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Determination of Hydration Numbers of Acids in Organic Phase by IR Spectrometry

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Abstract—By the precision infrared spectrometry the hydration numbers n were determined for a series of acids in 0.64 M tributyl phosphate (CCl_4) and acetonitrile at a concentration of free water 0.01–0.1 M. In tributyl phosphate n = 3.1±0.3 ($HAuCl_4$); 2.9±0.3 ($HFeCl_4$); 1.9±0.2 ($HClO_4$); 1.0±0.2 (HNO_3); 1.0±0.1 (HCl). In acetonitrile n = 3.1±0.7 ($HAuCl_4$); 1.1±0.4 ($HFeCl_4$); 2.1±0.2 ($HClO_4$), 0±0.05 (HNO_3); 0.1±0.15 (HCl).

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A method of IR spectrometry is used for the analysis of the state of water molecules in nonaqueous solutions and for measuring the total water content in organic solvents [1, 2]. However, it was rarely used for the study of equilibria and stoichiometry of the formed species [3], in contrast to the spectrophotometry in visible and ultraviolet regions, due primarily to the insufficient accuracy in the measurement of absorption. The number of water molecules in the composition of the studied form (hydration number) is an important characteristic, like the number of ligands in the complex. The most of known methods of determining hydration numbers are based on the data of extraction experiments [4]. For example, it can be calculated from the difference between the amount of water passing into the organic phase at the extraction of a studied component and without it. In other cases the total content of water in specially "dried" extracts can be found. The determination usually is carried out by Karl Fischer method [1]. Although the concentration of the component in organic phase can be quite high, the changes in the state of the studied medium commonly are neglected [4] that often leads to contradictory data and even to negative hydrate number. Thus, at the extraction of nitric acid into tributyl phosphate the total concentration of water in the organic phase with an increase in C_{HNO_3} decreases much stronger than it follows from the change in the water activity in solutions of HNO_3 [5]. In addition to the influence of the environment another possible reason for the apparent decrease in the water concentration is the reduced equilibrium concentration of the extractant (tributyl phosphate) as a result of its binding in solvate with the extracted component. Both factors (the influence of environment and the binding of the extractant) become significant at high concentrations of extracted components. Like the average number of ligand in the complex formation [6], the hydration number in a constant medium in the absence of polymeric forms depends only on the equilibrium concentration of water (free water) C_f in the organic phase. This implies a fundamental limitation of the methods based on extraction. If there is a balance between the aqueous and organic phases

$$H_2O_{(w)} = H_2O_{(org)}, \quad (1)$$

then $C_f = [H_2O]_{(org)}$ = const, and hence the average hydration number should be constant. Thus, using the extraction, we can determine the value of hydrate number at only one point at a given concentration C_f. It is possible to changing the C_f value by changing the water activity a_w in the aqueous phase by introducing an indifferent electrolyte in a high concentration. However, this will inevitably lead to environmental changes in the aqueous phase and, consequently, to uncontrolled change in all the characteristics, the equilibrium constants and distribution coefficients, of other processes in the system.

The method of IR spectrometry in the case of sufficient accuracy could provide much more extensive information and opportunities for the study of equilibria in the organic phase with involvement of water molecules and also reveal the stoichiometry of the forms. Special versions of the method have been used for the determining the hydration numbers of electrolytes in aqueous solutions [7]. The purpose of this study was to determine by means of precision infrared spectrometry the hydration numbers of some acids ($HAuCl_4$, $HFeCl_4$, HNO_3, $HClO_4$, HCl) in two organic media. As the first medium 0.64 M tributyl phosphate in CCl_4 was used. This system is often used for extraction. The polarity of the medium is low. The second medium is acetonitrile that has a higher polarity.

Figure 1 shows the spectra of water in 0.64 M tributyl phosphate in CCl_4 and acetonitrile.

The maxima of the bands of the stretching vibrations of water OH-groups in acetonitrile are located at 3543 and 3618 cm^{-1} with molar absorption coefficients 91 and 104 M^{-1} cm^{-1}, respectively, in the tributyl phosphate, at 3458 and 3686 cm^{-1}, the molar absorption coefficients are 102 and 88 M^{-1} cm^{-1}. Besides, at the addition of an acid often an additional broad band appears in the region of 3200–3300 cm^{-1} corresponding to hydrogen bonds. Its intensity depends strongly on the acid concentration C_{HX}. Therefore, it is probable that the hydrogen bonds are formed between the hydrogen ions of the acid molecules and oxygen atoms of water molecules.

As shown by conductometric data, all the studied acid HX at a given concentration of tributyl phosphate (0.64 M in CCl_4) are practically undissociated and exist in the form of associates $(HX{\cdot}nH_2O{\cdot}n_sTBP)_{org}$ where n_s is the solvate number, n is the hydrate number. For iron(III), despite the distribution of chloride complexes $FeCl_i^{3-i}$ in the aqueous phase, the organic phase contains only associates with X = $FeCl_4$ [4]. Gold(III) exists in the form of X = $AuCl_4$ in both phases. Absorption in the region of 3300–4000 cm^{-1} can be represented as

$$A/l = \varepsilon_f C_f + \varepsilon_b C_b = \varepsilon_f C_f + \varepsilon_b n C_{X(org)}, \quad (2)$$

where ε_f and ε_b are molar absorption coefficients, and C_f and C_b are the concentrations of free and bound water, respectively. For the bound water $C_b = nC_{X(org)}$, where $C_{X(org)}$ is the total concentration of HX in the organic phase, n is the hydration number.

The value of the product $\varepsilon_b n$ was determined from the results of extraction experiments. In these circumstances, there are two independent distribution equilibria: for acid and for water (1). The data on the extraction of water into tributyl phosphate from solutions of nonextractable salts show that at the unchanged environment the distribution of water in the organic phase follows the relation $C_f = C_f^0 a_w$, where a_w is the value of water activity in aqueous solution [5], C_f^0 is concentration of water in the organic phase at the extraction from pure water. Hence, water molecules do not form associates with each other in the organic phase. Therefore, for the extraction of acids, expression (2) can in general be represented as

$$A/l = \varepsilon_f C_f^0 a_w + \varepsilon_b n C_{X(org)} \quad (3)$$

and from experimental data [A, $C_{X(org)}$] the value of $\varepsilon_b n$ can be found.

Accounting for the activity of water is necessary, because for many acids the extraction was carried out from concentrated solutions. The data for the HX = $HAuCl_4$ at different wavenumbers are shown in Fig. 2.

The solid lines show the calculated behavior of the absorption that takes into account a decrease in $C_f = [H_2O]_{(org)}$ as a result of binding tributyl phosphate to associate and reducing its equilibrium concentration ([TBP] = $C_{TBP} - n_s C_{HX(org)}$, for $HAuCl_4$ n_s = 3 [8]). At the used concentrations $C_{HX(org)}$ these systematic changes are small. At ν = 3200 cm^{-1} (band of hydrogen bond) a significant increase in intensity is observed, which is natural, since the number of H-bonds increases with increasing $C_{HX(org)}$. Superposition of this band on the band of stretching vibrations of OH-bond at 3458 cm^{-1} leads to an increase in the measured

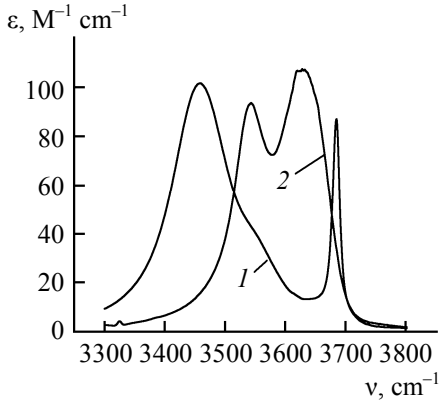

Fig. 1. Dependences of molar absorption coefficients of water on the wavenumber. (*1*) 0.64 M tributyl phosphate (CCl_4), (*2*) CH_3CN.

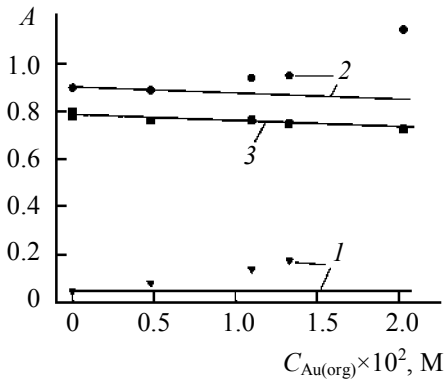

Fig. 2. Absorption of organic phase at the extraction of $HAuCl_4$ from aqueous solution (C_{NaCl} = 0.9 M, C_{HCl} = 0.1 M). (*1*) ν = 3200 cm^{-1}, (*2*) ν = 3458 cm^{-1}, and (*3*) ν = 3686 cm^{-1}.

intensity. Effect on the second band of stretching vibrations (3686 cm^{-1}) is small, and the change in intensity almost coincides with the calculated dependence. Therefore, just the high-frequency bands were selected for measuring. As follows from expression (3), the constancy of A at the increase in $C_{Au(org)}$ means that the value of the product $\varepsilon_b n \sim 0$. The same was observed for other acids: the bound water practically does not absorb at this wavelength.

Determination of hydration numbers in tributyl phosphate was carried out using the data from other (non-extraction) experiments. In anhydrous organic phase were dissolved certain small quantities of aqueous solutions of acids. As the water concentration in the initial aqueous solution is known, the total concentration of water in the organic phase, $C_{tot} = C_f + C_b$ is calculated according to the volumes of the additive and the organic phase. Equation (2) can be rewritten as

$$A/l = \varepsilon_f C_{tot} + (\varepsilon_b - \varepsilon_f) n C_{X(org)}. \quad (4)$$

With accounting for the result $\varepsilon_b n \approx 0$ obtained in extraction experiments, from the experimental data [A, C_{tot}, $C_{X(org)}$] the values of n were calculated. An example calculation for X = ClO_4 is shown in Table 1.

From these data follows that despite the marked random errors, the n value of $HClO_4$ is almost constant and close to 2 when $C_f > 0.01$ M. The data for all the acids in tributyl phosphate (CCl_4) are presented in Table 2. Here also are shown the ranges of total concentrations of water C_{tot} and HX in the organic phase.

In acetonitrile, HCl and HNO_3 do not dissociate and exist in the form of $HX \cdot nH_2O$. Other acids ($HAuCl_4$, $HFeCl_4$, and $HClO_4$) are dissociated almost completely and they probably exist as $\{H^+ \cdot nH_2O\}+X^-$, although, of course, in the framework of this study the hydration numbers of cation and anions cannot be determined separately, and only the overall n value can be found. Since in this case it is not possible to carry out the extraction experiments, then, as before, it was assumed that for the most short-wavelength band $\varepsilon_b \approx 0$, and for the calculations expression (4) was used. The values of hydration numbers are also presented in Table 2.

In the case of HCl and HNO_3 at C_{tot} = const the value of the absorption A is practically independent of C_X. As follows from (4) this means that $n \approx 0$. The acids dissociated in acetonitrile ($HAuCl_4$, $HFeCl_4$, $HClO_4$), have non-zero values of hydration number. This is expectable since the hydrogen ion is hydrated. For $HClO_4$ and $HAuCl_4$, the values of n were the same in both environments, although the forms of existence of these acids in tributyl phosphate and acetonitrile are quite different. The values of n in Table 2 refer primarily to the interval C_f = 0.01–0.1 M. At lower C_f the values of n should also decrease and, conversely, with increasing C_f they can grow. At the same time, in the given C_f range no significant systematic changes in n were observed for all acids (see, for example, Table 1).

Available information on the hydration numbers for both water [9] and organic media [10] is very controversial. For example, it is assumed that at the extraction of $HAuCl_4$ into tributyl phosphate [4] hydronium trihydrate [$H_3O^+ \cdot 3H_2O$] is formed, that is, n = 4.

Table 1. The calculation of hydration numbers for HX = $HClO_4$ in 0.64 M tributyl phosphate (CCl_4), ε_f = 88 M^{-1} cm^{-1}

$C_{tot}\times10^2$, M	$C_{X(org)}\times10^2$, M	A	n	$C_f\times10^2$
8.16	1.25	0.539	1.6	6.1
6.74	1.88	0.265	2.0	3.0
5.23	0.929	0.289	2.1	3.0
5.05	1.41	0.210	1.9	3.3
4.97	1.05	0.261	1.9	2.3
4.49	1.25	0.200	1.8	2.0
4.21	1.18	0.179	1.8	1.7
3.92	0.697	0.207	2.3	1.2
3.37	0.941	0.151	1.8	2.4
2.25	0.627	0.102	1.7	2.4
			Average n = 1.9±0.2	

Table 2. Hydration numbers of the acids HX in 0.64 M tributyl phosphate (CCl_4) and acetonitrile at C_f = 0.01–0.1

HX	Tributyl phosphate (CCl_4)			Acetonitrile		
	$C_{tot}\times10^2$, M	$C_{X\,(org)}\times10^2$, M	n	$C_{tot}\times10^2$, M	$C_{X\,(org)}\times10^2$, M	n
$HClO_4$	2.3–9.0	0.6–1.9	1.9±0.2	2.5–20	0.7–5.5	2.1±0.2
$HAuCl_4$	4.8–7.2	0.3–0.9	3.1±0.3	2.3–12	0.3–0.9	3.1±0.7
$HFeCl_4$	0.8–9.3	0.1–1.3	2.9±0.3	2.2–12	0.3–0.9	1.1±0.4
HCl	2.8–8.1	0.6–3.0	1.0±0.1	1.0–15	0.6–4.2	0.1±0.15
HNO_3	4.4	0.9–3.3	1.0±0.2	1.0–15	0.7–11	0±0.05

At the same time it is believed that at low concentrations of tributyl phosphate n = 0, and only upon approaching 100% concentration of tributyl phosphate the hydration number reaches a value of 3. There are also reports on the higher values of n. On the one hand, such diversity, of course, may be due to the difference in the experimental conditions. The change in concentration and, moreover, in the type of extractant and the organic component of the solution leads to a change in water concentration and, consequently, to changes in hydration and solvation numbers. However, other causes are also possible. One of them (the influence of the environment) was noted above. Another reason is the lack of informative techniques, which leads to the necessity of making assumptions and hypotheses. In this respect, the method of precision infrared spectrometry is one of the most reliable and containing no tentative assumptions. However, it has some natural limitations. Thus, for a cell with l = 1 mm the possible concentration of free water is restricted to 0.1–0.2 M, which is associated with reduced accuracy at measuring high absorption. In addition, the used solvents and extractants themselves should not contain OH bonds, which, of course, greatly narrows the range of possible objects of study.

EXPERIMENTAL

We used acids HNO_3, $HClO_4$, HCl, all of chemically pure grade. Concentrations of acids were determined by volumetric titration with NaOH. The initial iron(III) chloride solution (C_{Fe} = 4.27 M) was prepared from $FeCl_3$ (chemically pure) with the addition of the required amount of HCl in a small excess (C_{Fe}:C_{Cl} = 1: 4.1) . The content of chloride ions was determined gravimetrically as AgCl. The concentration of iron(III) was established spectrophotometrically after reduction with hydroxylamine and transformation into tris(dipyridyl)iron(II) complex (ε = 8640 M^{-1} cm^{-1} at ν = 18900 cm^{-1}). Aqueous solution of $HAuCl_4$ (C_{Au} = 4.59 M) was prepared by dissolving metallic gold in aqua regia followed by repeated evaporation with hydrochloric acid and then with water. The concentration of gold(III) in aqueous solutions was determined spectrophotometrically (ε = 5600 M^{-1} cm^{-1} at ν = 31800 cm^{-1}) on a Specord UV-VIS instrument. Densities of concentrated solutions were determined pycnometrically. Molar concentration of water in concentrated aqueous solutions was calculated as $C_w = (\rho - C_{HX}M_{HX})/M_{H_2O}$, where M is molar mass, ρ is the density of the solution (g l^{-1}).

At the extraction of $HAuCl_4$ the aqueous phase contained NaCl (0.9 M) and HCl (0.1 M); in the case of iron(III) it contained 5.5 M HCl. Other acids were extracted from their solutions of high concentrations (C_{HCl} > 6 M, C_{HClO_4} > 2 M , C_{HNO_3} > 2 M).

Tributyl phosphate was purified by washing with sodium carbonate solution, acid, and water. Water was removed by heating at 150ºC, and then storing over $CaCl_2$; as a diluent was used CCl_4 (extra pure). In the investigation was used a solution of tributyl phosphate with concentration 0.64 M (15 vol %).

Acetonitrile (extra pure) to remove water was boiled for 4 h over P_2O_5 in a flask with a reflux condenser, and then distilled. Residual water content in the organic phase was monitored by absorption in the IR region. The IR spectra (optical density) were recorded on one-beam Fourier spectrometer Scimitar FTS 2000 in a quartz cell with l = 1 mm. From the measured absorption of a solution was subtracted the absorption of the reference solution (anhydrous organic phase). Molar absorption coefficients of water were determined separately. Calibration dependences of A on C_f were linear [11].

For all the acids was measured electrical conductivity in the organic phase (conductivity meter OK-102/1). For solutions in tributyl phosphate it was below or near the lower limit of the instrument sensitivity that indicates absence of ionic forms. For solutions in acetonitrile it was found that hydrochloric and nitric acid are not dissociated, while $HClO_4$, $HFeCl_4$, and $HAuCl_4$ are dissociated almost completely [11].

In the case of acetonitrile in a test tubes with a glass stopper was placed 5–20 ml of acetonitrile, then with a microsyringe was injected 5 to 40 μl of acid and water, and then the spectrum was recorded.

Experiments with the tributyl phosphate consisted of two parts. In the first part extraction of acid from aqueous solution (3 min, 20°C) was carried out, then its content in both phases was determined and the absorption A of the organic phase. From these data the product $\varepsilon_b n$ was calculated, where n is the hydration number and ε_b is molar absorption coefficient of bound water. In the second part, to the water-free 15% solution of tributyl phosphate (5–10 ml) was added with the microsyringe portions (5–20 μl) of aqueous solutions of acids. After complete dissolution, A value was measured again and from these data were calculated n values.

As noted above, an important condition is the constancy of the environment in the organic phase in extraction experiments. This means that variations in the concentrations of components must be small enough. In the case of tributyl phosphate (C_{TBP} = 0.64 M, no ions) the concentration in the organic phase did not exceed: acid 0.02 M, water 0.1 M.

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