

THE COLLOIDAL STATE AND COHESION AT THE TIME OF SOLIDIFICATION.

BY JACQUES ERRÉRA.

Received 23rd November, 1927.

The hypothesis that certain bodies pass through a colloidal state of association during solidification, a condition which would remain persistent in the solid state in the neighbourhood of the point of fusion, seems justified.

Regarding this subject let me make the three following preliminary remarks:—

(1) In 1861 Thomas Graham¹ observed that the mechanical properties of ice in the neighbourhood of 0° were analogous to those of certain colloids. He compared the ice "to gum incompletely dried, to glue or any other firm jelly."

(2) Recently the experiments of Joffé² have shown that certain crystalline media, when we approach the point of fusion, are in a plastic state; we can bend rods of rock-salt and change their form, and this plasticity can be compared with that of a colloidal medium. Joffé says that it is not impossible, according to his experiments of diffraction of the X-rays, that there are plastic layers between the solid structures. He therefore finds no argument against the hypothesis of passage through a colloidal state.

(3) The passage through a state of colloidal association between the liquid state and the solid, would be analogous to the similar well-known effect which occurs under certain conditions of temperature and pressure between the gaseous and the liquid states and which is characterised by the appearance of the critical opalescence.

The experiments we have made on the variations of the Dielectric Constant of certain media having permanent dipoles in the neighbourhood of the point of fusion, seem to us to favour the hypothesis put forward at the beginning.

Let us remember that the *D.C.* of a pure liquid having permanent dipoles is caused by the sum of the effects of polarisation of the electrons, atoms, and permanent molecular dipoles. The frequency of the current corresponding to the *D.C.* must be so low as to be less than the time of relaxation of the permanent dipoles and to allow them thus to follow the inversions of the current. For example, for water, the frequency must be less than about 10^{11} . Recently we have shown that³ if we solidify a medium having permanent dipoles and measure its *D.C.* at about 10° below the point of fusion and with a current of frequency higher than about 10^6 , we find that the *D.C.* of the solid is noticeably smaller than that of the liquid, as the permanent dipoles no longer act: they no longer contribute to polarisation. For example, for water the *D.C.* falls from 87 in the liquid state to 2.5 in the solid state; for nitro-benzene, from 35 to 3.5 when we observe the conditions of frequency and of temperature indicated above.

¹ Thomas Graham works referred in Howard T. Barnes' paper in "Colloid Chemistry," edited by J. Alexander, 1926, p. 442.

² Joffé, *Report of the Physical Institute (Leningrad)*, 1926.

³ Erréra, *Compt. Rend.*, **179**, 155, 1924; *J. Physique*, **6**, 304, 1924.

This lowering of the *D.C.* in solidification is quite general for media having permanent dipoles, and we have called the "*D.C.* proper of the solid" that which corresponds to the sum of the electronic and atomic polarisations, to the exclusion of the polarisations due to other constituents.

We have also shown that if we measure the *D.C.* of solids arising from liquids with permanent dipoles near the point of fusion and with frequencies inferior to 10^6 , we find values of the *D.C.* higher than the *D.C.* proper of the solid. The two full-line curves in Fig. 1 show the increase of the *D.C.* of solid acetic acid with lowering of frequency, this increase being less and less as we get farther away from the point of fusion. The dotted line gives this same dispersion of the *D.C.* of liquid acetic acid.

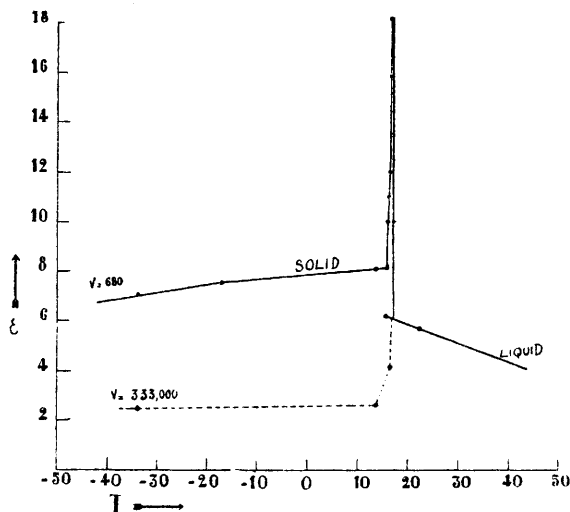


FIG. 1.

We, therefore, see that the *D.C.* of the solid can become higher than that of the liquid.

In order to make this fact clearer we give in Fig. 2 the variation of the *D.C.* of acetic acid with temperature at different frequencies.

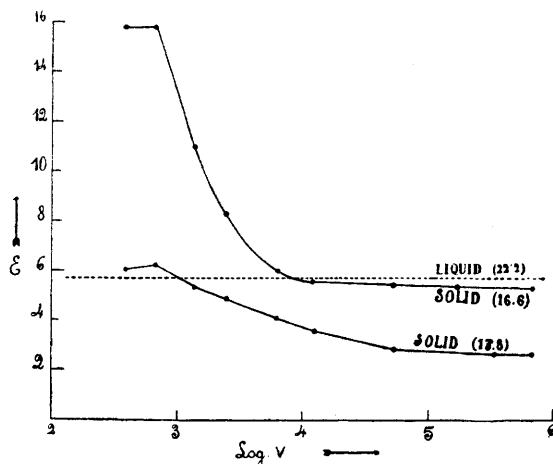


FIG. 2.

We see that for a frequency of 680 the *D.C.* during solidification jumps suddenly to a value of 18, and then drops within 0.2°C. to 8 when the *D.C.* of the liquid is 6.2.

We have found analogous facts for dimethyl sulphate, para-azoxyanisol and, taking the figures of the literature, for ice. The phenomenon is also produced at the moment of solidification when the liquid is supercooled. Other researches are being

made at different frequencies in other media.

We suggest in explanation of this rise of *D.C.*, which exceeds that in the liquid state, that there is formation, at the moment of solidification, of

structures in a state of colloidal association. First it is to be noticed that this rise of $D.C.$ is only found in media having permanent dipoles in the liquid state. It does not exist in media without permanent dipoles. We have made experiments on C^6H^6 , C^6H^{12} , CCl^4 , $TiCl^4$, $SnCl^4$, dichlorethylene, etc. The fact that there is no rise of $D.C.$ for these media is no proof that they do not also pass through an associated state during solidification, but shows that the associated structures, if they are formed, have not a truly permanent electric moment.

On the other hand we know that liquids having permanent dipoles are associated and that, when the temperature falls, the association of these molecules increases. At the moment of solidification there would therefore be a sudden increase of this association. There would therefore be no discontinuity in the increase of association which accompanies the falling of the temperature, but, rather, a sudden increase during solidification. Thus, associated structures would be formed in such a manner that their dimensions would cause them to come under the category of media in the state of colloidal division, that is to say, of which the particles have a diameter between a few $\mu\mu$ and about $500 \mu\mu$. Further, we must suppose 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.

Indeed we see by the curves in Fig. 2 that when the frequency increases, the rise of $D.C.$ which we believe to be due to the polarisation of the colloidal structures, becomes less and less, as if their time of relaxation were not reached. For high frequencies we find a continuous lowering of the $D.C.$ during solidification, without the $D.C.$ of the solid exceeding that of the liquid. These initial frequencies above which the rise of $D.C.$ is produced to a noticeable degree at the time of solidification are of the same order as those which we have proved to be necessary to produce the rise of $D.C.$ of certain colloidal solutions, such as the hydrosols of V^2O^5 (of which the $D.C.$ can reach the value of 1500), whose particles, which are rod shaped, have a high electric moment.

The substances considered, in passing from the liquid state to the solid, would pass through a state of colloidal association before arriving at the solid continuous state, as in the passage from the gaseous state to the liquid they can pass through a state where there are minute liquid drops having colloidal dimensions before arriving at the liquid continuous state. We suggest that these solid structures which, during their formation, pass through the state of colloidal association at the time of solidification, increase to such an extent as to result in structures having given dimensions by the plans of cleavage.

The absorption of electric energy which should accompany the rise of $D.C.$, consequent upon the fact that a new group of constitutive structures follows the reversals of current, cannot be demonstrated, owing to the sudden increase of resistance which accompanies solidification.

The hypothesis of the existence of colloidal structures in solids in the neighbourhood of the point of fusion is not inconsistent with that of the existence of free molecular dipoles in the solid. It rather verifies it in the case of media which are highly associated in the liquid state.

The experimental fact of the rise in $D.C.$ is independent of the hypothesis of the existence of colloidal structures, but it seems to us at the present time that the latter explains the fact most adequately.

Brussels.