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Proton conductivity of inorganic hydrates

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Abstract. A wide range of inorganic crystal hydrates possessing proton conductivity is analysed. The possible mechanisms of defect formation and proton transfer are considered, including those for a series of specific compounds. The main directions in the search of compounds having high proton conductivity at room temperature are outlined. The bibliography includes 65 references.

I. Introduction

One of the priority aspects of the development of modern chemistry is the elaboration of materials possessing special electrical properties; in particular, the search for solid electrolytes having proton conductivity. The prospects for their application are exceedingly wide. For example, they have been used to create high-performance fuel cells (with an efficiency approaching 100%) based on the oxidation of hydrogen,[1,2] water vapour electrolysers, devices for the extraction of hydrogen from water gas,[3] and highly sensitive sensors for hydrogen, carbon monoxide, and several other gases.[4,5] Recently a new field of application of proton-conducting materials was discovered: their use for the non-faradaic electrochemical modification of the catalytic activity (EMCA) of metal catalysts, resulting in a manifold increase in their activity and selectivity, e.g., in the 'catalytic cross-linking' of methane.[6] It should also be noted that the same requirements must be met for a compound to possess proton conductivity as those for the existence of acid – base catalytic activity in organic syntheses.[7] These properties are therefore directly correlated for many compounds,[8] and proton conductivity is used in several scientific centres as the primary test for screening proposed catalysts. The above factors led to a broad development of the search for and study of new solid proton-conducting electrolytes. Not only electrical conductivity but also other properties of the material, such as thermal stability, solubility, dispersity, etc., appear to be of primary importance.

If one considers the list of compounds possessing a high proton conductivity at the usual, relatively low temperatures, it is easy to see that virtually all of them, including all 'record holders', are hydrates of bases, acids, acid salts, or oxides with distinct acidic properties. For example, the highest proton conductivity at room temperature (0.17 S cm^{-1}) is exhibited by highly hydrated heteropolyacids.[9,10] The following compounds have conductivities lower by two orders of magnitude: uranyl phosphate,[11] some hydrated acid sulfates,[12] hydrates of sulfonic acids,[13] hydrated tetramethylammonium,[14] and certain finely dispersed materials, such as acid phosphates of zirconium, tin, antimony,[15–17] polyantimonic acid,[18] etc. Taking this into consideration, we shall devote most attention in this review to the proton conductivity of inorganic hydrates of acids, acid salts, and bases.

We shall present here several known general relations for ionic conductivity which will be used below. In the general case, electrical conductivity is defined by the following equation:

$$\sigma = \sum n_i q_i \mu_i, \quad (1)$$

where n_i is the number of the charge carriers, q_i is their charge, and μ_i is their mobility.

Temperature dependence of the number of carriers is expressed by the equation:

$$n_d = N\exp(-\Delta G_d/2kT), \quad (2)$$

where N is the overall number of possible sites for the formation of the carriers (most frequently proton defects in the case under consideration), ΔG_d is the free energy for defect formation, and k is the Boltzmann constant.

In its turn, the mobility of the charge carriers also depends on temperature:

$$\mu = (a^2 q/kT)\, v_0 \exp(-E_m/kT), \quad (3)$$

where a is the distance between the neighbouring positions in the structure, q is the proton charge, v_0 is the frequency of proton vibrations near the equilibrium position ($\sim 10^{14}$ s^{-1}), and E_m is the energy barrier to migration.

Thus the temperature dependence of the overall conductivity is defined by the equation

$$\sigma = (a^2 q/kT)\exp[-(\Delta G_d/2 + E_m)/kT]. \quad (4)$$

In practice, this equation is used in an abbreviated form adjusted to molar values and is known as the Frenkel equation:

$$\sigma T = A\exp(-E/RT). \quad (5)$$

To understand the essential nature of the proton conduction process, it is important to formulate the mechanisms for the formation of defects and their transfer in the structure of the substance.

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II. Formation of charge carriers

As a rule, the formation of charge carriers reduces to proton transfer from the ground state to an excited state characterised by a higher energy. Most often, this can be described by reactions of the following types:[19,21]

$$2HSO_4^- \rightleftharpoons H_2SO_4 + SO_4^{2-}, \quad (6)$$

or

$$O_3SO^{2-} - HOH_2^+ \rightleftharpoons O_3SOH^- - OH_2 . \quad (7)$$

The concentration of charge carriers for reaction (6) at room temperature can be estimated easily from the equilibrium constant, which is equal to the ratio of the successive dissociation constants of the corresponding acids in solution. This concentration is normally of the order $10^{-10}-10^{-6}$, although, strictly speaking, the corresponding values for a solid can differ significantly. The concentration for reaction (7) is determined by the difference between the proton-accepting capacities of water molecules and the anion. It can vary within very wide limits, reaching values close to 1 when the above capacities are equal. The proton transfer can occur along a chain of successively linked water molecules and oxonium ions, as in the case of highly hydrated molybdo- and tungsto-phosphoric acids. Since for the latter even the identification of the H_3O^+ ions in the structure is problematical, it can be assumed that all the acid protons act as charge carriers. Their absolute concentration, calculated from the unit cell volume, is 1.9×10^{21} cm^{-3} (or 3.2×10^{-3} mol cm^{-3}). If one takes the above considerations into account, the concentration of carriers in the hydrates of weaker acids is usually lower and can reach 10^{11} cm^{-3} or even less. For example, Chandra[20] suggests that the boundary between compounds with low and high concentrations of carriers lies at 10^{18} cm^{-3}. If the proton mobility is high, the former are assigned to the class of the so-called superionic conductors. However, the boundary between these and the usual ionic electrolytes is very arbitrary. Furthermore, proton defects can be formed due to the interaction of the compound with the molecules of water of hydration. A characteristic example is given by salts of heteropolyacids, in which the processes described by the reactions

$$PW_{12}O_{40}^{3-} + 7H_2O \rightleftharpoons PW_{11}O_{39}^{7-} + H_2WO_4 + 4H_3O^+, \quad (8a)$$

or

$$-W-O-W- + 3H_2O \rightleftharpoons 2-W-O^- + 2H_3O^+, \quad (8b)$$

result in a high effective concentration of the carriers even in the case of neutral salts.[21] Evidently, the same processes result in the existence of excess protons in the highly hydrated heteropolyacids, found by Ukshe et al.[22]

In addition, the concentration of defects is affected very strongly by various admixtures that can be present in solid proton-conducting electrolytes owing to various reasons. On the one hand, these materials normally exhibit ion-exchange properties. As a result, a portion of the protons can be replaced by various cations with a much lower mobility, which decreases the concentration of the carriers. This results in a decrease in the electrical conductivity of these compounds, as in the case of acid zirconium phosphate, even though the degree of hydration can increase.[23-27] On the other hand, doping the solid electrolytes with heterovalent cations can 'force' the generation of an excess concentration of the carriers correlated with the concentration of the admixture. A typical example of such doping is presented by oxygen-conducting materials based on the cubic modification of zirconium dioxide, stabilised with yttrium or calcium, as well as by halides. In this case Eqn (4) transforms into

$$\sigma = [N_0 + N \exp(-\Delta G_d/2kT)](a^2 q \nu_0/kT) \exp(-E_m/kT), \quad (9)$$

where N_0 is the number of admixture-generated defects. In contrast to individual compounds, the logarithmic conductivity plot for such a material consists of two straight lines intersecting at the point where the concentrations of the admixture- and thermally-generated charge carriers are equal. The effective activation energy is higher for the high-temperature branch. Unfortunately, the specific procedures used for the preparation of hydrates of inorganic acids and acid salts and their specific structure make it difficult to introduce doping ions into some materials and result in a high surface defectiveness of other materials. This makes it very difficult to investigate correctly the effect of doping with various admixtures on the electrical conductivity of these compounds.

III. Proton transfer

Like many other cations that can act as carriers in solid electrolytes, the proton is singly charged. However, it is distinguished by an exceedingly small radius, mass, small coordination number, and the absence of an electronic shell. It follows from these facts that the presence of large channels in the structure is not obligatory for the existence of proton conductivity. On the other hand, the activation energy for the transfer of charged species in structures with ionic conductivity passes through a minimum for cations with a radius of about 1 Å, as in β-alumina. The transfer of large cations encounters steric hindrance, whereas small cations 'stick' to the channel 'walls' forming fairly strong bonds. Therefore, proton transport is characterised by several specific features:

over a reasonable temperature range, the proton is always bound covalently to one of the electronegative atoms;

the hydrogen bond is always directed;

the proton can be effectively 'delocalised' between two electronegative atoms, and its oscillation along the H-bond, $O-H\cdots O \leftrightharpoons O\cdots H-O$, is an important step in the transfer reaction and can proceed by the tunnelling mechanism.

1. The 'carriage' mechanism

At present, the most common view is that a proton in a solid can move either by the 'relay' mechanism, i.e. by transfer from one electronegative atom to another, or by the so-called 'carriage' mechanism. The latter was suggested on the basis of the fact that the maximum proton conductivity at low temperatures is shown by compounds containing water or ammonia molecules together with protons. In this case, the formation of H_3O^+, NH_4^+, and other ions becomes possible. The authors of this theory suggest that these ions can migrate through the structure as a single whole structure, thus ensuring proton transfer.[28]

This view is fairly common and is supported by a number of facts. For example, the 'carriage' mechanism has been ascribed to uranyl phosphate tetrahydrate on the basis of the similarity of the activation energies for electrical conduction and the migration of oxygen atoms.[29] Although this view is popular, the existence of solid proton-conducting electrolytes with the 'carriage' transfer mechanism seems questionable, primarily because the actual time for a proton jump in uranyl phosphate is no more than 10^{-9} s,[30-32] whereas the lifetime of the oxonium ion is 10^{-12} s.[33] Furthermore, the environment of the H_3O^+ and $H_5O_2^+$ ions in the crystals is not restricted to oxygen atoms forming hydrogen bonds directly with these ions, but also includes at least one additional atom. The law governing this phenomenon can be readily understood from the fact that the energy of the dipole–charge interaction is inversely proportional to the cube of the distance between them, whereas that of the charge–charge interaction is inversely proportional to the distance. Hence, if the O^{2-} ion moves farther from the oxonium ion oriented towards it with its oxygen atom, then, starting from a certain distance, the attraction between them as oppositely charged species becomes the dominant effect. Moreover, in terms of the close-packed spheres structure, the oxonium ions are often located in tetrahedral cavities and more rarely in octahedral cavities with a somewhat distorted environment. This also implies that these ions are surrounded by more than three electronegative atoms.

The existence of such additional bonds in several real hydrates of acid salts has been demonstrated.[34] Assuming that the lengths of the three main H-bonds are 2.6, 2.8, and 2.8 Å (which is most typical for the hydrated oxonium ions) and that the mean statistical angles between them are 114°, one can find that the radius of an inscribed circle for the cross-sections formed by three oxygen atoms, through which the oxonium ion should pass, is 2.63–2.69 Å (less than the sum of two ionic radii of oxygen). Clearly, the diffusion process will involve substantial steric hindrance. When calculating the channel radius in real compounds, one has to take more atoms into account; hence this value can become even less. For example, the radii are 2.52 and 2.12 Å for the tetra- and monohydrates of indium bisulfate respectively.

Finally, there is also a direct method permitting an experimental choice between the 'carriage' and 'relay' proton transfer mechanisms. The replacement of oxonium ions or H_2O-H^+ fragments by NH_4^+ should result, in the case of the 'carriage' mechanism, in an increase in the concentration of carriers owing to the higher stability of the latter cation, and in an increase in their mobility owing to lower strength of the hydrogen bonds. On the other hand, in the case of the 'relay' mechanism, this change complicates the proton transfer owing to the high activation energy for its transfer from the ammonium cation to the anion. It has been shown, using this method, that the transfer in $D_3OZr_2(PO_4)_3$,[35] $Sn(HPO_4)_2.2H_2O$,[16] $H_3OM(SO_4)_2$ [12] (where M = Al, Ga, In, Tl, Ti, V, Mn, or Fe), and some other compounds occurs by proton jumps. A degree of probability of the carriage transfer mechanism can perhaps be retained only for the ammonium salts formed by acids in which the proton-accepting capacity of the anion is exceedingly low. This assumption is based on the fact that the electrical conductivities of ammonium, rubidium, and caesium perchlorates are similar. However, it is noteworthy that the analogous value for oxonium perchlorate is nine orders of magnitude higher.

2. The 'relay' mechanism

Unlike the situation with other ions, the transfer of the proton never occurs in one step, but normally consists of a series of jumps along the hydrogen bond and of rotations of proton-containing groups. It should be noted that a prerequisite condition for the transfer is an excess of potential hydrogen bonds in comparison with the number of protons present in the system. As was shown above, this condition should almost always be fulfilled for hydrates of inorganic salts and acid salts. 'Hydrogen bonds' of this type involving no proton are called the Bjerrum L-defects. In its turn, a Bjerrum D-defect is a hydrogen bond involving two protons. Their formation can be easily imagined if one rotates a water molecule in the structure of ice by 120° relative to any of the hydrogen bonds. The D-defects should have extraordinarily high energies. For this reason, some authors consider that their existence is, in principle, impossible. However, a hydrogen bond with a length of 1.91 Å has been found in $H_{3.33}Fe(CN)_6.2.7H_2O$.[36] The exceedingly short length of this bond is thought to be due to the fact that it incorporates two protons. Note that this ambiguous finding has not been supported by any other evidence.

Consider a hypothetical system containing oxonium ions and XO_4^{n-}, and assume that it already contains defects consisting of water molecules formed by the dissociation of oxonium. The transfer process in such a system can be represented by the scheme

$$\begin{aligned} &H_2O-H^+ \cdots O_a \cdots OH_2 \overset{a}{\rightleftharpoons} \\ &\rightleftharpoons H_2O \cdots H^+ - O_a \cdots OH_2 \overset{b}{\rightleftharpoons} \\ &\rightleftharpoons H_2O \cdots O_a - H^+ \cdots OH_2 \overset{c}{\rightleftharpoons} \\ &\rightleftharpoons H_2O \cdots O_a \cdots H^+ - OH_2 . \end{aligned} \qquad (10)$$

The process with the maximum activation energy should be the rate-determining step. The activation energy for proton transfer along the hydrogen bond (steps *a* and *c*) increases abruptly with increasing bond length,[33] whereas the activation energy for the rotation of the $X-O\diagup H$ moiety relative to the X–O bond (step *b*) actually decreases.[34] It follows that there exists an optimum length for hydrogen bonds, which should maximise the proton mobility. Using the data in Refs 33 and 34, one can conclude that, provided that the proton-accepting capacities of the oxygen atoms participating in the transfer are close, the systems with ~2.8 Å hydrogen bonds should have the lowest activation energies (of the order of 15–20 kJ mol^{-1}).

An example of proton transfer by this mechanism is provided by acid indium and thallium sulfate monohydrates $H_3OM(SO_4)_2$ (Fig. 1) described by us previously.[12] The *a*, *b*, *c*, and *d* indices refer to the states which the system adopts successively. The arrows indicate the directions of the movement of hydrogen ions resulting in these transformations (proton jumps and rotation of proton-containing groups). The environment of each oxonium ion incorporates six equivalent oxygen atoms of the anion, but only three of these can form hydrogen bonds with the oxonium ion simultaneously.[37] Thus the system initially contains three Bjerrum L-defects for three actually existing hydrogen bonds. The proton defects are formed by reaction (7). Judging from the equilibrium constant of this reaction, which can be easily estimated from NMR spectra at 77 K, ΔG for this process is close to 1.5 kJ mol^{-1}. The activation energy for the oxonium ion rotation in these compounds is only 18 kJ mol^{-1}; an excess of hydrogen bond acceptors plays an important role in decreasing this activation energy.[34] The rotation of the S–O–H moiety proceeds even more readily, since it requires the breaking of only one hydrogen bond and rotation around a S–O single bond. On the other hand, the proton transfer along hydrogen bonds with a length of 2.87 Å, formed by oxygen atoms possessing similar proton-accepting capacities, should be characterised[33] by an activation energy of ~ 33 kJ mol^{-1}, which determines the overall proton mobility in this case. Thus, the activation energy $E \sim 33 + 0.7 = 33.7$ kJ mol^{-1} can be obtained from Eqns (4) and (5) (cf. the experimental values of 30–34 kJ mol^{-1}).

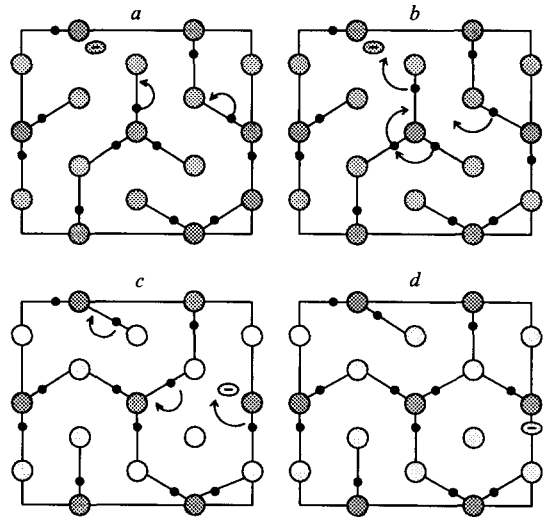


Figure 1. Schematic illustration of proton transfer in $H_3OM(SO_4)_2$: (*a*)–(*d*), consecutive conformations of the system; ◍ – oxonium oxygen; ○ – anion oxygen.

The proton transfer in a number of other hydrates of acids and acid salts, including oxonium perchlorate, occurs similarly.[38,39] The electrical conductivity of the latter compound increases abruptly in the first-order phase transition at 250 K,[33,38] after which the oxonium ions pass to the isotropic rotation state[40] and are surrounded by seven oxygen atoms at a distance of 2.86–3.40 Å.[41] It should be noted that the occurrence of phase

transitions resulting in an increase in proton conductivity is quite typical for these compounds.[19,39]

Usually, as in the above examples, the mobility of the proton is limited by the step involving its transfer along the hydrogen bond. However, the rotation of the proton-containing moieties is strictly necessary for the existence of proton conductivity. A typical example of a compound having an exceedingly low proton conductivity due to the hindered rotation of the proton-containing groups is provided by sulfuric acid octahydrate. The infinite planar networks $(H_9O_4)_n^{n+}$ in this compound are built up on the basis of the $H_5O_2^+$ ions with R(O—O) = 2.447 Å and with equivalent oxygen atoms. Each OH_2 moiety in these ions is a donor in hydrogen bonds with the anion and with a water molecule characterised by equal lengths of 2.654 Å. In turn, the water molecules form H-bonds with the anion (2.735 Å) and with similar molecules (2.762 and 2.765 Å). In the latter two bonds, each participant can act with equal probability as a proton donor or acceptor.[42] The proximity of a further two H_2O molecules not bonded directly is noteworthy. Thus the structure of $H_2SO_4.8H_2O$ seems to be ideal for proton conductors. However, the formation of numerous strong hydrogen bonds hinders the rotation of the proton-containing moieties. This inhibits in its turn the transfer of protons, which, according to our data,[43] do not pass to the mobile state below the melting point.

A number of solid proton-conducting electrolytes, whose conductivity is limited by different proton transfer steps, have been reported in the literature. Unfortunately, this assignment was not sufficiently well founded in most of the studies and was based merely on the activation energies for proton transfer (which is not always unreasonable). Some typical frequencies and activation energies for the elementary proton transfer steps reported in the literature are given in Table 1.

Table 1. Some typical frequencies and activation energies for the elementary proton transfer steps.

Process	Frequency/Hz	E_a/kJ mol^{-1}	Ref.
Reorientation of polyatomic ions	$10^{11}-10^{12}$	< 10	44
Reorientation of inter-layer water molecules or 'zeolite'-type water	$10^{7}-10^{12}$	20–30	30, 32, 44
Reorientation of coordinated water	10^{9}	20–30	44
Proton jumps	$10^{8}-10^{10}$	20	30, 32, 44
Oxygen diffusion	10^{9}	80	30

In our opinion, these data can be used for a preliminary comparison of the energetic and frequency parameters of conductivity-determining processes. For example, it follows from these data that the transfer process can normally be limited by the rotation of polyatomic ions such as HPO_4^{2-}, $HSeO_4^-$, etc. On the other hand, the parameters of these tabulated processes may be outside these limits for some compounds.[16]

In real structures, the proton should be transferred by ~3 Å in one step. By substituting this value, together with the previously estimated minimum activation energy of 15 kJ mol^{-1}, in Eqn (3), it is possible to obtain a proton mobility of 8×10^{-3} cm^{2}V^{-1} s^{-1}. On combining this with the maximum concentration of carriers, we obtain from the Frenkel equation (5) $A_{max} = 3.3$ S cm^{-1} and $\sigma = 2.5 \times 10^{-5}$ S cm^{-1} for the 'relay' mechanism.

3. The Grotthus mechanism

The structures of many solid proton-conducting electrolytes are characterised by a large number of virtually equivalent oxygen atoms, which nevertheless form different proton-containing groups (H_3O^+ and H_2O, OH^- and H_2O). The conditions for proton transfer are most favourable in such systems—ice might be an ideal proton conductor. However, the main obstacles to this are the low concentration of charge carriers (10^{-7}) and the low rotational mobility of water molecules in ice. The situation changes completely if oxonium ions or hydroxide ions are introduced into an ice-like structure. This results in the concentration of carriers and the proton mobility increasing abruptly; the rotational mobility of the proton-containing moieties is stimulated very strongly.[45,46] However, the combination of the above factors does not explain the anomalously high proton mobility, which is at least an order of magnitude higher than that of other ions in aqueous solutions and in a number of other compounds. It is also difficult to explain the difference between the maximum electrical conductivity for the 'relay' mechanism quoted in the previous section (2.5×10^{-5} S cm^{-1}) and the electrical conductivity of highly hydrated heteropolyacids (0.17 S cm^{-1}). One explanation for these facts is the equivalence of protons in H_3O^+ and H_2O. According to Haggins[47] and Zundel,[48] the transfer in these systems can be represented as structural migration of $H_5O_2^+$ ions (Fig. 2). This model is reminiscent of the familiar fairy tale about a race between a hedgehog and a hare, where a twin hedgehog awaited the exhausted hare at the finish. Zundel remarks that the proton jump occurs against the background of the vibration of the system of oxygen atoms, which leads to a shift of the shortest bond (the change from Fig. 2*b* to Fig. 2*c*). Undoubtedly, this condition favours proton migration,[48,49] although it is not essential.

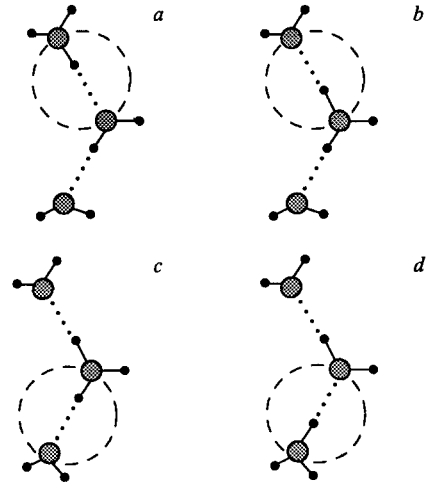


Figure 2. Schematic illustration of proton transfer by the Grotthus mechanism (the circles indicate the short hydrogen bond);[48] (*a*)–(*d*), consecutive conformations of the system.

Strictly speaking, the above scheme describes only the polarisation of the system, whereas proton conductivity requires, in addition, reorientation of the newly-formed proton-containing groups. It is easily seen that the rotation of any of these groups would result in a Bjerrum D-defect. Therefore, the view exists that such rotations occur in a concerted manner, i.e. the rotation of one water molecule initiates the rotation of a second molecule, then a third, etc., with a small phase lag. As a result, the D-defect migrates cooperatively in a wave-like manner (this is also called the soliton mechanism). The rapid overall proton transfer consisting of jumps between equivalent proton-containing groups alternating with their rotations was called the Grotthus mechanism. Combination of the above factors results in a

cooperative proton jump over an enormous distance, which in this case should be called more appropriately 'the length of the free path'. For example, this length for heteropolyacids estimated by Eqn (4) is 100 Å.

This mechanism is quite common not only for hydrates of acid salts[50,51] but also for bases.[14,52] The proton transfer in $CsOH.H_2O$ takes place in this way. This process is quite instructive and has been studied thoroughly, and so it seems reasonable to discuss it although formally this is beyond the scope of this review. Below 229 K, the compound crystallises in the monoclinic system with the structurally nonequivalent OH^- groups and H_2O forming a planar network (Fig. 3). This conclusion is also confirmed by ^2D NMR data.[52] However, above this temperature a phase transition occurs, which is accompanied by the transformation of the monoclinic crystal lattice into the hexagonal form with structurally equivalent oxygen atoms. The symmetrical hydrogen bond with $R(O-O) = 2.64$ Å is characterised by two possible positions of the proton 1 Å apart. The transfer between these positions is characterised by a frequency of 8×10^{10} Hz. When combined with the rotation of the proton-containing groups at a frequency of 2.8×10^9 Hz, this leads to the occurrence of two-dimensional proton diffusion in $CsOH.H_2O$, via the Grotthus mechanism.[52] Similar disordering is observed in $RbOH.2H_2O$, in which the hydroxyl groups participate in the formation of four hydrogen bonds with water molecules.[53]

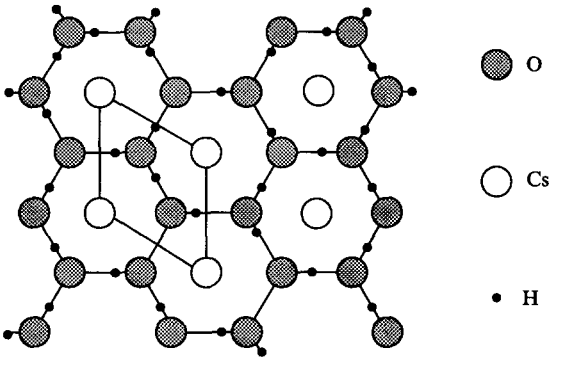


Figure 3. The structure of $CsOH.H_2O$.

A proton hydrate sublattice having the composition $H(H_2O)_n^+$ with a three-dimensional framework of hydrogen bonds is also formed in highly hydrated heteropolyacids. The existence of several variants of proton transfer ensures the extremely high electrical conductivity of these compounds, which decreases as the degree of hydration decreases.[9-11]

IV. Proton transfer on the surface of particles

Since in most cases the surface layer of particles of a compound constitutes a small proportion of the bulk, its contribution to the electrical conductivity is low. However, the situation changes completely when compounds such as hydrated oxides of polyvalent elements are considered. X-Ray microanalysis often indicates the presence of lines resembling those of the corresponding lines of oxides but differing mainly in having larger widths. This allows the assumption that the compounds have the globular structures[54,55] shown in Fig. 4 for tin hydroxide.

The composition inside the globules is close to that of the corresponding metal oxide. However, the surface of the globules incorporates fairly numerous OH groups, water molecules, and, possibly, anions trapped from the solution. The charged species located on the surface are highly reactive and can be readily exchanged when in contact with the solution.[54,55] A fraction of the water molecules are located in the intergranular space and,

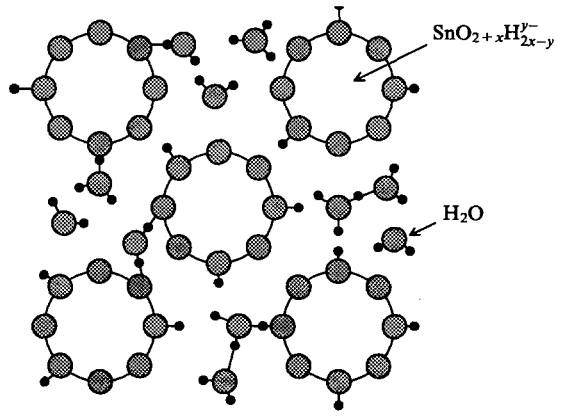


Figure 4. The structure of $SnO_2.nH_2O$.

being retained only by hydrogen bonds, are highly mobile.[55,56] The overall composition of tin hydroxide may be represented by the formula $SnO_{2-x}(OH)_{2x}.nH_2O$. In this composition there are $2+x$ oxygen atoms per tin atom. For 25 Å particles, $x = 0.6$, while for 100 Å particles $x = 0.15$.[54] There is a special term for these compounds in the English language literature, namely, 'particle hydrates'; in the Russian-language literature they are sometimes called 'globular hydrates', although this name is not generally accepted. The acidic nature of the hydroxyl groups in $SnO_2.nH_2O$ brings about their partial dissociation via the mechanism:

$$SnO_{2+x}H_{2x} + yH_2O \rightleftharpoons SnO_{2+x}H^{y-}_{2x-y} + yH_3O^+. \quad (11)$$

Thus the intergranular space contains a highly mobile solution with the composition $yH^+.nH_2O$ ensuring the high electrical conductivity of this compound, which reaches 3×10^{-4} S cm^{-1} at room temperature. Obviously the transfer itself occurs via the Grotthus mechanism.

The highly hydrated heteropolyacids are a prominent example of compounds with this type of proton transfer mechanism. In these, the heteropolyanions, in which all three OH groups are completely dissociated, act as globules whose radii are about 12 Å. Evidently this is why these compounds have the highest electrical conductivities.[9] Insoluble alkali metal tungsto-phosphates possessing cation-exchanging properties and a proton conductivity up to 10^{-2} S cm^{-1} form larger particles.[57] Ice doped with strong acids can be regarded as a system of this kind with a minimal core of particles (these are anions).

Hydrated acid zirconium phosphate is one of the best known proton conductors. Depending on the degree of crystallinity and atmospheric humidity, its electrical conductivity varies over five orders of magnitude, which indicates that the intercrystallite component plays the major role. The mobility of surface protons is four orders of magnitude higher than that of the bulk-phase protons.[58,59] The replacement of the OH groups by the $-C_xH_ySO_3H$ or $-C_xH_yCOOH$ fragments, or the sorption of bulky amines on some of them, significantly increases the interplanar distance in lamellar phosphates such as $Zr(HPO_4)_2.nH_2O$. In the opinion of some authors,[60-64] this might lead to the properties of the surface being acquired by almost the whole material. Unfortunately, this idea has not found practical confirmation. The maximum electrical conductivity of such compounds, which reaches 10^{-2} S cm^{-1} at room temperature and 90% humidity, is apparently also due to the surface component.[60-64] Furthermore, the authors postulated that proton transfer in compounds containing acid groups at the end of a flexible hydrocarbon moiety ($-C_xH_{2x}COOH$) can occur when the latter come closest together during their vibrations.

V. Some features of solid proton-containing electrolytes

Undoubtedly the presence and magnitude of proton conductivity in a compound depend primarily on its structural features. For example, the existence of a continuous network of hydrogen bonds, or the possibility of one being formed due to the rotation of hydrogen-containing groups, is a prerequisite. Furthermore, as shown above and by Potier,[39] the hydrogen bonds should have an optimum length, etc.

Despite these requirements, one can outline fairly confidently the range of hydrates and acid salts among which materials with a high proton conductivity should be sought at comparatively low temperatures. It is convenient to use the classification proposed by us,[65] based on the proton-accepting capacity of the acid residue and its spatial structure in the compound. For example, both the formation of carriers and their transfer are hindered in the salts of weak acids (class I, $pK_a > 3$).

The class II compounds ($-3 \leqslant pK_a \leqslant 3$) are much more suitable for this purpose, since the proton transfer from the anion to water molecules and vice versa occurs comparatively easily. The behaviour of the class IIa compounds (where the proton is localised on the oxygen atom of the anion in the ground state) is often restricted by the low degree of hydration. Therefore, these compounds usually exhibit a high electrical conductivity only in a finely dispersed state [$Zr(HPO_4)_2 . nH_2O$]. In the class IIc compounds with isolated anions, the latter form fairly strong hydrogen bonds with the hydrated proton, which significantly restricts its mobility. The class IIb compounds with a bulky anion forming skeletal structures are good proton electrolytes. The majority of these compounds have layered structures ($MH(SO_4)_2 . nH_2O$, $MH(PO_4)_2 . nH_2O$, $UO_2HPO_4.4H_2O$).

The hydrates of strong acids ($pK_a < -3$) tend to form hydrogen bonds between the H_3O^+ or $H_5O_2^+$ ions and water molecules and hence to exhibit a high degree of hydration.[65] Consequently, despite some hindrance to proton transfer from the proton-hydrate sublattice to the anion (which, incidentally occurs comparatively easily, for example, in oxonium perchlorate), proton transfer by the Grotthus mechanism is most probable in this case ($H_3PW_{12}O_{40} . nH_2O$). This is why compounds possessing the maximum proton conductivity have been found among these compounds. The search for proton-conducting electrolytes among highly hydrated class III compounds is especially advisable. However, their tendency to change their hydrate composition (dehydration in air or absorption of moisture) can be a limiting factor in their employment.[65]

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