

THE DIELECTRIC PROPERTIES OF ADSORBED WATER LAYERS ON INORGANIC CRYSTALS

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Received 21st August, 1950

Small amounts of adsorbed water have been found to cause peaks at about -30°C in the variation with temperature of the dielectric constant and power factor of a number of inorganic crystals. A note is added on the dielectric changes accompanying the λ -point transition of $(\text{NH}_4)_2\text{SO}_4$.

As a parallel investigation to that described in the previous paper,¹ the dielectric properties of various materials exhibiting hydrogen bonding were studied over a temperature range from -100°C to 0°C . No significant variations were found for powdered crystals of boric acid, urea, fumaric acid, pentaerythritol, resorcinol and benzoic acid, but the results are inconclusive for the reason of gradation of temperature in the specimen discussed earlier.¹ During the course of the work, however, it was discovered that very small amounts, probably unimolecular layers, of adsorbed water gave rise to sharp peaks at about -30°C in the temperature variation of both the dielectric constant ϵ/ϵ_0 and power factor $\tan \delta$ of powdered crystals of a number of inorganic salts. The effect was not confined to hydrogen-bonded materials and it was found in NaHCO_3 , NaHSO_4 , Na_2SO_4 , NaCl , KHCO_3 , KHSO_4 , NH_4Cl and $(\text{NH}_4)_2\text{SO}_4$, these being the only sodium, potassium and ammonium salts to be examined.

Experimental

The dielectric measurements were made on the specimens *in vacuo*, at a frequency of 3000 c/sec. with a Schering bridge, the apparatus being that described in the previous paper¹ for measurements over the temperature range. The test specimens were powdered crystals and the quality of all the materials was of A.R. standard.

With a rotary oil pump, a pressure of approximately 10^{-3} mm. Hg was obtained in the system. The vacuum was later improved by incorporating a liquid-air trap and a Metropolitan-Vickers oil diffusion pump into the system so as to give an ultimate pressure of $<10^{-4}$ mm. Hg. In order to allow a reasonable rate of cooling of the test condenser by the liquid air, the system after evacuation was filled to a suitable pressure with dry oxygen obtained by warming a side-tube containing potassium permanganate.

Results

The results for NaHCO_3 , NaHSO_4 and NaCl are plotted in Fig. 1-3, similar curves being obtained for the other materials as indicated. The peaks occurred as the specimens warmed up in the vacuum obtained with the rotary pump. The heights of these peaks differed between the substances studied and, with NaCl at least, the height depended upon the extent of cooling (see Fig. 3). No peaks were found, however, when measurements were made as the specimens cooled down and they were completely eliminated with the improved vacuum obtained with the diffusion pump and trap.

¹ Bayley, *Trans. Faraday Soc.*, preceding paper.

The results suggested that condensation of a vapour, which was not removed by the rotary pump, was occurring in the poorer vacuum and experiments were therefore performed on samples of NH_4Cl and NaHCO_3 after evacuation by the diffusion pump and subsequent exposure for several hours at room temperature to various vapours. The vapours tried were (dry) CO_2 , water, and the vapour

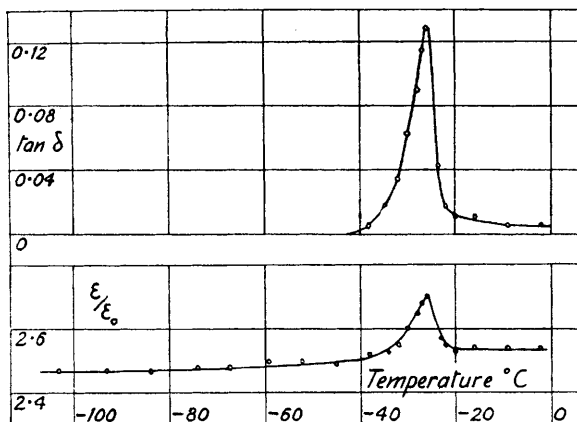


FIG. 1.— NaHCO_3 : Results for dielectric constant and power factor over a temperature range in the vacuum obtained with the rotary oil pump. Similar results to these were obtained for KHCO_3 and KHSO_4 .

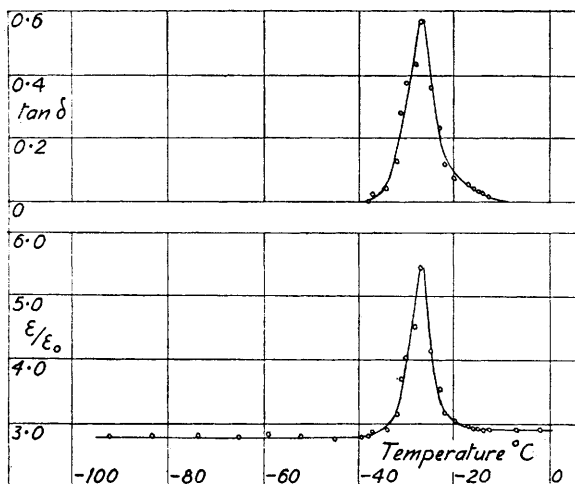


FIG. 2.— NaHSO_4 : Results for dielectric constant and power factor over a temperature range in the vacuum obtained with the rotary oil pump. Similar results to these were obtained for Na_2SO_4 .

from an oil at 90°C , the oil being similar to that used in rotary pumps. For both materials the peaks were reproduced with water vapour, and negative results were obtained with CO_2 and oil vapour.

Owing to the gradation of temperature mentioned above, the sudden dielectric changes occurring at the λ -point of NH_4Cl were not detected. If more accurate temperature control were used, the peaks here considered would probably prove to be extremely sharp.

Discussion

The peaks in the temperature variation of the dielectric properties of the materials examined appear to be due to extremely thin, probably uni-molecular layers of adsorbed water. An explanation of this phenomenon in terms of a Debye relaxation process² is precluded by both the sharpness of the power factor peak and the existence of a corresponding peak in the curve for the dielectric constant.

The occurrence of these peaks may mean that some widespread change in the forces binding the adsorbed water molecules takes place at this point, resulting in either

- (a) increased freedom of orientation and hence enhanced polarization,
- or (b) ionic effects on the surface of the crystals causing corresponding increases in dielectric constant (cf. ref. (1)).

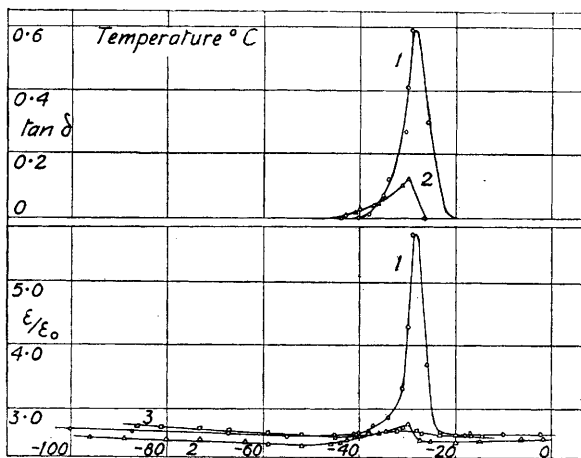


FIG. 3.—NaCl: Results for dielectric constant and power factor over a temperature range in the vacuum obtained with the rotary oil pump. Curves 1, 2 and 3 show the behaviour for initial cooling to temperature of -105°C , -103°C and -101°C respectively. The size of the peaks at -30°C for NH_4Cl and $(\text{NH}_4)_2\text{SO}_4$ were similar to those of curve 1.

The forces exerted on the adsorbed molecules will arise from neighbouring adsorbed molecules as well as from the adsorbent molecules so that co-operative effects will occur. Explanation (a) would therefore mean that the peaks mark a transition from an ordered, possibly localized, system of adsorbed water molecules to a disordered state, the dielectric absorption being due to the breaking-down of the ordered structure. A similar process would be involved in the second explanation, except that here ionic conduction occurs when the ordered structure is broken down and the water molecules have become mobile. In actual fact, the strongly polar nature of the adsorbate may exclude the first explanation since the molecules may be too rigidly oriented on the crystal surface to allow re-orientation. The sudden decrease at the higher temperature side of the peaks would be accounted for by the evaporation of the adsorbed layer.

The curves for NaCl (Fig. 3) suggest that condensation of water vapour only occurs below a critical temperature of about -105°C (cf. the results of Cockcroft³ for the condensation of metallic vapours on surfaces). The existence of critical temperatures for the other substances was not confirmed. With NaCl, the very large temperature difference between the

² Debye, *Polar Molecules* (Reinhold Publishing Corp., New York, 1929).

³ Cockcroft, *Proc. Roy. Soc. A*, 1928, **119**, 293.

condensation and the possible evaporation of the water layer at -30°C therefore implies an extremely large hysteresis for the adsorption-desorption process, which may be due to co-operative forces between adsorbed molecules preventing desorption until a much higher temperature.

The close similarity in temperatures at which the peaks for different salts occur suggests that this desorption process depends largely on the univalent positive ion present. It would be interesting, therefore, to compare these results with the behaviour of salts of metals of other valencies. Measurements of greater accuracy are required in order to study the desorption process more fully, and in this respect the frequency-dependence of the peaks and also the accompanying heat exchanges would be valuable. Nevertheless, the existence of these peaks may provide a useful method of investigating the sorption of vapours on crystal surfaces.

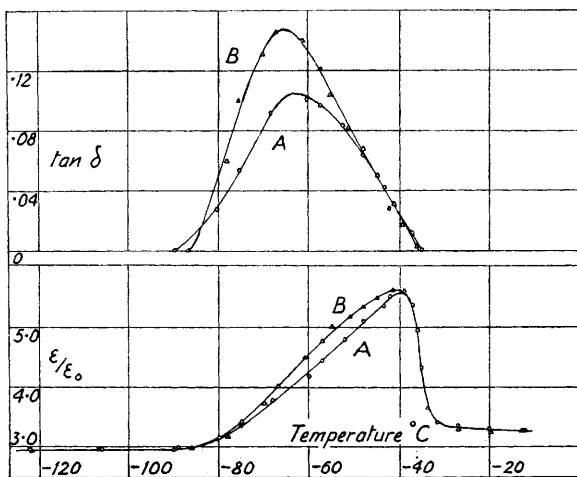


FIG. 4.— $(\text{NH}_4)_2\text{SO}_4$: Results for the variations in dielectric constant and power factor in the region of the λ -point transition (pressure $< 10^{-4}$ mm. Hg).

Curve A—Measuring voltage approximately 130 V/cm.

Curve B—Measuring voltage approximately 470 V/cm.

Dielectric Properties at the λ -Point of $(\text{NH}_4)_2\text{SO}_4$.—Besides the effects at -30°C discussed above, $(\text{NH}_4)_2\text{SO}_4$ exhibits a much broader peak in the dielectric properties at low temperatures, due to a λ -point phase transition at -53.4°C . A typical set of curves from the results obtained for the variation of dielectric constant and power factor in this temperature region is given in Fig. 4. The height of the power factor maximum was found to depend upon the measuring voltage applied across the condenser (see curves A and B) and there was a slight tendency for the difference in temperature between the maxima for dielectric constant and power factor to increase with increasing voltage.

The only previous references to these dielectric changes at the λ -point of $(\text{NH}_4)_2\text{SO}_4$ are two papers by Guillien^{4, 5} who also used crystalline powder specimens. This author found that the maxima in dielectric constant and power factor, which coincided at the λ -point (-53.4°C) were not due to spontaneous polarization and that their magnitudes decreased with increasing frequency. The effect of large static fields on the maxima was studied with negative results, but the variation with different oscillatory voltages was not considered.

⁴ Guillien, *Compt. rend.*, 1939, **28**, 980.

⁵ Guillien, *Ann. Physique*, 1942, **17**, 334.

Although the method of temperature control and measurement used here is inaccurate, the present results differ from Guillien's in that the maxima for the dielectric constant and the power factor do not coincide. This difference would be explained if the oscillatory measuring voltage used by the previous author, which is not reported, were small and the tendency found here for the temperature difference between the maxima to vary with the measuring voltage were real. The peak in the dielectric constant does not appear to shift with varying voltages, which suggests that the present temperature measurements were in error by about 13°C .

The work described here formed part of that submitted for a degree of Ph.D. in the University of London. The author wishes to thank Prof. J. T. Randall, F.R.S., for his interest and advice throughout this research.

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