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Abstract

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ON THE QUESTION OF THE NATURE OF SUBSTANCES WITH INTERMOLECULAR HYDROGEN BONDING

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According to existing views, the relatively high values of the dielectric permittivity of water, alcohols, and a number of other substances with intermolecular hydrogen bonds are usually explained by dipole polarization and by the influence of "association." But these views contradict, in particular, the following experimental facts.

1. The dielectric permittivity of water in static fields and at constant volume, ε_{SV}, is a linear function of $1/T$, where T is the temperature in °K (for water, it is possible to reduce the values of ε_S to the condition $V = \text{const}$, since the dependence of ε_S on V is known over a wide temperature interval (^{1,2})).
2. The static dielectric permittivity ε_S of a number of low-molecular alcohols in the liquid and solid phases, and also of ice, is a linear function of $1/T$.
3. The main region of dielectric relaxation of water and alcohols, within the limits of experimental error, follows the Debye equations, i.e., it can be characterized by one single value of the relaxation time τ.
4. The main region of dispersion of the dielectric permittivity of solutions of methyl and propyl alcohols in each other is likewise described by only one value of τ, although the relaxation times for the pure liquids differ by a factor of 50 or more (^{3}).

In addition, the existing views do not explain, for example, the experimentally observed dependence of τ of alcohols on temperature (^{3}), the sharp increase in the high-frequency limit $\varepsilon_{\infty 1}$ of the main region of dielectric relaxation when intermolecular hydrogen bonding arises, and a number of other facts. Let us also note that a fully satisfactory theory of the hydrogen bond has not yet been developed (see, for example, (^{4})).

The facts cited above show that the dielectric relaxation of water, alcohols, and, apparently, many other substances with intermolecular hydrogen bonding is, in its main part, a collective process, not directly dependent on the reorientation of dipoles, and proceeding in such a way that the individual elementary components of this collective process are statistically equivalent. The data on the dielectric relaxation of water, a number of alcohols, etc., directly indicate this, and the linear course of the dependence of the dielectric permittivity on $1/T$ does so on the basis of the following considerations. If $\varepsilon_{SV} = \varepsilon_0 + c/T$, where ε_0 and c are constants, the density of the internal energy of a dielectric U in a field E is equal to:

$$U = U_0(T) + \Delta U_E = U_0(T) + \frac{\varepsilon_0 E^2}{8\pi}. \tag{1}$$

Here T and E^2 are independent variables, the volume $V = \text{const}$, and ΔU_E is the change in U upon application of a static electric field E. In the general case, for $V = \text{const}$, and if in the temperature interval under consideration the structure of the dielectric molecules does not change, i.e., the mean deformation polarizability of the molecules a does not depend on T, ΔU_E can be represented

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as a function of the statistical mean cosine of the angle θ between the direction of the electric moment of an arbitrarily chosen molecule $\vec{\mu}$ and the direction of the field E. With a linear dependence of ε_{SV} on $1/T$ or of ε_S on $1/T$ (see (1)), it follows from equation (1) that

$$\frac{\partial \Delta U_E}{\partial T} = \left(\frac{\partial \Delta U_E}{\partial \overline{\cos\theta}}\right)_{a,T,V} \frac{d\,\overline{\cos\theta}}{dT} = 0.$$

If the molecules have a permanent electric moment and the dielectric polarization is associated with a redistribution of dipole orientations, then $\overline{\cos\theta} = f(T)$, and consequently $d\Delta U_E/d\overline{\cos\theta} = 0$, i.e., the internal energy of the dielectric does not depend on the manner of mutual orientation of its molecules. Any mutual orientations of the molecules of such a dielectric are energetically equivalent and therefore equally probable, just as in the dilute gas. But such a conclusion would obviously be incorrect for ice and for the glassy phase of alcohols, where the linear dependence of ε_S on $1/T$ is retained, while order in the distribution of molecular orientations exists. Therefore it remains to assume that $d\,\overline{\cos\theta}/dT = 0$, and consequently that the process by which dielectric polarization is established in water, alcohols, and a number of other substances is not connected with reorientation of dipoles, but has another nature.

As is known, owing to the interaction between particles, the energy levels of the particles making up molecules (electrons, protons, etc.) in condensed systems are transformed into energy bands. It may be assumed that for protons entering into the composition of molecules, as for electrons, in addition to the valence band there is also a conduction band, while the band of forbidden states between the valence band and the conduction band (see Fig. 1) is usually large, so that protons do not enter the conduction band. But if the molecules contain atoms O, N, F, Cl, S, then in a number of cases (with a favorable structure and composition of the molecules) these atoms cause the appearance of an intermediate band, analogous to an impurity band in electronic semiconductors (see

Fig. 1

Figure 1: Fig. 1

Fig. 1). Then the transition of protons from the valence band to the conduction band becomes possible and takes place in two stages. First the proton can pass into the above-mentioned intermediate band, and then, under the influence of thermal motion, into the conduction band. The motion of a proton in this band in the field of negatively charged residues of molecules or atoms (and neutral particles) occurs relatively freely, similarly to the motion of electrons in the conduction band, with the difference that a proton gas is not pronounced at ordinary temperatures, since protons are almost 2000 times heavier than electrons. The transition of a proton from the valence band of the proton donor into the intermediate band, where the proton is located at the proton acceptor (an O, N, F atom, etc.), occurs by means of a tunneling effect (5) with the corresponding orientation of the molecules, when the donor and acceptor atoms are in direct contact with each other. As a result of thermal motion this contact may be broken at a moment when the proton is at the acceptor atom, so that ions H_3O^+ and OH^- arise in water, or ROH_2^+ and RO^- in alcohol (R is a hydrocarbon radical). The proton remains for some time in the intermediate band and, under the influence of thermal motion, may pass further into the conduction band. Jumps of the proton from the donor atom to the acceptor atoms, accompanied by rupture of hydrogen bonds, lead to migration of ions and, in the absence of protons in the conduction band, could constitute the basis of the mechanism of dielectric polarization. However, as calculations based on experimental data on τ show, the free enthalpy

Fig. 1

The activation $\Delta\Phi_{\varepsilon}^{++}$ of this process for water considerably exceeds the free enthalpy of activation for the transition of a proton from the intermediate zone into the conduction zone. The latter for water is only about 2 kcal/mol. For a number of aliphatic alcohols, $\Delta\Phi_{\varepsilon}^{++}$ for the process of proton transition from the intermediate zone into the conduction zone lies in the interval 3–5 kcal/mol.

With the aid of the concepts set forth here, the previously mentioned features of dielectric polarization and relaxation for water, alcohols, and a number of other substances with intermolecular hydrogen bonding receive a simple explanation. As has already been said, in these substances some of the protons are in the conduction zone, and there exists a temperature-dependent dynamic equilibrium between the proton gas and the protons located in the intermediate zone. When a weak external electric field is applied, a small redistribution of protons occurs in the direction of the field. As a result, electric polarization arises. Since the mean free path of protons in the conduction zone is small, this process can formally be regarded as a redistribution of dipole orientations, as is usually assumed. But the energy expended in such a redistribution is practically equal to zero; therefore, despite the presence of hydrogen bonds between molecules, the dielectric constant in static fields proves to be a linear function of $1/T$.

The time of proton relaxation, according to what was said above, does not depend on the mutual orientations of the molecules. It is determined by the difference between the energy levels of the protons in the conduction zone and in the intermediate zone. This difference, far from the critical region, is approximately the same for all protons in the liquid, and therefore proton relaxation should obey the Debye equations. In solutions it is necessary to distinguish cases in which the acceptor atoms are identical and the molecules of the components are similar in structure, as occurs in mixtures of methyl and propyl alcohols, from cases in which the acceptor atoms are different, or in which the types of molecular structures containing acceptor atoms are different. In the first case the corresponding energy levels of the acceptor atoms merge into one common intermediate zone and, consequently, proton relaxation should, as before, be characterized by a single value of τ.

In the second case, between the valence zone and the conduction zone there may be several intermediate energy levels or zones and, correspondingly, a series of values of τ. When water freezes, all or almost all molecules are connected by hydrogen bonds. For the formation of OH_3^+, it is necessary to break at least one of the hydrogen bonds. The free enthalpy of activation of proton relaxation (as well as the enthalpy and entropy) increases discontinuously (thus, $\Delta\Phi_\varepsilon^{++}$ increases from 2 to 10 kcal/mol). Therefore the time of proton relaxation sharply decreases. However, the number of structural defects is reduced, and the mean free path of the proton increases. As the temperature is lowered, alcohols gradually pass into a glass-like state. In this process the number of broken hydrogen bonds gradually decreases, while the minimum energy required for rupture of the hydrogen bonds that form gradually increases to values on the order of 11 kcal/mol and higher. Correspondingly, the entropy of activation of proton relaxation, $\Delta S_\varepsilon^{++}$, also increases. This explains the specific course of the dependence of τ for alcohols on temperature, noted in ([3]). Since the dependence of the viscosity of alcohols on temperature is explained mainly by the same causes, the reason for the observed parallelism in the course of the dependence of the free enthalpy and the enthalpy of activation of viscous flow becomes evident.

Owing to the anomalous mobility of the proton in substances with intermolecular hydrogen bonding, the deformational polarizability of these substances must be anomalously large, as is indeed observed experimentally.

In addition, there is a dispersion region associated with the rotational vibrations of polar molecules. In water and alcohols at ordinary temperatures this region merges with the principal dispersion region. At low temperatures, the indicated second dispersion region is clearly observed in alcohols.

Thus, water, alcohols, and a number of other substances with intermolecular hydrogen bonding apparently constitute **proton semiconductors**. In these substances there is a proton analogue of the metallic bonding of electrons—**pro-**

ton metallic bonding, i.e., a collective interaction between the "proton gas" and the system of negative ions. Further analysis will show how far this parallelism extends. A number of properties of water, alcohols, and other substances are caused not by "association," but by the presence of proton metallic bonding, i.e., by protons in the conduction band.

The existing ideas about the nature of substances with intermolecular hydrogen bonding apparently require some revision.

Here we have given mainly a qualitative description of the results of the investigation carried out. A more detailed analysis will be presented in another paper.

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