CCLX.—*The Electrokinetic Potential between the Solid and Liquid States of a Single Substance.*

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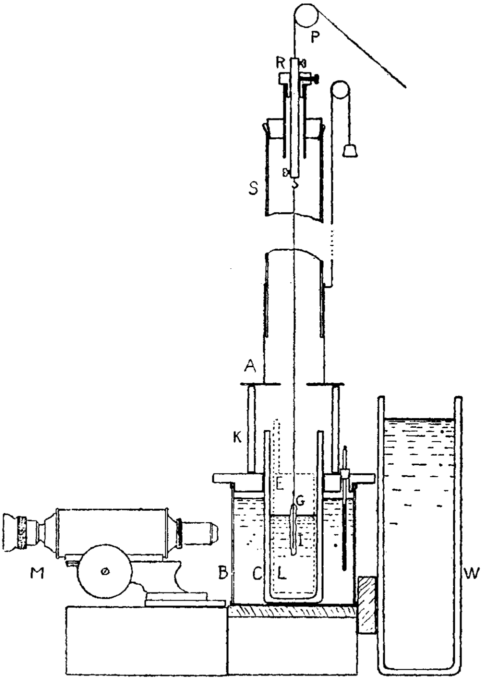
THE first observation of the production of an electric charge by the friction of a liquid against the same substance in the solid state appears to have been made in 1843 by Faraday ("Experimental Researches," **2**, No. 2131, p. 122), who, in the course of his researches on the production of electricity by escaping steam and air, allowed "undried common air" to issue under pressure from an orifice and flow along a cone of wood or metal which thereby became electrified, acquiring a negative charge. He showed that this electrification was due to the "particles of water suddenly condensed from the expanding and cooled air rubbing against the metal or wood" and that dry air produced no such electrification. When, however, undried air was let out against *ice*, it rendered the ice positive in contrast to the negative charge given to wood or metal.

Sohncke (*Wied. Ann.*, 1886, **28**, 550), on account of its bearing on the production of storm electricity, examined closely by different methods the electrification produced by the friction of water against ice. He allowed a jet of water from the ordinary tap to flow along a plate covered with ice, and also forced water through a capillary formed along the axis of a rod of ice. By both methods he found the water to be negatively charged, thus confirming the results of Faraday.

The phenomenon seemed worthy of attention on account of its bearing on the structure of the interface between a solid and the melt from which it is crystallising or into which it is passing, as well as of its bearing on the general question of interfacial potentials. The sign of the electrokinetic potential of ice against water has therefore been examined by another method which has also permitted of the experiments being extended to other substances, with the result that, not only have the experiments of Faraday and Sohncke been confirmed, but in all cases where an electrokinetic potential was detected the solid was found to be positively charged relatively to the liquid.

FIG. 1.



EXPERIMENTAL.

Modifications of the stream potential method of Sohncke were tried but were discontinued on account both of the experimental difficulties and of the uncertainty of interpretation of experiments which included the friction of the liquids against the electrodes. Electroendosmosis measurements were also attempted with little success. The chief difficulty here lay in the preparation of suitable capillaries or diaphragms, and in their retention for a time sufficiently long to permit of the determination of the direction of electroendosmosis. The observations now recorded were made by a cataphoresis method. In essentials the method is somewhat similar to that used by Kleeman and Fredrickson (*Physical Rev.*, 1923, **22**, 134) for the determination of the sign of the electrocapillary charge on thin metallic wires in water.

The apparatus employed is shown in Fig. 1. A rod or " icicle " I of the solid, formed round a thin glass rod G, was suspended at the end of a single unspun silk fibre, 141 cm. in length, in the corresponding liquid L. The glass rod was 3 cm. in length and 0·3 mm. in diameter. About three-quarters of the length of the rod of solid was immersed in the liquid, which was contained in the parallel-sided glass observation cell, C. This cell with its contents was surrounded by a water-jacket, B, with glass windows and a tightly fitting lid, whereby the liquid could be kept at a suitable temperature. With the present apparatus it was impracticable to keep the temperature at the triple point where solid, liquid, and vapour are in equilibrium. Temperatures slightly above or slightly below the melting point were therefore used, so that the rod of solid gradually melted away during the observations or gradually grew in size. This continual formation of a fresh interface also reduced the probability of erroneous observations conceivably due to the possible deposition of atmospheric moisture on the rod of solid during its formation. An electric field of 400 volts, giving about 50 or 100 volts per cm. according to the position of the electrodes, was applied through the electrodes, E, in a direction perpendicular to the plane of the paper. These electrodes in the preliminary experiments were of copper, but were later replaced by platinum electrodes, consisting of platinum foil stretched over rectangular frames of glass rod, and " soldered " in position by small globules of fusible lead glass. The suggestion that the observed effect might be due in part to the electrostatic attraction of such part of the suspended system as lay above the surface of the liquid but within the electric field, was carefully examined and eliminated by control experiments. The lateral movement of the rod of solid in the electric field was followed by means of the microscope, M, which was provided with an ocular micrometer. The suspended system was protected from draughts by the glass tube, S, over the lower end of which passed an earthed brass tube with a wide flange, A. The latter fitted on to the top of a light wooden box, K, formed on the top of the water-jacket lid. Slots were cut in the sides of this box to allow of the passage of the ends of the electrodes. A large glass cell W, filled with acidified ferrous sulphate solution, minimised the passage of heat from the lamp used for illumination. The rod of solid was formed as follows. A glass tube, about 4 cm. long, 2 mm. internal diameter, and closed at one end, was cleaned with chromic–sulphuric acid, washed with distilled water, and dried at 130° before each experiment. The tube was then filled with the liquid under investigation and arranged in the position later to be occupied by the rod of solid, and the glass rod lowered into the liquid. For this purpose the observation cell with its contents and jacket was removed and the suspended system raised and lowered by a small winch operating a cord passing over a small pulley P. The weight necessary to the system was provided by a brass rod R working in a brass collar. The liquid was then allowed to solidify. For most purposes, in particular with substances melting below 30°, it was found advantageous to surround the small tube with dry, solid carbon dioxide. This quickened solidification and greatly facilitated the arrangement of the glass rod G in a central position in the "icicle." With substances melting above 30°, the final results were the same whether or not solid carbon dioxide was used. When the liquid was frozen, the glass tube was gently warmed with the fingers and the solid next to the glass melted sufficiently to allow the withdrawal of the remaining rod of solid. (In the case of substances melting above 30° this operation was usually carried out by immersing the tube in a small quantity of the warm liquid.) The observation cell was then replaced, the rod of solid lowered into the liquid, and the cover A placed in position. Usually about 15 seconds elapsed between the removal of the rod from the mould and its focussing in the field of the microscope. By means of a reversing switch, observations were taken with the electric field in both directions. Only observations which showed a definite reversal of direction of movement with reversal of the applied potential were taken as indicative of the electrokinetic charge. In all such cases the solid was positively charged whether melting in a liquid a little warmer than itself or growing in a supercooled liquid. In no case was a reversible movement observed in a direction indicating that the solid had a negative charge. On the other hand, in every case, except in benzene and in *o*-chlorophenol, the (cleaned) glass rod alone in the liquid moved as if negatively charged, giving reversible deflexions usually greater than those of the rod of solid in the same liquid.

The width of the cell and the diameter of the rod of solid substance were such as to render negligible the effect of electroendosmosis along the walls of the observation cell. In any case this would tend to produce an effect in a direction opposite to that actually observed.

The choice of substances for examination was somewhat restricted. With the present form of apparatus it was inconvenient to use substances melting below 0° or above 40°. In the second place, it was very desirable to use substances which formed coherent crystalline rods. Several substances which were tried gave only soft, noncoherent masses or very viscous liquids. In all the observations now recorded, even with the rapid cooling employed, it could be observed that the icicle was a compact *crystalline* mass, except in the case of ice, which had the usual glassy form. The materials other than water were obtained initially in a fairly pure condition and were carefully fractionated after having been dried with the appropriate reagents, phosphoric oxide being used where permissible. No attempt, however, was made at intensive drying.

In the following table are given the substances examined, together with the typical deflexions from the mean position in terms of the divisions of the eyepiece micrometer, ten such divisions corresponding to an actual movement of 0·5 mm. In all cases, except with pure benzene and *o*-chlorophenol, for which no movement could be detected,* the sign of the charge on the solid was *positive*.

TABLE I.

Substance.	Dielectric constant.	M. p.	Electric field, volts/cm.	Typical deflexion.
Water	88·2 (0°) *	0°	50	10·0
Acetophenone	18·1 (21°) †	20	50	10·0
Nitrobenzene	37·5 (16°) ‡	5	50	2·0
Guaiacol	—	31	50	2·0
Anethole	—	21	100	2·0
p-Cresol	13 (40°) §	35	100	2·0
o-Cresol	8 (40°) §	31	100	1·0
o-Chloronitrobenzene	17·8 (33°) **	32	100	2·0
o-Chlorophenol	6·31 (25°) ‖	7	100	—
Benzene	2·28 (15°) ¶	5	100	—

* Drude, *Wied. Ann.*, 1896, **59**, 17.
† Walden, *Z. physikal. Chem.*, 1910, **70**, 569.
‡ Abegg and Seitz, *ibid.*, 1899, **29**, 242.
§ Philip and Haynes, J., 1905, **87**, 998.
‖ Sayce and Briscoe, J., 1926, 2623.
¶ Kerr, *ibid.*, p. 2796.
** Cauwood and Turner, J., 1915, **107**, 276.

The deflexion is greatest in the cases of water and acetophenone, and non-existent for *pure* benzene. It seems justifiable to conclude that it is only with " polar " compounds that the effect is observable, and that the more polar the substance is, the greater is the deflexion likely to be.

The movement in the case of acetophenone may seem surprisingly great compared with that of the other substances examined. The solid phase, however, owing to the manner of crystallisation when the rod was allowed to grow, had generally a very large surface compared with its weight. The positive charge on the solid acetophenone was also confirmed by the following observations. When slowly crystallising from a slightly super-cooled liquid, acetophenone forms large, very thin plates; when solidification was allowed to proceed in an electric field, it was clearly seen that more crystallisation occurred round the negative electrode than

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* Another sample of benzene, which had not been completely freed from thiophen, gave indications of a positive charge on the solid state.

round the positive electrode. Also, plates of the solid lying in the surface of the liquid could occasionally be seen to move towards the negative electrode, reversing their movement when the direction of the applied potential was reversed.

In the case of *p*-cresol and *o*-chloronitrobenzene, too, small crystals in the interior of the liquid were seen to move towards the negative electrode.

The present data do not permit of any quantitative estimation of the charge on the solid, but an idea of the magnitude of the electrification may be gained from the fact that on the application of a field of 50 volts/cm., the small glass rod G alone, when suspended in distilled water, moved through 21 divisions of the eyepiece scale, having a negative charge. The electrification between the solid and liquid states of a substance is thus generally much less than the electrocapillary charge of glass in distilled water.

Discussion.

Some uncertainty exists regarding the change of dielectric constant on passing from the liquid to the solid state at the moment of solidification. There is considerable evidence from the results of several authors to show that at a temperature several degrees below the melting point, the dielectric constant of many solids is much less than that of the corresponding liquid, particularly when the latter is large, but that, as the melting point is approached, the dielectric constant of the solid becomes dependent to a greater extent upon the frequency of the measuring current, and may at low frequencies approach that of the liquid state. At the lower temperatures, the degree of freedom of the permanent dipoles in the solid is insufficient to permit of their contributing much to the dielectric constant.

If we regard the dielectric constant of the solid as being below that of the liquid during a change of state, then the observations now recorded are in contradiction to the rule formulated by Coehn (*Wied. Ann.*, 1898, **64**, 217), according to which the phase with the higher dielectric constant should become positively charged. Coehn (*loc. cit.*) realised this apparent anomaly in the case of ice and water, and suggested in explanation that probably it was not a matter of water rubbing against ice, but of water at a higher temperature rubbing against cooler water which was adhering to the ice. It seems very improbable, however, that the temperature coefficient of the dielectric constant of liquid water could account for such a degree of electrification as exists.

On the other hand, some recent work by Errera (*Trans. Faraday Soc.*, 1928, **24**, 162) indicates that in the neighbourhood of the melting point, the dielectric constant of a polar substance in the solid state may, when measured at low frequencies, be even higher than in the liquid state. His figures for acetic acid show a sharp rise to a dielectric constant of 18 at a frequency of 680 cycles, in the neighbourhood of the solidification point, the dielectric constant of liquid acetic acid measured at the same frequency being about 6. Errera suggests in explanation of this rise that there is a formation at the moment of solidification of structures in a state of colloidal association, and he assumes further that " the arrangement of the molecular dipoles inside the colloidal structures is such that these last have a high electric moment, higher indeed than that of the molecular dipoles." If this phenomenon is general with polar substances, whatever its cause, then the sign of the electrification between the liquid and solid states of the same substance follows the general rule of contact electrification between different dielectrics as given by Coehn (*loc. cit.*).

It would appear, however, to be a general rule that, where there is an electrokinetic potential between the liquid and solid states, the solid is positively charged relative to the liquid.

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