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PHYSICAL CHEMISTRY

1965

SovietRxiv

Abstract

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UDC 541.20

PHYSICAL CHEMISTRY

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STUDY BY THE METHOD OF NUCLEAR MAGNETIC RESONANCE OF THE POSITION OF HYDROGEN IONS IN CERTAIN HETEROPOLY COMPOUNDS

A number of controversial questions concerning the structure of heteropoly compounds are associated with the number and position of hydrogen ions, their interaction with the anion and with water molecules included in the elementary cell. The role and arrangement of a considerable amount of water in crystalline hydrates of heteropoly compounds are also unclear. To investigate the state of water and hydrogen ions we have applied the NMR method.

In studying phosphomolybdic acid (PMA) ([1]) with various contents of hydration water, a regular increase was observed

Table 1

Water content in samples of SiWA and PWA obtained at different dehydration temperatures

Temperature, °C	Number of H_2O molecules according to analysis	Formula	Temperature, °C	Number of H_2O molecules according to analysis	Formula
20	15	$H_3[PW_{12}O_{40}]\cdot 13.5H_2O$	20	15	$H_4[SiW_{12}O_{40}]\cdot 13H_2O$
80	10	$H_3[PW_{12}O_{40}]\cdot 8.5H_2O$	70	10	$H_4[SiW_{12}O_{40}]\cdot 8H_2O$
120	7	$H_3[PW_{12}O_{40}]\cdot 5.5H_2O$	100	8	$H_4[SiW_{12}O_{40}]\cdot 6H_2O$
140	6	$H_3[PW_{12}O_{40}]\cdot 4.5H_2O$	120	7	$H_4[SiW_{12}O_{40}]\cdot 5H_2O$
175	5	$H_3[PW_{12}O_{40}]\cdot 3.5H_2O$	140	6	$H_4[SiW_{12}O_{40}]\cdot 4H_2O$

Fig. 1

Figure 1: Fig. 1

Temperature, °C	Number of H_2O molecules according to analysis	Formula	Temperature, °C	Number of H_2O molecules according to analysis	Formula
200	4	$H_3[PW_{12}O_{40}]\cdot 2.5H_2O$	175	5	$H_4[SiW_{12}O_{40}]\cdot 3H_2O$
225	3	$H_3[PW_{12}O_{40}]\cdot 1.5H_2O$	200	4	$H_4[SiW_{12}O_{40}]\cdot 2H_2O$
275	2	$H_3[PW_{12}O_{40}]\cdot 0.5H_2O$	250	3	$H_4[SiW_{12}O_{40}]\cdot 1H_2O$
380	1.5	$H_3[PW_{12}O_{40}]$	380	2	$H_4[SiW_{12}O_{40}]$

in the intensity of the component of the corresponding spectra in the field region of $\$\pm 2 gaussashydrationwaterwasremoved. Itwasfurtherestablished({}^{\{2\}})thatthespectraofheteropolycompoundscompi
{}^{4}).

In order to trace in detail the dependence of the absorption line of hydrogen ions on the content of hydration water, preparations of STA and PTA with different contents of bound water were obtained (Table 1). The synthesis and analysis of the initial compounds are given in ([2]). Samples of STA and PTA with different water contents were obtained by prolonged holding at a definite temperature until constant weight was reached (Table 1). The water content was checked by calcination at 700° C. Weighed portions of the obtained samples, 1 g in mass, were sealed in glass ampoules. Derivatives of the proton absorption lines were recorded at 90° K on a spectrometer for broad lines ([5]). Figure 1 gives derivatives of the absorption lines of STA samples with different contents of hydration water. The character of the changes in the spectra of STA and PTA is the same. The intensity of the central narrow line increases and reaches its maximum value in completely dehydrated preparations.

Figure 2 shows the dependence of the intensity A and width δH of the narrow lines on the water content per one molecule of STA and PTA. The intensity was measured as the peak-to-peak distance of the derivative and was taken as a percentage of the line of the anhydrous sample. The regularities found can be divided into two regions—below and above the point corresponding to the content of 4 molecules of hydration water. The dependence of the intensity of the narrow line on the water content in the first region is linear, while the line width is practically constant.

Fig. 1. Derivative absorption lines of samples of silicotungstic acid with different contents of hydration water:

Fig. 2

Figure 2: Fig. 2

a –$H_4SiW_{12}O_{40} \cdot 4H_2O$,
b –$H_4SiW_{12}O_{40} \cdot H_2O$,
v –$H_4SiW_{12}O_{40}$.
The scale of Fig. 1b along the ordinate axis is reduced by a factor of 2.5 in comparison with Fig. 1a.

The increase in the intensity of the narrow line in the spectra under consideration, associated with the removal of a strictly definite amount of hydration water, is due to a sharp change in the proton environment of the hydrogen ions.

Fig. 2. Dependence of the intensity (A) and line width (δH) of the absorption of H^+ ions at 90° K on the content of hydration water: on the left—in phosphotungstic acid; on the right—in silicotungstic acid.

In accordance with our measurements, it should be concluded that in STA and PTA samples containing, respectively, 4 and 3 molecules of hydration water per one molecule of acid, all protons are arranged in groups $n \cdot (H^+ + H_2O)$, where $n = 4$ for STA and $n = 3$ for PTA. Upon removal of all n water molecules, the absorption line is determined only by the arrange-

···of the remaining hydrogen ions. In (2) we estimated the smallest distance between H^+ ions as a value exceeding 3 Å. The distance between the $H^+ + H_2O$ groups may likewise be regarded as exceeding 3 Å.

As follows from Fig. 2, the change in intensity of the narrow line for PVA and SVA in the first region is somewhat different. This is due to the fact that in PVA one water molecule is not bound to an H^+ ion and is the last to leave upon dehydration.

The second region of the dependences in Fig. 2 must be considered together with the total spectrum of the system $n \cdot (H^+ + H_2O)$ (Fig. 1, a). Without pausing here to analyze the lines in samples containing 4 or more molecules of hydration water, we note that the derivative of the absorption line of an isolated H_2O molecule has another form ([6]). The absorption line of the system $n \cdot (H^+ + H_2O)$ also does not correspond to the known form of oxonium ([7]). Probably, in our case the three protons are arranged in a deformed triangle.

In work ([8]), Keggin determined by X-ray diffraction the structure of 5-water PVA. Later the same was done for SVA ([9]). These acids in their low-water forms have a unit cell of the body-centered-cube type with parameter 12.14 Å. Two acid molecules are located in it. According to Keggin' s data, two variants of anion arrangement in the unit cell are possible. They correspond to the Fedorov groups T_d^3—$I43m$ and O_h^4—$Pn3m$. In the case of T_d^3 symmetry, 14 water molecules are placed in the cell. Eight of them are situated between anions on the threefold axes of the cube with tetrahedral symmetry, in the

positions aaa, $\bar{a}\bar{a}a$, $\bar{a}a\bar{a}$, $a\bar{a}\bar{a}$, where $a = 3.28$ Å. In the case of O_h^4, 10 water molecules are placed in the cell, with 4 of them on the threefold axes in the positions $aa\bar{a}$, $\bar{a}aa$, $a\bar{a}a$, aaa, where $a = 3.03$ Å. In both variants, 6 water molecules occupy the centers of the edges and faces of the elementary cube.

The arrangement of anions in the unit cell in accordance with the Fedorov group T_d^3 makes it possible to place eight H^+ ions at the positions of the eight water molecules. To estimate the position of H^+ ions in the unit cell of SVA, PVA, and PMA from the experimental values of the second moment, the following considerations may be stated:

1. The form of the absorption line in anhydrous structures is determined only by the mutual arrangement of the hydrogen ions and the central atom.
2. The SVA anion contains 4 H^+ ions; PVA and PMA contain 3 H^+ ions.
3. In hydrated forms of the heteropolyacids studied, the H^+ ions are located next to eight, for SVA, and six, for PVA, H_2O molecules in the unit cell.
4. The packing of anions in the unit cell occurs with symmetry T_d^3—$I43m$.
5. The most probable arrangement of H^+ relative to the anion is tetrahedral for SVA and an equilateral triangle for PVA.

The expression for the second moment of the acids investigated may be written as follows:

$$\Delta\overline{H}_0^2 = \Delta\overline{H}_{\mathrm{H-H}}^2 + \Delta\overline{H}_{\mathrm{H-X}}^2 + \Delta\overline{H}_{\mathrm{H-H'}}^2 + \Delta\overline{H}_{\mathrm{H-X'}}^2, \tag{1}$$

where $\Delta\overline{H}_0^2$ is the experimental value of the second moment; $\Delta\overline{H}_{\mathrm{H-H}}^2$ is the contribution from the interaction of protons of one anion; $\Delta\overline{H}_{\mathrm{H-X}}^2$ is the contribution from the interaction of protons with the magnetic moment of the central atom $(\mathrm{Si}, \mathrm{P})$; and $\Delta\overline{H}_{\mathrm{H-H'}}^2$, $\Delta\overline{H}_{\mathrm{H-X'}}^2$ are contributions from the interaction of spins of neighboring anions.

Since the dimensions of the anion are large, $R_{\mathrm{an}} \simeq 5$ Å ([10]), the last two terms in equation (1) may be neglected without significant error.

Using Van Vleck' s general expression for the second moment of a rigid lattice of a polycrystal [11], in the case of KVA we obtain:

$$\overline{\Delta H_0^2} = \frac{57}{r^6} + \frac{6.24}{r^6}, \tag{2}$$

where r is the distance from the H^+ ion to the central atom. For PVA, with the H^+ ions arranged as an equilateral triangle,

$$\overline{\Delta H_0^2} = \frac{26.6}{r^6} + \frac{26}{r^6}. \tag{3}$$

Fig. 3. Arrangement of H+ ions and eight water molecules in the unit cell of silicotungstic acid

Figure 3: Fig. 3. Arrangement of H+ ions and eight water molecules in the unit cell of silicotungstic acid

The same expression is obtained for PMA. The values of $\Delta\overline{H_0^2}$ for KVA, PVA, and PMA are given in [(2)] and are equal, respectively, to 0.38, 0.17, and 0.30 G^2. The values of r for KVA, PVA, and PMA calculated according to equations (2) and (3) are given in Table 2. Figure 3 shows the arrangement of H^+ and H_2O in the unit cell of KVA. The positions of the anions are given by the central tetrahedra SiO_4. The H^+ ions are arranged, as are the H_2O molecules, on the threefold axes. In this case the distance between the H^+ ion and the oxygen of the water molecule is indeed small, namely 2.49 Å (KVA), 2.23 Å (PVA), and 2.47 Å (PMA). The proposed arrangement of the H^+ ions can be checked after determining the interproton distances in the group $H^+ + H_2O$.

Fig. 3. Arrangement of H^+ ions and eight water molecules in the unit cell of silicotungstic acid

Thus, the investigation carried out makes it possible to refine the ideas about the structure of KVA, PVA, and PMA. The H^+ ions contained in the unit cell are located in the immediate vicinity of eight water molecules in KVA and six water molecules in PVA and PMA. On the basis of our results and of structural data known earlier, the most probable packing of anions in the cell is assumed to have the symmetry $T_d^3 - I\bar{4}3m$. In accordance with this, and using the experimental values of the second moment for the anhydrous structures, the distances H^+—P, H^+—Si were calculated (Table 2). The H^+ ions are located on threefold axes inside the sphere of the heteropolyanion.

Table 2

Substance	Calculated distance H^+— central atom, Å	Calculated distance between H^+ ion and one anion, Å
$H_4SiW_{12}O_{40}$	2.35	3.80
$H_3PW_{12}O_{40}$	2.60	4.50
$H_3PMo_{12}O_{40}$	2.36	4.10

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Received
25 V 1965

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Note: Figure translations are in progress. See original paper for figures.