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Abstract

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STUDIES OF THE STATE OF HYDROGEN IN AQUOPOLYCOMPOUNDS OF TUNGSTEN BY THE METHOD OF NUCLEAR MAGNETIC RESONANCE

The study of the state of water in aquopolycompounds is essential for understanding their structure. Numerous studies of dehydration under various conditions have not been able to resolve this question completely. During dehydration, a significant rearrangement of the original hydrate structure occurs, accompanied in some cases by partial decomposition of the substance. Proceeding from the fact that on heating the last 1-2 molecules of water are removed with the greatest difficulty, a conclusion was drawn about their special position in the original molecule. Taking into account the results of dehydration and formally using the provisions of coordination theory, Copaux (^{1}) and Rosenheim (^{2}) assigned to the most typical aquopolycompounds of tungsten—sodium paratungstate and sodium metatungstate—the following formulas: $Na_5H_5[H_2(WO_4)_6] \cdot xH_2O$ and, respectively, $Na_6H_4[H_2(W_2O_7)_6] \cdot xH_2O$. In these structures the central complex-forming species is the ion ${H_2}^{2+}$, which lacks physical justification, since the indicated ion cannot exist in a stable form.

Recently, the method of nuclear magnetic resonance (NMR) (^{3}) has begun to be used to study the state of water in crystalline hydrates. Aquopoly- and heteropolycompounds have not yet been investigated by this method. Among substances close to them, molybdic (^{4}) and tungstic acids (^{5}) have been studied by the NMR method.

We obtained derivatives of the NMR proton signals for the following substances: normal sodium tungstate (n.s.t.) $Na_2WO_4 \cdot 2H_2O$, sodium paratungstate (p.s.t.) $Na_{10}W_{12}O_{41} \cdot 28H_2O$, sodium metatungstate (m.s.t.) $Na_2W_4O_{13} \cdot 10H_2O$, and yellow tungstic acid (y.t.a.) $WO_3 \cdot H_2O$ (Fig. 1). The starting product for the synthesis of these compounds was $Na_2WO_4 \cdot 2H_2O$ of chemically pure grade, which was recrystallized several times from water. Yellow tungstic acid was prepared by the usual procedure (^{6}). P.s.t. and m.s.t. were synthesized by the gradual addition of yellow tungstic acid to a boiling solution of Na_2WO_4, respectively to pH 7 and 2.5-3, followed by crystallization. The preparations obtained were analyzed for the content of H_2O, WO_3, and Na_2O. The analytical results were close to the theoretical values.

Derivatives of the NMR absorption signals from protons were recorded on a spectrometer constructed at the Institute of Physical Chemistry of the Academy of Sciences of the USSR. The spectrometer used a permanent magnet with a field strength of 5500 gauss and inhomogeneity of ~0.03 gauss/cm^3. As the radio-frequency generator and signal detector, Robinson' s circuit (^{7}) was used. The rate of frequency change when passing through the line corresponded to a field-change rate of 1 gauss/min. The level of radio-frequency voltage on the working coil was set at 0.1 V. The constant magnetic field was modulated at a frequency of 81 Hz and an amplitude of 0.1 gauss. The signal, proportional to the first derivative of the absorption line, was amplified by a narrow-band amplifier and fed from the phase detector to the recorder. The samples were taken in the form of powder placed in an ampoule with a working volume of 0.4–0.5 cm^3.

The second moments ΔH_2^2 were calculated from the derivative of the absorption line.

The error in the calculation did not exceed 5%. The shape of the NMR absorption and, consequently, the second moment are affected by thermal motions of the atoms and by lattice vibrations. However, in a number of works (^{3}) it was shown that at temperatures below 120°K this effect is negligibly small, and the NMR absorption line below this temperature may be regarded as corresponding to the rigid proton structure of the substance. Therefore the spectra of all compounds were recorded at 77 and 293°K (Table 1).

Table 1

Second moments and line widths (δH) of proton NMR

Compound	δH (gauss) 293°K	$\overline{H_2^2}$ (gauss^2) 293°K	$\overline{H_2^2}$ (gauss^2) 77°K
$Na_2WO_4 \cdot 2H_2O$	–	–	17
$Na_{10}W_{12}O_{41} \cdot 28H_2O$	0.8	24	29
$Na_2W_4O_{13} \cdot 10H_2O$	0.8	11	25
$WO_3 \cdot H_2O$	0.6	12	27
$Al(OH)_3$	0.6	17	23

The shape of the absorption lines and the magnitude of the second moments in paratungstate hydrate, metatungstate hydrate, and tungstic acid are typical of crystalline hydrates with an average H—H distance in the water molecule of 1.58–1.60 Å (^{3}). These compounds differ from "pure" crystalline hydrates by a component of the line in the region of fields $\Delta H = \pm 3$ gauss. According to (^{8,9}), this component indicates the presence of hydroxyl groups, in the present case bound to the W atom. Here the H—H distance is 2–2.5 Å. The number of protons entering into the hydroxyl groups amounts, for paratungstate hydrate and metatungstate hydrate, to approximately 2–3%, and in tungstic acid to 1% of the total number of hydrogen atoms in the substance.

Fig. 1. Derivatives of the proton NMR absorption lines in solid tungsten compounds. Temperature 77°K: 1 –Na10W12O41 • 28H2O; 2 –WO3 • H2O; 3 –Na2W4O13 • 10H2O; 4 –Na2WO4 • 2H2O; 5 –Al(OH)3. Temperature 293°K: 1′ –Na10W12O41 • 28H2O; 2′ –WO3 • H2O; 3′ –Na2W4O13 • 10H2O; 4′ –Al(OH)3.

Figure 1: Fig. 1. Derivatives of the proton NMR absorption lines in solid tungsten compounds. Temperature 77°K: 1 –Na10W12O41 • 28H2O; 2 –WO3 • H2O; 3 –Na2W4O13 • 10H2O; 4 –Na2WO4 • 2H2O; 5 –Al(OH)3. Temperature 293°K: 1′ –Na10W12O41 • 28H2O; 2′ –WO3 • H2O; 3′ –Na2W4O13 • 10H2O; 4′ –Al(OH)3.

Fig. 1. Derivatives of the proton NMR absorption lines in solid tungsten compounds. Temperature 77°K: 1 –$Na_{10}W_{12}O_{41} \cdot 28H_2O$; 2 –$WO_3 \cdot H_2O$; 3 –$Na_2W_4O_{13} \cdot 10H_2O$; 4 –$Na_2WO_4 \cdot 2H_2O$; 5 –$Al(OH)_3$. Temperature 293°K: 1′ –$Na_{10}W_{12}O_{41} \cdot 28H_2O$; 2′ –$WO_3 \cdot H_2O$; 3′ –$Na_2W_4O_{13} \cdot 10H_2O$; 4′ –$Al(OH)_3$.

At room temperature, part of the water molecules in the crystalline hydrates of metatungstate hydrate and tungstic acid passes into a more mobile state, which is accompanied by the appearance of a central narrow line (Fig. 1).

Of note is the small difference in the values of the second moments and in the general form of the absorption curve for paratungstate hydrate at 77 and 293°K. Evidently, in this case the appearance of a new motion in the system, affecting the shape of the NMR line, is associated only with a small change in the vibrational motion of the lattice, which only slightly changes the distribution of the proton correlation times. In contrast to the other compounds, the water molecules in paratungstate hydrate are arranged very densely, and raising the temperature from 77 to 293°K has little effect on changes in their mobility.

An unexpected result was obtained in the study of sodium tungstate hydrate. The second moment (17 gauss^2) proved to be considerably smaller than that observed in crystalline hydrates. To estimate the H–H distance one can use the Van Vleck equation for polycrystalline structures (^{3}):

$$\overline{\Delta H_2^2} = \frac{6}{5} I(I+1) \frac{g^2 \mu_0^2}{N} \sum_{j>k} r_{jk}^{-6}, \tag{1}$$

where I is the nuclear spin quantum number, g is the splitting factor, and r is the H–H distance. Since the main contribution to $\Delta\overline{H_2^2}$ is made by the smallest H–H distance, in formula (1) the terms with larger r may be neglected. Substituting into relation (1) the values of all quantities and taking $N = 2$ (the number

of the H atoms in the cell, which make the largest contribution to the second moment), we obtain the equation $\Delta\overline{H}_2^2 = \frac{348}{r^6}$, which has been used by a number of authors (^{10,11}) to estimate r in low-water hydrates. For N.V.N. r proved to be 1.65 Å, which is appreciably larger than the analogous distance for molecules of free water (1.58 Å).

The anomaly found can be explained by the fact that the water molecules in $Na_2WO_4 \cdot 2H_2O$, owing to the considerable affinity of the protons for the anion WO_4^{2-}, as well as the formation of hydrogen bonds between the WO_4^{2-} anion and the water molecules, are in a stretched state. The latter is also confirmed by the fact that the NMR line shape for N.V.N. is very similar to the line shape of typical aluminum hydroxide $Al(OH)_3$ (Fig. 1). Consequently, in N.V.N. a peculiar "hydrolysis" occurs, as it were, within the crystal lattice itself.

Thus, the results obtained by us indicate the absence in tungsten aquopolycompounds of a special rigid proton structure with a small H—H distance, which, according to the views of Copaux—Rosenheim, should have been observed in them. These conclusions, refuting one of the basic propositions of the Copaux—Rosenheim hypothesis, are in agreement with other published works ($^{12-15}$).

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