

of any isobestic points rule out the possibility of a chemical equilibrium between two forms which shift with solvent composition. *cis*[Coen₂(SCN)₂](SCN) behaves similarly in water-methanol mixtures. Evidence for a true solvent effect is also found in the fact that light absorption in the various solvents does not show any time effect.

That a crystal field band of a saturated complex ion only to a slight degree is dependent on the solvent can be predicted from the theoretical expression for λ_{\max}

$$1/\lambda_{\max} = \text{const. } \mu/r^6$$

(see *e. g.* Ballhausen⁵) where μ is the point dipole moment and r the distance of the ligand from the central atom. Denoting the quantities in the first and second spheres by μ' , μ'' , and r' , r'' , respectively, the relative contribution of the second sphere to the wavelength is given by

$$\frac{\Delta\lambda_{\max}}{\lambda_{\max}} = \frac{\mu''}{\mu'} \cdot \left(\frac{r'}{r''}\right)^6$$

Now introducing $\mu' \gtrsim \mu''$ and $r'' = 2r'$, we get

$$\frac{\Delta\lambda_{\max}}{\lambda_{\max}} \lesssim \frac{1}{64}$$

According to this estimation the displacement of a crystal field band of a saturated complex should always be smaller than 2 % in agreement with what is found experimentally. The greater variability of the electron transfer band found in some cases is quite natural considering that the orbitals of the solvent molecules are closer to the orbitals of the ligands than to the electron systems of the central atom.

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On the Proton Conductivity in Water

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It is commonly agreed that the large mobilities of the H_3O^+ and OH^- ions in water must be explained by a proton transfer over hydrogen bridges. By assuming this proton transfer mechanism, Gierer and Wirtz^{1,2} derived the following equation to explain the mobility as a function of temperature:

$$u = \frac{C}{T} f(T) \exp\left(-\frac{q}{RT}\right) \quad (1)$$

Here u is the mobility of the H_3O^+ or OH^- ion in excess of the value expected for ions of that size. C is a factor which incorporates some constants of the system, T is the absolute temperature and q is the activation energy of the rate determining process. $f(T)$ is a function of temperature (and also pressure), which describes the influence of the liquid structure upon the mobility.

If this equation is to be useful, the structural influence $f(T)$ should be known. Gierer and Wirtz used Eucken's structure model of water³ for their treatment. Eucken assumed that the water structure consisted of a few definite types of molecular species. There is very little evidence to support this assumption, however. An alternative derivation of $f(T)$ from the model of water proposed by Grjotheim and Krogh-Moe⁴ shall therefore be suggested.

If the proton transfer across a hydrogen bridge is the rate determining process, one might expect $f(T)$ to be proportional to the total number of hydrogen bonds present in water. Contrary to this assumption the extra mobility increases with temperature in a certain temperature interval, though the number of hydrogen bonds decreases monotonously. By assuming that $f(T)$ is proportional to the number of water molecules with only one hydrogen bond established, consistent results may be derived. This is reasonable if the breaking of the hydrogen bond is the rate determining process. When a proton transfer over a hydrogen bridge has occurred, a reorientation of the water molecule is necessary if the molecule is to participate in further proton transfers. A water molecule

with only one hydrogen bond reorientates readily when the bond breaks.

The description of excess mobility presented here implies a number of assumptions, of which the following are the most important:

1) The model of water applied³ is assumed adequate for the purpose, though it is only a rough idealization of the real conditions. Hence x , the ratio of the number of established hydrogen bonds to the number of possible bonds, is known.

2) It is assumed that the H_3O^+ ions and the OH^- ions in dilute solutions have the same structural environment as the water molecules.

3) A random distribution of the hydrogen bonds between the molecules will be assumed. The ratio w of one-bonded molecules to the total number of molecules is then given by the following equation:

$$w = 4x(1-x)^3 \quad (2)$$

Any coupling between the breaking of the bonds is disregarded in deducing this equation.

4) The assumption that the factor $f(T)$ in equation (1) is proportional to the number of molecules with one hydrogen bond is only valid within a limited temperature interval. For instance differences in mean chain lengths for transfers taking place over chains of hydrogen bridges are not taken into account. Coupling between the breaking of bonds is again disregarded.

5) Eqn. (1) is not quite exact, but assumed to be adequate.

In view of these assumptions and approximations the results obtained should be regarded as of only a semiquantitative nature. However, by plotting $\log u + \log T - \log x(1-x)^3$ against $1/T$, using the values of u given for the H_3O^+ ion by Gierer and Wirtz¹ or by Bjerrum⁵ and the values of x given by Grjotheim and Krogh-Moe⁴, a straight line is obtained for temperatures up to 200° C. The slope of the line corresponds to an activation energy of 1.7 kcal/mole. This value compares favourably with the values 1.3–2.6 kcal/mole obtained by Grjotheim and Krogh-Moe for the breaking of a bond in water. It should be noted that this value for the hydrogen bond includes only the part of the total interaction responsible for the tetrahedral configuration of the water molecules.

The activation energy for the OH^- ion conductivity is shown to be 0.6 kcal/mole higher than that for the H_3O^+ ion¹. This

means that an OH^- ion cannot have quite the same surroundings on average as the H_3O^+ ion. The energy of the hydrogen bond appears to be slightly different in these two cases. Rather than a single energy, however, we have in these systems an energy distribution. A single hydrogen bond energy seems to be a fairly good approximation, however.

The previous considerations enable us to understand why the extra mobility increases with pressure in a certain temperature range. In this temperature range the breaking of a hydrogen bond results in a decrease in volume⁴. Therefore increased pressure means a smaller number of bonds in the liquid. This leads to a larger number of water molecules with only one bond, as may be seen by introducing into eqn. (2) the appropriate values of x . Consequently an increase in extra mobility with pressure is expected. If the factor $f(T)$ of structural influence in eqn. (1) were proportional to the number of established hydrogen bonds, the pressure dependence of extra mobility could not be explained.

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The Vitamin Content of Pollen after Storing

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In a previous paper¹ the results of an investigation concerning the content of some B-vitamins in pollen from different plants were given. The samples examined were obtained from *Zea mays*, *Alnus glutinosa*, *A. incana* and *Pinus montana*. The following vitamins were determined: riboflavin, nicotinic acid, pantothenic acid, pyridoxine, biotin and inositol. The determinations were carried out during October