Transitions in Camphor and Chemically Related Compounds. I. Dipole Rotation in Crystalline Solids

BY W. A. YAGER AND S. O. MORGAN

The measurement of the dielectric constant may often provide a means of determining both the structure of molecules and the physical changes which take place in the material as it undergoes a phase change, either from liquid to solid or from one solid form to another. This paper points out how dielectric studies on certain solids have disclosed phase changes not heretofore known and how these phase changes contribute to our knowledge of dielectric behavior. In a companion paper[1] it is pointed out that the dielectric evidence of phase changes in these solids is confirmed by density and specific heat measurements and the nature of these changes is discussed in more detail.

The dielectric constant ϵ of a pure polar liquid which freezes sharply usually decreases abruptly, upon solidification, to a value equal to the square of the optical refractive index. For most organic materials this refraction value of ϵ is between 2 and 3. In nitrobenzene, an example of this class of material, which has been measured by several investigators,[2,3] ϵ decreases from 36 to 3 at the melting point, as a result of the inability of the polar nitrobenzene molecules to orient in the solid. The ability to orient is determined by the magnitude of the inner friction, which in normal crystalline solids becomes so high immediately on solidifying that orientation is impossible even at very low frequencies. Therefore in this class of materials the change from high to low ϵ is usually independent of frequency. In certain crystalline solids such as ice[4,5] and in some materials having water of crystallization,[6] as well as in substances such as glycerol[7] which solidify to glasses instead of crystallizing, the inner friction in the solid is still low enough to permit orientation at low frequencies. In these cases anomalous dispersion is always observed. Other crystalline solids are known in which the inner friction is so low that

orientation is possible even at high radio frequencies. In these materials the dielectric constant characteristic of the liquid does not decrease to the refraction value at the freezing point but does so, without dispersion, at a lower temperature where a solid-solid transition occurs.

The significance of this behavior was made apparent by the work of Pauling[8] on the rotational motion of molecules in crystalline solids. As was pointed out by Pauling, the distinction between the two solid forms may be recognized, in the case of polar materials, by dielectric measurements. This fact has served both to explain the dielectric behavior of some crystalline materials and to provide a useful tool for the investigation of phase changes in solids. Since there are no very satisfactory criteria of the moments of inertia and intermolecular forces involved in the rotation of complex organic molecules, a convenient starting point for this dielectric investigation has been polar materials known to have solid-solid transitions. The work of Wallerant[9] on the crystal structure and Bridgman[10] on phase changes has shown that camphor is polymorphic. This paper discusses the interpretation of phase changes in camphor and some related compounds by means of dielectric measurements.

Experimental Details.—The experimental work to be described consists of measurements of the variation of dielectric constant and conductivity of camphor and some related compounds with frequency and temperature. The frequency range was from 1 to 100 kc. and the temperature range from liquid air temperature to somewhat above the melting points. Direct capacitance and conductance measurements were made with a capacitance bridge described by Shackelton and Ferguson.[11]

The original measurements on camphor in parallel plate and cylindrical condensers gave values of ϵ which were consistently about half those of corresponding measurements on pressed disks, due presumably to unusually great con-

(1) White and Morgan, THIS JOURNAL, 57, 2078 (1935).

(2) Smyth and Hitchcock, ibid., 54, 4631 (1932).

(3) Sun and Williams, Trans. Am. Electrochem. Soc., 65, 121 (1934).

(4) Errera, J. Phys., [6] 5, 304 (1924).

(5) Murphy, Trans. Am. Electrochem. Soc., 65, 133 (1934).

(6) Errera and Sack, Trans. Faraday Soc., 30, 687 (1934).

(7) Morgan, Trans. Electrochem. Soc., 65, 109 (1934).

(8) Pauling, Phys. Rev., 36, 430 (1930).

(9) Wallerant, Compt. rend., 158, 597 (1914).

(10) Bridgman, Proc. Am. Acad. Arts Sci., 52, 91 (1916).

(11) Shackelton and Ferguson, Bell System Tech. J., 7, 70 (1928),

traction on cooling from the liquid state, although precautions were taken to solidify the material as uniformly as possible. That the dielectric constant obtained for pressed disks of camphor was not due to any change produced by pressing was shown by a number of experiments on sheets pressed at different pressures, and by the fact that the high value was also obtained on a section cut from a cast specimen of the material. The dielectric data presented here are for pressed disks, except for camphoric anhydride, which pressed with such difficulty that recourse to melting the material into a cylindrical condenser was necessary.

Homogeneous disks 1.0 to 1.3 mm. thick and reason-ably free from entrapped air were prepared by pressing the materials under 7.5 to 30 tons ram pressure in a 4.4 cm. circular mold. Tin foil disks were placed between the material and the plungers to facilitate removal from the mold and also to ensure good electrical contact between electrodes and dielectric. Two disks of each material, with tin-foil electrodes in place, were clamped one on top of the other between two brass disks 10 mm. thick and 6.35 cm. in diameter, by an arrangement of pins and springs as shown in Fig. 1. The object of the springs was to pro-

vide constant clamping pressure upon the disks of the dielectric so as to minimize void formation on cooling. The brass plates constituted the ground electrodes and the tin foil between the disks of dielectric the high tension electrode, which was connected to the bridge by a shielded lead insulated from the brass plates. The error due to edge effects in this arrangement was found to be negligible.

The cylindrical condenser employed for the measurements on camphoric anhydride is shown diagrammatically in Fig. 2. It was so designed that, by making direct capacitance and conductance measurements, all fixed and stray capacitances and conductances were eliminated.

Fig. 1.—Arrangement of condenser for direct capacitance and conductance measurements on pressed disks of dielectric.

The usual procedure in making preliminary measurements at low temperatures was to place the condenser containing the specimen in a Dewar flask, cool with liquid air, then remove the liquid air and allow the sample to warm up slowly. Capacitance and conductance were measured at 1 and 100 kc. alternately as the system warmed up, no attempt being made to hold the temperature constant. For bornyl chloride and d-camphor drifting measurements only were made with ascending tempera-

tures. For the other materials measurements were made at constant temperature with both increasing and decreasing temperatures, the specimen being equilibrated in a simple liquid air thermostat. Good agreement was obtained between the values with a drifting temperature and those equilibrated at fixed temperatures. For measurements above room temperature an oil thermostat was used for the pressed disks and an aluminum block thermostat for measurements with the cylindrical condenser.

Materials.—The d-camphor was a refined commercial gum camphor which was recrystallized twice from absolute alcohol, dried and resublimed.

The dl-camphor was refined synthetic camphor from the du Pont Company and was used without further purification. A sample of refined synthetic camphor from the Eastman Kodak Company gave identical results and a sample of this camphor, which was recrystallized twice from alcohol and then resublimed, also gave the same dielectric constant, though slightly different dielectric loss.

Borneol and isoborneol from Fritzsche Brothers were measured as received.

d-Camphoric anhydride from Eastman Kodak Company was measured as received.

Eastman Kodak Company pinene hydrochloride (bornyl chloride)[12] was recrystallized from absolute alcohol and dried over calcium chloride.

Fig. 2.—Cylindrical condenser for direct capacitance and conductance measurements on liquids or solids.

Experimental Results and Discussion

The temperature dependence of the dielectric constant of d-camphor is shown graphically in Fig. 3 for low temperatures. With descending temperature (Curve A) ϵ was found to increase to a maximum value of 14.9 at $-37°$. The temperature was maintained constant at $-37°$ for at least two hours, but ϵ retained its high value with no indication of falling off. On lowering the temperature a degree or two, however, ϵ decreased abruptly to a value of 2.82, which remained constant to liquid air temperature. With ascending temperature (Curve B) the same value of ϵ, independent of temperature, was observed up to $-32°$. At this temperature it increased rapidly to a maximum of 12.4 at $-25°$ and subsequently decreased with further increase in temperature. Within the experimental error the 1 and 100 kc. dielectric constants fall on the

(12) According to Brooks, "Non-Benzenoid Hydrocarbons," p. 438, what is commonly called pinene hydrochloride, m. p. 127°, is bornyl chloride.
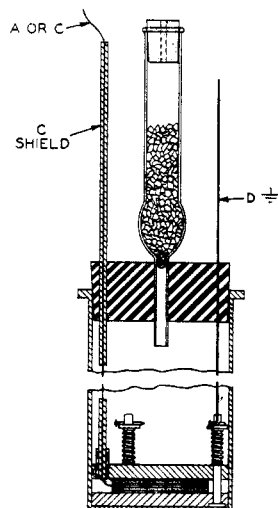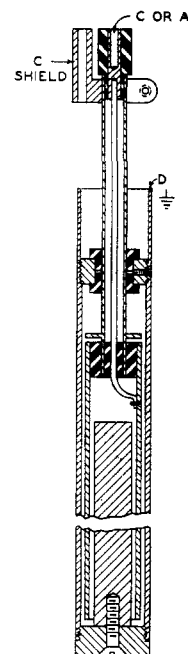
same curves with no evidence of an anomalous dispersion even in the transition interval. The conductance, which is a more sensitive test for anomalous dispersion, was low so that changes could not be followed through the transition interval due to inability to balance the bridge, because of the rapidly changing capacity. It can be safely said, however, that the variation in conductance, if any, was extremely small. The dielectric constant at 18 megacycles, measured at room temperature, was also found to agree with the value at lower frequencies. It appears, therefore, that the relaxation time of the polarization which accounts for the value of ϵ above the transition is less than 9×10^{-9} seconds at room temperature.

The fact that the transition occurred at $-37°$ on cooling, but at $-32°$ on heating, can probably be attributed to an overstepping of the transition point in both directions as is often observed in solid–solid transitions.[13] The curve a-b of Fig. 3 was obtained by continuing the measurements which gave curve B from the point b, going first in the direction of descending and then in the direction of ascending temperature. The points all fall on the same curve, showing that after completion of the change to the high temperature form there is no hysteresis above the transition temperature.

The abrupt change in dielectric constant of d-camphor at the transition is accompanied by a large change in heat content, as revealed by heating and cooling curves. The first break in the heating curve occurred at $-32°$ and the second at $-27°$, checking remarkably well the range determined from the dielectric data. On cooling, the transformation began at $-37°$ and was practically complete at $-40°$, again in good agreement with the dielectric data.

In 1914, Wallerant,[9] studying the crystallography of d-camphor, found that if it is made to crystallize by fusion it assumes four different states. Upon first solidifying the crystals are cubic, transforming into rhombohedral at 97°. Small crystals, also rhombohedral, then develop on these large crystals and are to be considered the stable form as an inverse transformation never takes place at any temperature. Since these new crystals are produced by crystalline supercooling, the transformation takes place near

(13) Findlay, "The Phase Rule and Its Applications," Longmans, Green and Co., New York City, 1923, p. 27.

90° instead of 97°. Finally at $-28°$ these crystals are again transformed into very birefringent crystals which are also rhombohedral. Bridgman[10] found that d-camphor is polymorphic with six possible solid phases depending upon the temperature and pressure. At atmospheric pressure a solid–solid transition was found at 87°, and another in the neighborhood of $-40°$. The dielectric data for camphor serve to define the lower of these phase changes more clearly than the earlier work, but tell very little about the change near 90°.
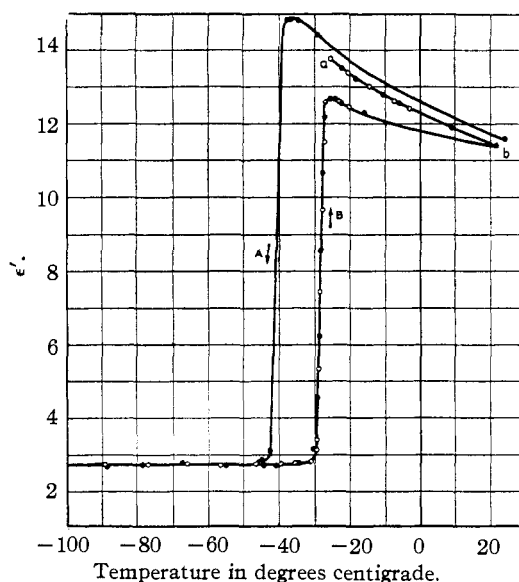

Fig. 3.—Dielectric constant of d-camphor as a function of temperature: Curve A, descending temperature; Curve B, ascending temperature. O, 1 kc.; ●, 100 kc.

The temperature dependence of the dielectric constant of d-camphor at temperatures including the melting point and the transition in the neighborhood of 90° is shown in Fig. 4. A cylindrical condenser was employed for the measurements in the liquid state, and the disk condenser for the measurements in the solid state up to 168°. At these temperatures the vapor pressure of the camphor is so high as to cause excessive evaporation at the edges of the disks. To cover the range between 168° and the melting point (177.6°), the cylindrical condenser was again used, precautions being taken to solidify the material from the bottom up. The data up to 168° and above the melting point are shown as solid lines in the figure, and that of the intermediate region as dashed lines, there being some uncertainty as to the absolute values in this region.

The dielectric constant of solid d-camphor was observed to decrease with increasing temperature in a manner very similar to that of polar liquids, where the decrease is supposedly due to decreasing density and greater hindrance to dipole orientation. Up to approximately 75° ϵ is practically independent of frequency (between 1 and 100 kc.) and the dielectric loss may be accounted for entirely by direct current conductance. Between 90 and 100°, where the rhombohedral crystals should be transformed to cubic crystals, there is still no discontinuity in the higher frequency curves but the 1 kc. curve shows a slight break.
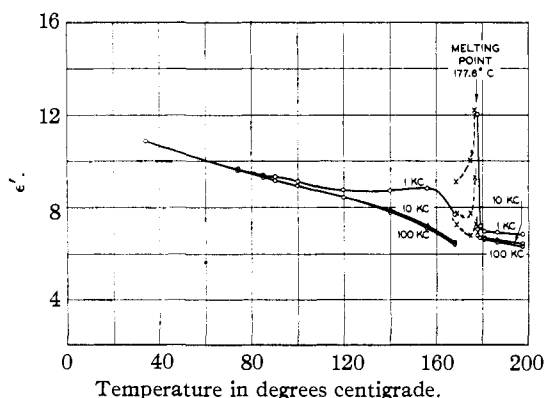

Fig. 4.—Dielectric constant of d-camphor as a function of temperature and frequency above room temperature.

The fact that ϵ at the higher frequencies decreases more rapidly as the melting point is approached than at lower temperatures, is probably due to the decrease in area of the test specimen as a result of evaporation. The 1 kc. value, although subject to the same percentage error, increases to a maximum at approximately 156° and then decreases rapidly. This maximum indicates the presence of an anomalous dispersion which, however, does not appear to be present at 10 and 100 kc. The conductivity data are too uncertain to assist in analyzing this behavior. In the neighborhood of the melting point there are two regions of anomalous behavior both of which are probably the result of interfacial polarizations due either to impurities or to the formation of two layers. The lower may be due to solid–air layers produced by contraction of the solid and the upper to the coexistence of a liquid and solid phase near the melting point.

Impurities present might give rise to a liquid phase just below the melting point but failure to attain temperature equilibrium is a more probable

cause. As the system is allowed to cool gradually, a solid layer will form on the outer electrode giving in effect a two layer dielectric composed of a solid layer in series with a liquid layer. As cooling proceeds, the solid layer will increase in thickness at the expense of the liquid layer until the entire mass between the electrodes has solidified. The dielectric constants of the liquid and solid phases are essentially the same but the conductivity, γ, of the solid phase is less than that of the liquid phase so that the necessary condition for the existence of a Maxwell–Wagner interfacial polarization, namely, that $\epsilon_1\gamma_2 - \epsilon_2\gamma_1$ be either greater or less than but not equal to zero, is fulfilled. Furthermore, the conductivity is of the right order for the anomalous dispersion to occur in the frequency range of these measurements. It can be shown from the equations for a two-layer dielectric, that a behavior analogous to that observed may be obtained if the ratio of the thickness of the solid layer to the total electrode separation be allowed to increase progressively from 0 to 1. The reverse procedure of gradually heating the system through the melting point will give precisely the same results.

Apart from the uncertainties in the values near the melting point, the data indicate clearly that there is no appreciable change in value of ϵ for camphor on solidifying. They indicate that the same polarization which exists in the liquid state also is present in the solid. The melting point, usually supposed to represent the place where the molecules align themselves into a crystal pattern, does not introduce any appreciable interference with the ability of the molecules to orient. The restraint to rotation sets in at the transition point some 215° lower.

There is no evidence to indicate that any difference should have been expected between the dielectric properties of the natural d-camphor and the synthetic dl-camphor. Figure 5 shows that the two are very similar, though not identical. The transition for dl-camphor is displaced to lower temperatures, and ϵ undergoes but half the sharp drop shown by d-camphor at the transition. ϵ then decreases more gradually with descending temperature through a region of anomalous dispersion before finally reaching the state corresponding to the refraction polarization at $-180°$. There apparently is no temperature hysteresis in the region of anomalous dispersion as the data for ascending and descending temperatures fall

on the same curves, but at higher temperatures a slight hysteresis appears, which is probably associated with the transition as in the case of d-camphor. The dielectric loss factor, ϵ', is shown for the region of anomalous dispersion below the transition temperature. At higher temperatures ϵ'' was too small to be significant.
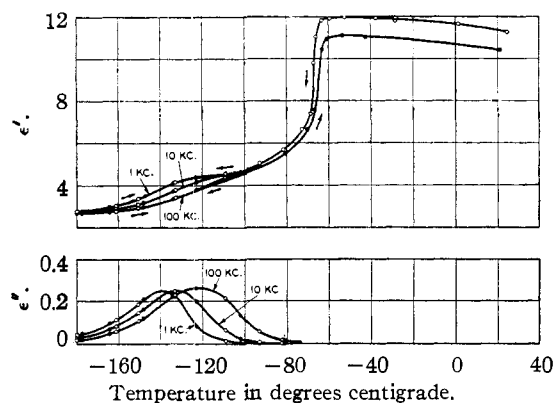

Fig. 5.—Dielectric constant and dielectric loss factor of dl-camphor as a function of temperature and frequency below room temperature; ●, ascending temperature; ○, descending temperature.

The anomalous dispersion below the transition was at first thought to be due to the presence of impurities. However, no systematic variation in ϵ'' with degree of purification was found. For a purified sample, which was recrystallized twice from absolute alcohol and then sublimed, ϵ'' was reduced somewhat in magnitude but by no means eliminated. The loss factor of a sample which, in addition to being recrystallized twice from absolute alcohol was recrystallized once from hexane, and subsequently sublimed, was higher than that of the unpurified sample and was shifted to somewhat higher temperatures. It appears that this dispersion below the transition is not entirely due to the presence of impurities in the usual sense of the term.

Heating and cooling curves for dl-camphor show breaks which are much less pronounced than those of d-camphor, in accord with the more gradual falling off of the dielectric constant in passing through the transition. From these data the transition interval appears to be between -65.7 and $-66.7°$ on cooling and between -65.4 and $-64.4°$ on heating, in fair agreement with the dielectric data.

A point of considerable interest is that the transition of dl-camphor occurs at a considerably lower temperature than that of d-camphor. Un-

published work in this Laboratory indicates that the transition of d-camphor is displaced to lower temperatures when it is one component of a solid solution, whereas its transition temperature is unaffected when it is one component of a eutectic mixture. This is in agreement with the usually observed behavior of transitions in metals. Whether or not the transition temperature is altered when it forms a compound with another material has not been determined. However, it appears that dl-camphor is either a racemic compound or a pseudo-racemic mixed crystal and[13] (p. 177) not a racemic mixture.

The dielectric data for samples of borneol and isoborneol are presented in Fig. 6. The data indicate a dielectric transition in borneol with a change in ϵ from 3.02 at 70° to 3.67 at 75°. The transition is less critical to temperature than those of the camphors as evidenced by the gradual increase in ϵ with temperature both above and below the transition proper. It is interesting to note that no temperature hysteresis was found in this case. There is also no evidence of an anomalous dispersion, between 1 and 100 kc., over the range of temperature shown, including the transition interval. Furthermore, ϵ'' and d. c. conductivity remained very low, even up to 100°.
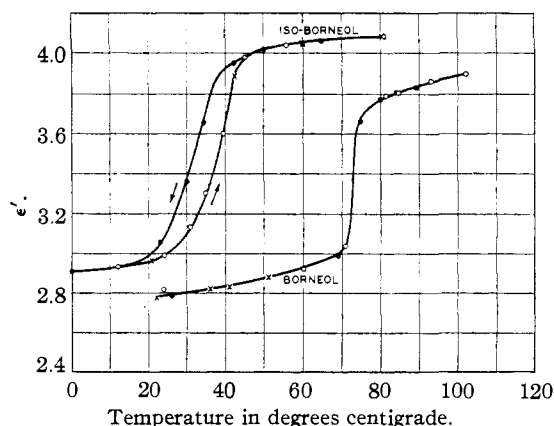

Fig. 6.—Dielectric constant of borneol and isoborneol as a function of temperature: x, ascending tempera ture—first run; ○, ascending temperature—second run; ●, descending run.

The data for isoborneol indicate a dielectric transition in which ϵ increases from 2.9 at 12° to 4.0 at 46° with a pronounced temperature hysteresis through this interval. There is no anomalous dispersion, between 1 and 100 kc., over the temperature range shown. In isoborneol also ϵ'' and the d. c. conductivity remain low, even up to 80°.

No transitions corresponding to those observed in borneol and isoborneol have been reported in the literature. As is shown elsewhere,[1] a change of volume accompanies this transition in both materials.

The fact that the dielectric constants of borneol and isoborneol decrease below their transition points to values somewhat higher than the refraction values (2.5 to 2.6) leads to further low temperature study of these materials. In both cases a second decrease of ϵ to the refraction value, and showing anomalous dispersion, was observed between about -50 and $-100°$. A similar small decrease of ϵ with a dispersion has also been observed in this Laboratory in other solids, particularly those having OH or OCH_3 groups. Since this change occurs at very nearly the same temperature in widely different compounds containing these groups it is believed that this is evidence of group rotation.
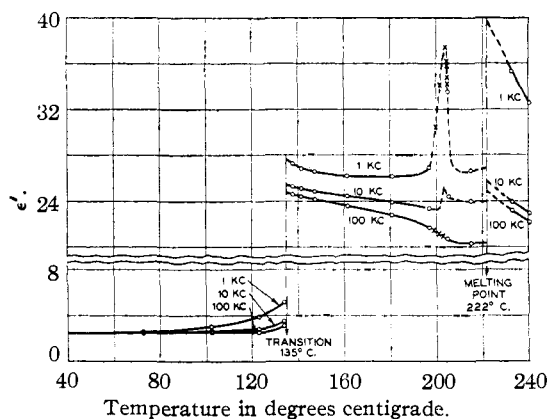

Fig. 7.—Dielectric constant of d-camphoric anhydride as a function of temperature and frequency.

The dielectric constant data for d-camphoric anhydride are presented in Fig. 7. They reveal a dielectric transition at 135°, at which ϵ suddenly increases, with no evidence of an anomalous dispersion, from a value of 3.2 to 24.8 at 100 kc., and to somewhat higher values at lower frequencies. Above 135° the dielectric constant at 1, 10 and 100 kc. shows the typical decrease with temperature characteristic of polar liquids, but between 190 and 210° some anomalous results are obtained. The 1-kc. dielectric constant increases rapidly to a maximum and then decreases again with equal rapidity. This anomalous behavior was much less pronounced at 10 kc. and apparently absent at 100 kc. The relative spacing of the 1, 10 and 100 kc. curves between 205° and the melting point suggests an anomalous dispersion.

The d. c. conductivity in this range is so large as to mask the accompanying dielectric absorption so that the loss factor cannot be used to confirm the existence of the anomalous dispersion. At the melting point the dielectric constant increases somewhat, with no evidence of an anomalous dispersion, and exhibits the typical decrease with increasing temperature in the liquid state. There is, however, marked evidence of electrolytic polarization. The peculiar behavior of the dielectric constant some 20° below the melting point is similar to that observed for d-camphor about the same distance below the melting point. As in the case of camphor also, the change of ϵ at the melting point is so small compared to that at the transition as to indicate that dipole orientation is taking place in the solid, between the melting and transition temperatures.

The temperature dependence of the conductivity of d-camphoric anhydride is illustrated in Fig. 8. A discontinuity in the 1, 10 and 100 kc. curves is observed at both the transition and melting points, the conductivity increasing suddenly by a factor of approximately 10 in each case. However, the d. c. conductivity, measured with a microammeter after a one-minute application of 50 volts, apparently shows no discontinuity at the transition point. It seems, therefore, that the ionic conductivity which increases exponentially with temperature is essentially unaffected by the solid–solid transition. Above the melting point the conductivity is predominantly ionic and hence independent of frequency.
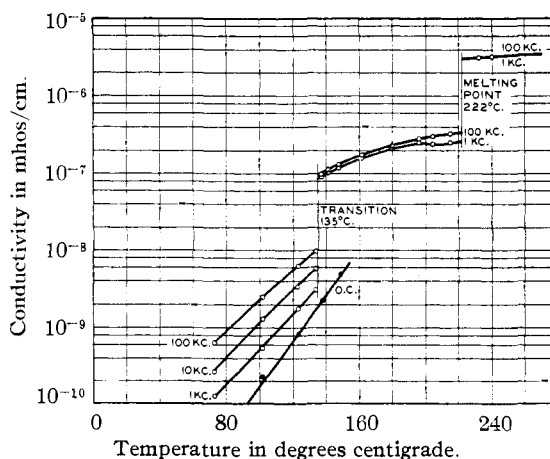

Fig. 8.—Conductivity of d-camphoric anhydride as a function of temperature and frequency.

The dielectric data for bornyl chloride are reproduced in Fig. 9. This behavior closely re-

sembles that of *dl*-camphor, in that ε drops suddenly at the transition only part way to its refraction value and then passes through a region of anomalous dispersion with further decrease in temperature. ε″ curves of the same type as for *dl*-camphor are also obtained. The dispersion in bornyl chloride was very much altered by purification, a result contrary to that for *dl*-camphor. The unpurified sample showed an anomalous dispersion starting so close to the transition as to mask it.

The anomalous dispersion observed immediately below the transitions for *dl*-camphor and bornyl chloride probably arises from the restricted rotation of dipoles in the solid. Several causes of this restricted rotation suggest themselves. The initial decrease of ε without dispersion suggests that it may result from the separation of the material into two or more components, one of which has an inner friction of the correct magnitude to produce dispersion. Alternatively, it may be that following the transition of a part of the material to the low temperature form the resultant inner friction becomes large enough to restrict the rotation of the remainder. It must also be considered that the dispersion may be due to an interfacial polarization resulting from the existence of more than one solid phase. Since the free-ion conductivity of the solid phases is very low this explanation requires that there be a polarization conductivity of considerable magnitude. There appears to be little doubt that the high dielectric constants above the transition temperatures are a result of orientation of dipoles and that the inner friction opposing rotation is small compared to that below the transitions. The absence of an anomalous dispersion immediately above the transition temperature in the camphor compounds may be regarded as evidence of the sharpness of the change from the high temperature form, having low inner friction forces, to the low temperature form, where inner friction forces are too large to permit rotation.

The type of dielectric behavior described in this paper fits very closely into the picture provided by Pauling's theory. From consideration of the thermal properties, Pauling predicted that the polar hydrogen halides would have high dielectric constants in the solid state, the values and their temperature variation being those predicted by the Debye theory. Experimental

study has confirmed this prediction.[14,15] In addition to hydrogen chloride, bromide and iodide this dielectric behavior has been reported for hydrogen sulfide, dimethyl sulfate and methyl alcohol.[16] All of these materials are known to show specific heat changes at their transition points, these changes, in fact, being used as an indication of expected dielectric constant change. The heat capacity measurements on the materials studied in this work, as far as they have been made, also show that a change of specific heat accompanies the solid–solid transitions.
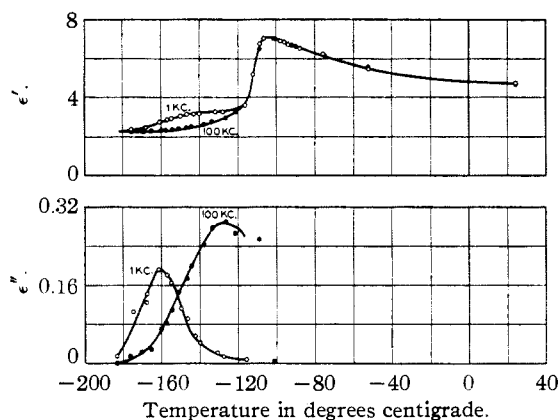

Fig. 9.—Dielectric constant and dielectric loss factor of bornyl chloride as a function of temperature and frequency.

The dielectric behavior of camphor and related compounds differs from that of many other crystalline solids, such as ice, for example, in the effect of frequency. In ice there is an anomalous dispersion at all temperatures below the freezing point. This has been observed by several experimenters.[2,4,5,17,18] Furthermore there is no discontinuity in the specific heat or density of ice which would lead to the prediction that the dielectric constant should change suddenly. It is to be expected that the gradual decrease in heat capacity and density would necessitate a gradual increase of the forces opposing dipole rotation and hence that anomalous dispersion should result.

The phase diagram of ice suggests the possibility that if the dielectric constant were studied with decreasing temperature at high pressure, a discontinuity might be expected at the temperature where a change from phase I to phase II takes place. This assumes that phase I is a high and

(14) Cone, Denison and Kemp, THIS JOURNAL, **53**, 1278 (1931).

(15) Smyth and Hitchcock, *ibid.*, **55**, 1830 (1933).

(16) Hitchcock and Smyth, *ibid.*, **55**, 1296 (1933).

(17) Wintsch, *Helv. phys. acta*, **5**, 126 (1932).

(18) Oplatka, *ibid.*, **6**, 198 (1933).

phase II a low dielectric constant form, which seems probable.

The molar polarization of these materials likewise undergoes a change at the transition point and is a linear function of $1/T$ in the range between the transition and melting temperatures. This is in agreement with the prediction of the Debye dipole theory but nevertheless is of doubtful significance except as qualitative evidence that a dipole polarization is present in these solids. Qualitative evidence that dipole rotation is contributing to the dielectric constant is also given by the correlation between the magnitude of ϵ and the dipole moment. No values are available for the moment of camphoric anhydride but it is safe to predict that it is the highest of this group of materials, probably between 4 and 5 D. The moment of camphor, 2.7 D, is higher than either bornyl chloride or borneol, as is its dielectric constant.

Summary

A study of the dielectric properties of d-camphor, dl-camphor, d-camphoric anhydride, borneol, isoborneol and bornyl chloride has shown that these materials undergo solid–solid transitions. These transitions have not been previously reported in the literature, except for d-camphor. Above the transition the value of the dielectric constant of the solid is that normally expected of the polar material in the liquid state. Below the transition the dielectric constant has a low value, approximately equal to the square of the optical refractive index. This dielectric behavior is explained by the rotation of dipoles in the solid.

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Transitions in Camphor and Chemically Related Compounds. II. Vibration of Atomic Groups

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Introduction

In 1914 Wallerant[1] observed at $-28°$ a transition of d-camphor from rhombohedral crystals of slight birefringence to similar crystals of pronounced birefringence, upon cooling. P. W. Bridgman[2] studied this transition at higher temperatures and pressures, and designated the solid phases stable above and below it as phase II and phase III, respectively.

Linus Pauling[3] has shown that some crystalline transitions accompanied by thermal phenomena may be explained by assuming that molecules or atomic groups begin to rotate at the transition when the crystal is heated. The possibility that a rise of molecular rotation is responsible for transitions occurring in crystals of complex organic molecules, as well as in the simple molecular lattices studied by Pauling, was the original subject of this investigation.[4] Activity was centered on the above-mentioned transition in d-camphor, at which dielectric constant undergoes a change similar to that predicted by Pauling for the transitions in crystals composed of simpler polar molecules.[5]

The molecule of d-camphor is so much more complex than that of hydrogen, which Pauling studied, that a mathematical discussion of the possibility of its rotation in the crystal would not be very informative. However, Pauling's theory suggests three lines of attack which should help to determine experimentally the mechanism responsible for the transition in d-camphor.

1. Heat capacity measurements through the transition should yield information as to any increase in mobility of units whose motion is restrained below the transition.

2. Specific volume and thermal expansion measurements should reveal any general loosening up of structure such as may accompany increased mobility of its units.

3. Dielectric measurements, interpreted in the light of the Debye[6] theory, should give some information as to the specific type of motion involved, and particularly as to whether the motion is rotational or translational.

(1) Wallerant, Compt. rend., 158, 597 (1914).

(2) P. W. Bridgman, Proc. Am. Acad. Arts Sci., 52, 91 (1916).

(3) Linus Pauling, Phys. Rev., 36, 430 (1930).

(4) Yager and Morgan, THIS JOURNAL, 57, 2071 (1935).

(5) Morgan, Yager and White, ibid., 55, 2171 (1933).

(6) Debye, "Polar Molecules," Chemical Catalog Co., New York City, 1929.