

study and KRAMERS-KRONIG analysis of the infrared absorption spectrum. He arrived at the remarkable conclusion that 3/4 of the difference between the optical and microwave refractive indices, respectively 1.31 and 1.18, arises from vibrations of frequency less than 10^{13} (325 cm^{-1}). This means that a change in the length of a hydrogen bond (0 — 0 distance) produces a large electric moment, with proportionality constant of about 0.3 electronic charges, as WHALLEY observed. Some of us may have suspected such an effect, but hardly anybody realized how big it was. The molecular models which underly present theories of dielectric constants do not incorporate this important property of the hydrogen bonds. In a realistic theory we must recognize it: on the whole it seems easier now to understand the large dielectric constant of water.

A. R. Ubbelohde. — To what extent does the abnormal mobility of protons and OH^- ions, found in water under ordinary conditions, persist to higher temperatures and pressures? As is well known, this mobility gives important information about the cluster structure of water, and about other cooperative effects between H_2O molecules in assemblies, of high density, whether liquid or gaseous. The frequencies at which these mobilities begin to show relaxation dependence may likewise give significant information. Has any frequency dependence been observed at higher temperatures and pressures?

E. U. Franck. — We have tried to measure the abnormal mobility of protons in aqueous solutions up to about 300 °C and up to about 5 kbars. Beginning with normal conditions, the increase of temperature as well as the increase of pressure cause an increase of the abnormal mobility, which may perhaps be ascribed to a facilitation of structural diffusion of clustered areas because at elevated temperatures and pressures more simple water molecules are available.

(This would be in accordance with the assumption that high pressure breaks up voluminous clusters).

The increase of extra mobility of protons however appears to level off at temperatures beyond 200 or 300 °C and also at pressures beyond several kbars. Thus it is likely that the proton mobility in aqueous solutions cannot be increased by more than perhaps a factor of about three by an elevation of temperature and pressure only.

The abnormal proton mobility has so far at high temperatures and pressures only been investigated up to about 100 kilocycles. As could be expected no relaxation has been observed in this range. An extension of such measurements to higher frequencies at elevated temperatures and pressures would be very difficult but very interesting and rewarding.

T. Ackerman. — I wonder whether Dr ROTH has made an attempt to observe an additional continuous absorption due to « excess » or « defect » protons in the IR spectra of solutions of acids and bases in the high pressures region at elevated temperatures.

What is the meaning of the term « freely rotating water molecules » used in the discussion of the infrared spectra shown in slide N° 2.

E. U. Franck. — So far Dr ROTH in our Laboratory has only investigated the infrared absorption of pure water and of several alcohols at wave numbers not smaller than about 2 500. Mr BUBACK has used the same cell to investigate the absorption of pure HCl up to 150 °C and 1 000 bars in the range of absorption of the HCl vibrations. Extension of measurements to lower wave numbers than about $2\,200\text{ cm}^{-1}$ was not possible because of the absorption of the sapphire windows with about 10 mm thickness. Also the corrosion of acidic solutions at high temperatures would cause considerable difficulties in the all-metal cell. It may, however, be possible to do such measurements in the future using silicon windows.

In this presentation the term « freely rotating » molecules has only been used to describe molecules which because of their rotation give rise to an observable rotational structure of the vibrational absorption band. It is not excluded that there may be rotating molecules which because of certain

interactions with neighbours cannot be detected specifically by such spectra.

H. Friedman. — With regard to the very interesting data on conductivity of aqueous KCl on isochores of nearly constant viscosity, it would be of interest to compare with the theory of the effect of dielectric relaxation on ionic mobility. This is the theory to which a number of people have contributed, but most recently R. W. ZWANZIG. I wonder whether you have considered this problem?

E. U. Franck. — We should like very much to follow your suggestions to try to study experimentally the effect of dielectric relaxation on ionic mobility in a region of conditions where the density of the fluid is high and where the viscosity of the fluid varies only slightly with density and temperature. The results of such measurements would certainly be very rewarding.

As is demonstrated by the diagram shown, however, such relaxation experiments should be made at temperatures of 400 °C and higher and at pressures of several kilobars (unfortunately). At the present time the experimental difficulties seem to be very high or even prohibitive. Corrosion is one of the major obstacles. We should, however, think about it again.

J. C. Justice. — Professor FRANCK has shown experimental results for association constants for KCl in argon — water mixtures indicating the rare gas component in the solvent was « inert » in opposition to dioxane — water mixtures studied by FROSS *and al.* where dioxane, being a structure breaker, led to further complications.

In fact, though simple as may look argon atoms, it is known that in water they lead to a reinforcement of the water structure. In that respect they cannot be considered as inert; their influence though opposite to that of dioxane in water leads also to further complications. A really « inert » second component that would not affect at all water structure seems even inaccessible since the mere fact to introduce (in imagination) « vacuum cavities » in water would tend to reinforce water structure in the immediate outer vicinity of the surface of such cavities. To what extent this consideration may be of negligible consequences?

E. U. Franck. — I agree that argon atoms in water may well be not an inert component and may well influence the structure of the surrounding water considerably. Such effects, however, are very probably restricted to relatively low temperatures. We assume that at the temperature applied here (440 °C) and at the applied densities which were somewhat below 1 g/cm^3 any effects of the argon on the structure of the surrounding water are too small to be detected. This would certainly be different in the range of gas hydrate formation.

A. R. Ubbelohde. — If the density of the system is fairly high one might expect the different space requirements for the insertion of different inert gas atoms into the mixture to result in notable differences in certain physical effects. For example the breaking up of clusters of water molecules by different inert gases at the same concentrations should show same effects of atomic size. Have any comparisons been made say, between neon, argon, and xenon in these respects? In the case of molten salts, insertion of inert gases involves considerable work to displace the ions. One might expect the additional space requirements for xenon, say compared with argon, to outweigh the higher polarisability of xenon; its solubility at the same temperatures should be smaller than that of argon. Unfortunately experimental tests do not yet appear to have been made.

E. U. Franck. — I am very happy about the encouragement which we receive from your suggestion to investigate mixed aqueous solvents, which contain larger atoms than argon as the second component. We shall try to do it.

Before using such mixed solvents for conductance experiments we have to know the two-phase range and critical curve of such a system. For that purpose we have started to make these thermodynamic measurements with the system xenon-water. Since Dr LENTZ in our Laboratory has developed a very small apparatus for simultaneous visual observation and determination of PVT-data of such mixtures we need only

small quantities of the expensive xenon. Since the sample space mounted is horizontally and because of the continuous control by observation through a sapphire window, we believe to be able to avoid errors caused by gravitational forces.

The apparatus of Dr LENTZ is described in a paper of LENTZ and myself,¹⁷⁾

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