an inert diluent. This method was probably first employed by Peppard[53]. It consists essentially in the application of an expression which can be derived on the basis of the law of mass action: $D = A[S]^m$, where $D$ is the partition coefficient, [S] the equilibrium concentration of free active solvent in the organic phase, $m$ the solvation number, and $A$ a constant. Since this expression represents an equation to a straight line ($\log D = \log A + m \log [S]$), the value of $m$, numerically equal to the slope of the straight line, is usually found graphically. A necessary condition for application of the method is that all other conditions should be constant, primarily the composition of the equilibrium aqueous phase. Use of this procedure presupposes that the activity coefficients of solvent and solvate are equal to unity.

Difficulties often arise in applying this method. It is usually applicable only at comparatively low concentrations of active solvent. Deviations from linearity ($\log D = f \log [S]$) at high solvent concentrations are ascribed[54] to a deviation from ideal behaviour (variation of activity coefficients of solvent and solvate).

Sometimes deviations from linearity are observed even at low solvent concentrations. This was observed, for example, by Zvyagintsev and Zakharov-Nartsissov[55] in a study of the solvation number of hydrogen cyanoaurate(I) in the system water–cyclohexanone (or pentanol)–benzene; as the concentration of cyclohexanone in the benzene was changed from 0.3 M to 5 M the "solvation number" increased from 1 to 6. Kertes and Kertes[20] noted that the concentration of TBP in the diluent affected the solvation number of several acids, and Goroshchenko and Babkin[56] that the solvation numbers of the acids $HNbF_6$ and $HTaF_6$ were influenced by the cyclohexanone concentration. According to Fomin and Morgunov[42] $HFeCl_4$ is extracted by undiluted octan-2-one from a hydrochloric-acid solution of a definite concentration in the form of a pentasolvate, and by a solution of the octanone in benzene in the form of a trisolvate (or a tetrasolvate).

Maslova and Fomin[45] observed deviations from additivity in the systems $HNO_3$– ethers–$C_6H_6$–$H_2O$. Dilution of ethyl propyl and of dipropyl ethers with benzene somewhat lowers their "specific extractive capacity" (the amount of substance extracted per mole of active solvent).

The "slope" often depends also on the nature of the diluent. This applies, for example, to the system $HClO_4$–TBP–diluent–$H_2O$, studied by Schevchenko *et al.*[21] Casey *et al.*[57] studied the composition of the solvates formed by iron during extraction with 2,4-dimethylpentan-3-ol, and showed that the "slope" differs with the diluent (heptane, benzene, $CCl_4$).

The difficulties in applying the slope method to determine the solvation number of strong acids (simple and complex) seems to be fully explicable in the light of the ideas examined above on the mechanism of extraction. Furthermore, acceptance of the hydrate–solvate mechanism as fundamental in the extraction of strong acids leads to the conclusion that this graphical method is not strictly applicable at all to the study of the solvation number of the extracted acids.

Let us examine this in greater detail. If the organic solvent adds on *via* water, the solvation number should be linked with the hydration number. The above data on the variation in hydration and solvation numbers with rise in acidity probably confirm this. But does the hydration number remain constant with change in concentration of the active solvent? General considerations and available experimental data indicate that the hydration number should depend on the concentration of the solvent.

In fact, as was noted above, the degree of hydration depends on the degree of dissociation of the acid in the organic phase. For a given acid the degree of dissociation is in turn determined by the properties (composition) of the organic phase, increasing with increasing dielectric constant of the latter. An increase in concentration of an active solvent in an inert diluent is accompanied by an increase in dielectric constant and in degree of dissociation of the acid in the organic phase. This should lead to an increase in the hydration number. It is also possible that the hydration number is linked with the total content of "free" water in the organic phase, and will vary with increase in concentration of the acid in the organic phase, *i.e.* ultimately with increase in concentration of the active solvent. Thus the degree of hydration may vary with increase in concentration of the active solvent. The nature of the diluent should also, of course, influence the degree of hydration.

Let us refer to some data, indicating the correctness of the above considerations concerning the variation in degree of hydration. Maslova and Fomin[45] showed that, with increasing concentration of ethyl propyl and dipropyl ethers in benzene, the proportion of hydrated solvates rises; the opposite situation is observed with the less active dibutyl ether, which dissolves water less well[46]. Fomin and Morgunov[42] showed that hydrochloric acid is extracted from 7–8 M HCl by octan-2-one in the form of $HCl.3H_2O.S$; on dilution of the ketone with benzene, however, the degree of hydration is diminished; in extremely dilute solutions of the ketone, extraction takes place without water. A similar situation occurs in the extraction of $HFeCl_4$ with octan-2-one: the pure ketone extracts $HFeCl_4.4H_2O.5S$ (at a definite acidity, of course), and a solution of the ketone in benzene removes $HFeCl_4.3H_2O.3–4S$.

The change in degree of hydration with increase in concentration of active solvent may lead to a change in the solvation number, as is evident from the last example. It is this variation which explains the inapplicability of the method in some of the cases cited at the start of this section.

Acceptance of the hydrate–solvate mechanism as the main mechanism enables us to suggest that numerical values of the solvation and hydration numbers themselves are to some extent devoid of meaning. In any case, these numbers characterise the system only under certain concrete conditions (concentration of acid and active solvent, nature of diluent, etc.).

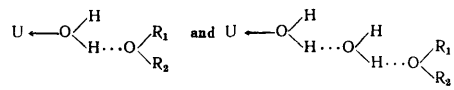
## 6. EXTRACTION OF SALTS

This section deals with salts formed by anions of simple and complex acids with metal cations. The question of the extraction of salts of complex acids has been discussed in part by Diamond[8].

It has already been mentioned that, since the ion–water interaction is stronger than that between the ion and the organic solvent, the ion can more advantageously pass into the organic phase together with its primary hydration shell. In the organic phase the hydrated ion would be solvated by molecules of the organic solvent. It is probable that sometimes water can be displaced by the organic solvent with the formation of a structure in which the solvent is directly coordinated to the metal atom.

A mechanism involving bonding of the solvent with the metal through water has been established for the extraction of uranyl nitrate with not too basic organic solvents. The data on this well-studied system are worth detailed consideration.

Glueckauf and McKay[58] put forward the idea that, in the extraction of uranyl nitrate with ether, a hydrogen bond may be formed between the hydrogen atom of the water of hydration and the oxygen atom of the organic solvent. This hypothesis was later proved by the work of Ryskin *et al.*[59] and especially of Vdovenko and his collaborators[12,60–65], which showed that two molecules of water enter the inner sphere of the complex (are directly coordinated with the uranium). To these water molecules, which are strongly polarised in the field of the uranium, molecules of the organic solvent are attached by means of hydrogen bonds. In several cases the hydration number exceeds 2, but the "extra" water molecules are present in the second hydration layer, and organic solvent is already attached to them. The structures thus formed are:




(XVI) (XVII)

As Vdovenko and Suglobova[60] noted, the water molecules entering the inner sphere are strongly deformed, and acquire acidic properties. The solvent molecules possess the properties of a base, and can therefore interact with the coordinated water.

The degree of hydration of the uranyl nitrate depends, as Vdovenko and Smirnova showed[62], on the nature of the organic phase, *i.e.* the nature of the active solvent, its concentration in the diluent, and the nature of the diluent. The "specific extraction capacity" of the solvent decreases on dilution with an inert diluent, the decrease varying in the sequency $C_6H_6 < CCl_4 < CHCl_3$; these workers link this with a change in degree of hydration of the salt. The hydration number decreases with decreasing concentration of active solvent, the nature of which plays an important part. In the case of solvents having appreciable proton-acceptor properties, in which water is soluble, this decrease is greater than in the case of feeble proton-acceptors, in which water is sparingly soluble. The degree of hydration in undiluted solvents is also linked with the nature of the solvent; the hydration numbers with diethyl ether, methyl butyrate, ethyl butyrate, and dibutyl ether are 4, 4, 3.3, and 2.5 respectively. It is readily seen that the degree of hydration depends on the proton-acceptor capacity of the solvent.

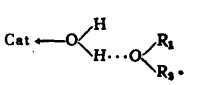
Anhydrous uranyl nitrate is insoluble in ethers, but dissolves in ketones, esters, and alcohols[63]. Thus direct attachment of solvent to the uranium atom is obviously possible, but under the actual conditions of extraction, addition takes place only *via* water. We are dealing with a system resembling in its behaviour one containing $HFeCl_4$.

Very active solvents displace water from the inner sphere of the uranyl ion. Tributyl phosphate extracts anhydrous uranyl nitrate, two TBP molecules entering the positions usually occupied by two water molecules — composition of solvate $UO_2(NO_3)_2.2TBP$. However, uranyl perchlorate is extracted[66] as a dihydrate with two or more TBP molecules. A possible explanation of this is that perchlorate ions create steric hindrance to TBP molecules but not to water. It is also possible that substitution of the anion results in a change in charge density on the central atom of the uranyl ion, and hence in a change in the extent of bonding of water. In the perchlorate the organic solvent is again linked apparently through water.

Tervalent iron is extracted quite well not only from hydrochloric-acid solutions but also from lithium-chloride solutions in the almost complete absence of hydrochloric acid, the Fe : Li ratio in the extract being close to unity. Iron is extracted, although not as well, also from $MgCl_2$, $CaCl_2$,[27] and $AlCl_3$ solutions. According to Specker and Cremer[27] the Fe : Ca ratio in the organic phase, in the extraction of iron with TBP from $CaCl_2$ solutions in the absence of acid (in order to eliminate competition by $HFeCl_4$), is close to 2 at low and intermediate $CaCl_2$ concentrations, and to 1 at high concentrations. Iron is present in the extracts in the form of $FeCl_4^-$. It may be assumed that mainly $Ca(FeCl_4)_2$ is extracted in the former case, and a mixture of $Ca(FeCl_4)_2$ and $CaCl_2$ in the latter.

More detailed study has been made of $FeCl_3$–LiCl–ester systems[3-5]. The infra-red spectra of the extracts show practically the same shift in the band due to stretching vibrations of the C=O group of the solvents as in the case of hydrochloric-acid solutions. This indicates that the organic solvent is combined in the extract. The spectrum of the solutions undergoes the same changes with time as in the case of hydrochloric-acid solutions: the spectrum undergoes analogous changes on being heated and exposed to ultra-violet radiation. Thus in the case of LiCl solutions, too, the organic solvent probably forms part of the compounds extracted. Since, as has been shown, water is also combined, the mechanism of the addition of the organic solvent can be regarded as analogous to that considered above.

The mechanism of the extraction of acids and uranyl nitrate, and also apparently of salts of $HFeCl_4$, shows common features. It is obvious that in all cases a structure is formed of the general type



(XVIII)

In some (comparatively rare) cases water is absent.

A mechanism of this type should not be peculiar to the cations considered above. It can obviously operate when the cation combines quite firmly with water, while the total amount of water in the system is not sufficiently large for it to form second, third, etc., hydration layers. The latter is achieved in systems having a high concentration of cations combining with water. Another condition is the ability of the organic solvent to form hydrogen bonds with the water molecule.

It is quite possible that compounds containing "intermediate" water may be extracted, under otherwise identical conditions, even more readily than anhydrous compounds. The size of the cation is an important factor. Passage from the aqueous to the organic phase proves to be easier with large ionic structures, among which are the hydrated forms. It is also noteworthy that these forms, in which the water is screened by organic molecules, have to a considerable extent lost their hydrophilic character.

Considerations of size are especially important in connection with the anion of the extracted ion pair. For a given cation (with anions of equal charge) a salt should be extracted more readily the larger the anion§. Anions are weakly hydrated. This is associated with the fact that the water molecule is bent; it is oriented with its oxygen atom towards a metal cation, and here is concentrated the negative pole of the molecular dipole, so that ion–dipole interaction is supplemented by donor–acceptor interaction. However, the water molecule is oriented with its hydrogen atoms towards the anion, and in this case only ion–dipole interaction is present. This interaction is intensified by increasing charge on the anion. As a result, only singly charged anions are extracted well, double charged anions are already feebly extracted, while triply charged anions are hardly extracted at all by oxygen-containing solvents.

Thus it would appear in principle that any salts should be extracted provided that the cation can firmly bind water, the anion has a small charge and is not too small in size, while the organic solvent possesses sufficient donor capacity. Salts containing large ions can be extracted in non-coordinating solvents having a high dielectric constant. Two opposite tendencies exist: when solvents with coordinating ability are used, salts with small cations capable of considerable solvation should be extracted better (for example Li > Cs); with non-coordinating solvents of high dielectric constant, on the other hand, extraction should improve with increase in size of the cation (Li < Cs).[9] In practice the two factors operate simultaneously, but sometimes these tendencies are very clearly expressed. An example is provided by Boyd and Larson's results[67] on the extraction of septivalent technetium from 1 M nitrate solutions with tributyl phosphate and from 1 M chloride solutions with nitromethane (Table).

Let us cite some other experimental data on the extraction of salts. The extraction of sodium chloride by TBP is very poor, but sodium perchlorate is extracted from 3 M solution by a 2.3 M solution of TBP in benzene with a partition coefficient of 0.068;[21] lithium perchlorate will probably be extracted still better. Baldwin *et al.*[68] studied the distribution of a series of alkali-metal halides between an aqueous solution and tributyl phosphate, and determined the equilibrium amount of water in the organic phase. It was shown that all the halides carry water along with them on passing into the organic phase. The quantity of water in the organic phase depends on the nature of the cation, diminishing in the sequence H > Li > Na > K. The hydration number depends also on the anion. The sequence of extractability is HI > HBr > HCl; LiI > LiBr > LiCl; HX > LiX > NaX > KX > CsX. The extent of extraction

§ The dielectric constant of the organic phase plays an important part here. For a more detailed account, see Diamond[9].

TABLE. Extraction of technetium from 1 M salt solutions with tributyl phosphate and with nitromethane.

| TBP, 1 M nitrate solutions of Tc | D | Nitromethane, 1 M chloride solutions of Tc | D |
|---|---|---|---|
| H | 28.3 | Li | 0.55 |
| Li | 14.7 | Na | 1.2 |
| $NH_4$ | 4.6 | H | 1.6 |
| Na | 2.2 | K | 2.1 |
| K | 1.1 | Rb | 2.5 |
| Ca | 15.6 | Cs | 3.7 |
| Cu | 5.4 | | |
| Al | 4.4 | | |

increases with increasing halide concentration in the aqueous phase; even LiCl, when its concentration in the aqueous phase is 13 m, is extracted in amount corresponding to a concentration of it in the equilibrium organic phase (TBP) of the order of 1 m (*i.e.* with a partition coefficient close to 0.1). So that there may be no doubt whether the extraction of salts can be considerable, we stress that LiI is extracted by TBP even better than is hydrochloric acid. It is readily established that these results correlate fairly well with the views set out above.

When basic oxygen-containing solvents are used (with which we are mainly concerned here), salts are usually extracted less well than the corresponding acids¶. The reason is that molecules of the water of hydration are usually more weakly bound to the metal cations than in the extraction of acids (the positive charge of the cation is diffuse, and there is no migration of the proton in the hydrates).

It is interesting that long ago Werner also gave expression to the thought that several coordination spheres can form around a positive ion. He argued that when water molecules form a coordination sphere around a positive ion, a negative charge is induced on the inner surface of the sphere, so that the outer surface bears a positive charge, just as the metal ion itself does. This enables it to attract another sphere of water molecules, which will likewise bear an induced charge. The process may be repeated several times (quoted from Bailar and Busch[69]).

If the salt is extracted together with "intermediate" water, the "slope method" for determining the solvation number may not give a satisfactory result. The reasons are the same as in the case of acids considered above. Determination of the solvation number by the slope method encounters less difficulty with the anhydrous solvate formed by uranyl nitrate with TBP than with hydrated uranyl perchlorate. Shevchenko *et al.*[21] showed that the slope method is inapplicable to the system $UO_2(ClO_4)_2$–TBP–$H_2O$–diluent. As already mentioned, the work of Vdovenko and his collaborators has shown that the degree of hydration of uranyl nitrate on extraction with ethers and esters varies with the concentration and nature of the diluent. It must be supposed that the solvation number, too, will vary.

In the investigation of the extraction of acids as a function of hydrogen-ion concentration, a constant ionic strength (*i.e.* concentration of chlorides, for example) is sometimes maintained by means of lithium salts. This apparently should not be done, since lithium itself can be extracted by basic solvents to a greater extent than, for example, sodium or potassium. As a result, the data obtained do not reflect the relation under investigation. Deviations would be especially large at low hydrogen-ion concentrations; at higher concentrations, the acid will be extracted preferentially (for example, $HFeCl_4$, not the salt $LiFeCl_4$), and the relative error will diminish.

¶ The position may change when non-coordinating solvents of high dielectric constant are used, as Diamond[9] has shown.


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## COLLOID-CHEMICAL MECHANISM OF THE SEPARATION OF SOME ELEMENTS BY EXTRACTION

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Extraction processes are of very great value in radiochemistry, inorganic and analytical chemistry, and also for the fissile materials industry and in chemical technology. Establishment of the mechanism of the extraction of various elements is therefore of great theoretical and practical interest, since it will make possible a systematic choice of extractants and determination of the optimum conditions for the process. In some cases a colloid-chemical mechanism is possible for the extraction of a series of elements. Some elements on passing into the organic phase may be extracted in the form of highly disperse colloidal particles (submicroscopic sols).

The extraction of elements by a colloid-chemical mechanism is due to the diminution in free surface energy of the system when hydrophobic colloidal particles pass from the aqueous phase into the organic phase, and is governed to a first approximation by the difference in surface tension at the aqueous medium–disperse phase boundary of the sol and at the disperse phase–organic solvent boundary.

Thus good extractants should generally have a comparatively low surface tension ($\gamma$ = 15–25 erg cm$^{-2}$). In fact, however, this relation is more complex in character.