tive index of ethylene distearate[17] at 75° is 2.07, which is only slightly lower than the dielectric constant found for the solid ester. The increase in density accompanying solidification could easily account for this difference. Very little change in dielectric constant with temperature is evident in these solids.

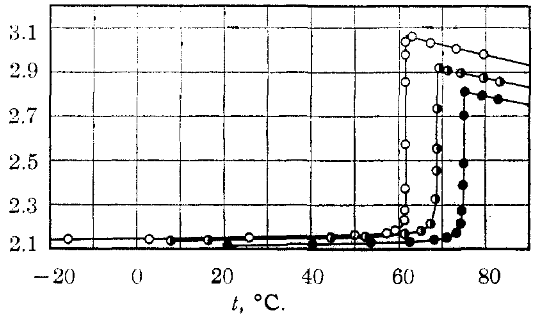

Fig. 11.—The variation of the dielectric constants at 5 kc. of ethylene dimyristate (hollow circles), ethylene dipalmitate (half-filled circles) and ethylene distearate (filled circles) with decreasing temperature.

**Stearic Acid.**—The dielectric behavior of stearic acid is shown graphically in Fig. 12. Due to the strong tendency of the carboxylic acids to form non-polar dimers in the liquid phase, their dielectric constants are always lower than they would be if only monomers were present. Several investigators have reported that, in the lower acids, the dielectric constant of the liquid increases with increase in temperature due to the thermal dissociation of the dimers,[27,28] resulting in an increase in orientation polarization. With stearic acid, however, the polar group is diluted to such an extent by the long hydrocarbon chain that this effect may be overbalanced by the normal decrease in dielectric constant resulting from decrease in density and increase in thermal agitation of the dipoles. Thus there is a small net decrease in dielectric constant for this compound with increase in temperature even though the total polarization probably increases under these conditions. The sharp peak in the dielectric constant of stearic acid at the freezing point is analogous to those found by Piekara[29] for palmitic acid, stearic acid and oleic acid. The phenomenon may be the result of interfacial polarization between liquid and solid which coexist during the solidification process. As can be seen in Fig. 12, the dielectric constant of solid stearic acid is significantly higher than that of the liquid, probably because of the higher density. Piekara, on the other hand, reports a much lower value for the solid than for the liquid, probably because of the presence of voids. It has been found in this Laboratory that errors due to void formation can be greatly reduced by repeated melting and freezing of the samples before the final measurements are made, since this procedure tends to expel dissolved gases.

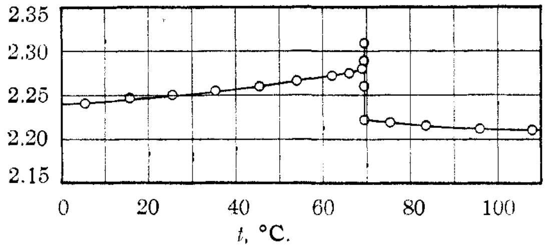

Fig. 12.—The variation of the dielectric constant at 5 kc. of stearic acid with decreasing temperature.

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(27) C. P. Smyth and H. E. Rogers, This Journal, **52**, 1824 (1930).

(28) A. Piekara and B. Piekara, *Compt. rend.*, **198**, 1018 (1934).

(29) B. Piekara, *Physik. Z.*, **37**, 624 (1936).

Princeton, New Jersey Received March 31, 1951

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[Contribution from the Frick Chemical Laboratory, Princeton University]

# The Dielectric and Polymorphic Behavior of Cyclohexanol, Cyclohexanone, Chlorocyclohexane and Cyclohexane[1,2]

By Robert W. Crowe[3] and Charles P. Smyth

The dielectric properties of cyclohexanol, cyclohexanone, chlorocyclohexane and cyclohexane have been investigated over a wide temperature range at frequencies from 0.5 to 100 kilocycles. Cyclohexanol was found to exist in three solid forms instead of two as had previously been reported. In the high temperature form, the molecules possessed freedom of orientation comparable to that observed in the liquid. Both low temperature forms possessed low dielectric constants, indicating an absence of molecular freedom. In the supercooled high temperature form the orientation process involves a small distribution of relaxation times similar to that reported for solid cyclopentanol. Cyclohexanone and chlorocyclohexane were found to exist in two solid forms, with evidence of rotational mobility in their high temperature forms. The rotational transition in chlorocyclohexane was found to be enantiotropic instead of monotropic as had previously been reported. The unusually low value of the dielectric constant of the low temperature form of cyclohexane suggests that the force fields in the crystals increase the binding forces on the electrons so as to decrease the molecular polarizabilities, the effect becoming more pronounced as the density of the solid increases.

It has been known for a number of years that cyclohexane and some of its derivatives are capable of existing in more than one crystalline form. In this respect, they resemble compounds such as *t*-butyl chloride,[4,5,6] *t*-butyl bromide,[4,6] methylchloroform,[7,8] 2,2-dichloropropane,[7] 2-chloro-2-nitropropane[8] and others whose molecules are ap-

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(1) This research has been supported in part by the Office of Naval Research. Reproduction, translation, publication, use or disposal in whole or in part by or for the United States Government is permitted.

(2) This paper represents a part of the work submitted by Mr. R. W. Crowe to the Graduate School of Princeton University in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

(3) Procter and Gamble Fellow in Chemistry, 1949–1951.

(4) W. O. Baker and C. P. Smyth, This Journal, **61**, 2798 (1939).

(5) W. P. Conner and C. P. Smyth, *ibid.*, **63**, 3424 (1941).

(6) L. M. Kushner, R. W. Crowe and C. P. Smyth, *ibid.*, **72**, 1091 (1950).

(7) A. Turkevich and C. P. Smyth, *ibid.*, **62**, 2468 (1940).

(8) R. W. Crowe and C. P. Smyth, *ibid.*, **72**, 4009 (1950).

TABLE I

PHYSICAL CONSTANTS OF COMPOUNDS

| | This research | | | Literature | | |
|---|---|---|---|---|---|---|
| Compound | B.p., °C. | M.p., °C. | $n^{20}D$ | B.p., °C. | M.p., °C. | $n^{20}D$ |
| $C_6H_{12}$ | 80.6 | 6.5 | 1.42650 | 80.7[15] | 6.2,[16] 6.4[17] | 1.42648[15] |
| $C_6H_{11}OH$ | 160.6 | 23.0 | ..... | 161.1[18] | 25.15[18] | ...... |
| $C_6H_{10}O$ | 155.5 | −32.0 | 1.45097 | 155.65[18] | −31.4,[12] −32.0[19] | 1.4507[20] |
| $C_6H_{11}Cl$ | 142.5 | −44.4 | 1.46265 | 142.5[20] | −43.0[12,19] | 1.46264[20] |

proximately spherical in shape. Such compounds have been shown to possess molecular orientational freedom for some distance below their freezing points, this behavior leading to abnormally high melting points and abnormally low heats and entropies of fusion.[9] Although the existence of polymorphism has been definitely established in solid cyclohexanol, cyclohexanone, chlorocyclohexane and cyclohexane,[10-14] there appears to be some disagreement concerning the transition temperatures and the reversibility of these transitions. It, therefore, seemed of interest to reinvestigate the dielectric properties of these substances over a wide temperature range in an effort to determine whether these discrepancies are the result of variations in the thermal histories of the samples or whether they are caused by the presence of impurities.

## Purification of Materials

**Cyclohexanol.**—Material from the Matheson Company was refluxed for 24 hours over freshly burnt lime and fractionally distilled at atmospheric pressure. The sample was then heated with a small piece of sodium metal and again fractionally distilled. Since this compound is extremely hygroscopic, the final product was placed in a desiccator until ready for use.

**Cyclohexanone.**—Material from the Matheson Company was dried for 24 hours over anhydrous sodium sulfate and fractionally distilled twice at atmospheric pressure.

**Chlorocyclohexane.**—Material from the Matheson Company was washed several times with dilute sodium bicarbonate solution and repeatedly with distilled water. The sample was then dried over calcium chloride and fractionally distilled at atmospheric pressure.

**Cyclohexane.**—Material from the Paragon Testing Laboratories was washed several times in the cold with a mixture of concentrated nitric acid and sulfuric acid. This procedure introduced nitro groups into any benzene that might have been present as an impurity. The hydrocarbon was then washed repeatedly with distilled water and finally fractionally distilled over sodium metal.

The physical constants of these substances as measured in this investigation are compared with reliable literature values in Table I.

### Experimental Method and Results

The dielectric constant and loss measurements were made with the aid of an impedance bridge operating between 0.5 and 100 kilocycles. The details of this method have been described elsewhere.[21,22] Measurements were made with both increasing and decreasing temperature. The data are plotted in Figs. 1–7. Dielectric constant values at two or three temperatures for each substance in the liquid state are given in Table II. These liquid values showed no variation with frequency between 0.5 and 50 kc.

TABLE II

DIELECTRIC CONSTANTS OF LIQUIDS

| $t$, °C. | $\epsilon'$ | $t$, °C. | $\epsilon'$ |
|---|---|---|---|
| $C_6H_{12}$ | | $C_6H_{11}Cl$ | |
| 6.5 | 2.049 | −44.2 | 10.43 |
| 9.0 | 2.045 | −15.3 | 9.22 |
| 16.2 | 2.035 | 20.6 | 8.00 |
| $C_6H_{11}OH$ | | $C_6H_{10}O$ | |
| 23.5 | 16.48 | −28.1 | 19.19 |
| 31.4 | 15.23 | − 8.3 | 17.50 |

## Discussion of Results

From heat capacity measurements on solid cyclohexanol, Kelley[10] has shown that this compound exists in two polymorphic forms separated by a sharp thermal transition involving a $\Delta H_t$ = 1.96 kcal./mole at about −10°. He found that the high temperature form, if cooled sufficiently rapidly, could be supercooled down to the temperature of liquid hydrogen without difficulty. The heat capacity of this supercooled phase resembled that observed for glasses.[23] White and Morgan[11] have investigated the dielectric properties of cyclohexanol and observed behavior similar to that reported by Kelley. They found that the dielectric constant was, within experimental error, continuous through the freezing point and continued to increase with decreasing temperature, anomalous dispersion appearing below −25°. At about −60°, this form transformed rapidly to the low temperature form as evidenced by a rapid decrease in dielectric constant. On subsequent warming, they observed a sharp rise in dielectric constant at about −27° corresponding to transformation from the low temperature form to the high temperature form. They suggested that this was essentially the transition which Kelley observed at −10° and ascribed the difference to the presence of impurities in their sample (m.p. 18°). It seems unlikely, however, that impurities would have such a pronounced effect on the transition temperature, especially when a great deal of care had been taken in the purification procedure. In view of this behavior and especially of the peculiar absence of any change in dielectric constant at the freezing point, it was decided to reinvestigate this compound, emphasizing the effects of variation in thermal history.

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[9] W. O. Baker and C. P. Smyth, THIS JOURNAL, **61**, 1695 (1939).

[10] K. K. Kelley, *ibid.*, **51**, 1400 (1929).

[11] A. H. White and S. O. Morgan, *ibid.*, **57**, 2078 (1935).

[12] A. Van de Vloed, *Bull. soc. chim. Belg.*, **48**, 229 (1939).

[13] A. H. White and W. S. Bishop, THIS JOURNAL, **62**, 8 (1940).

[14] O. Hassel and A. M. Sommerfeldt, *Z. physik. Chem.*, **B40**, 391 (1938).

[15] G. Egloff, "Physical Constants of Hydrocarbons," Vol. II, Reinhold Publishing Corp., New York, N. Y., 1940, p. 78.

[16] G. S. Parks and H. M. Huffman, *Ind. Eng. Chem.*, **23**, 1138 (1931).

[17] J. Smittenberg, H. Hoog and R. A. Henkes, THIS JOURNAL, **60**, 17 (1938).

[18] M. J. Timmermans and Mme. Hennaut-Roland, *J. chim. phys.*, **34**, 693 (1937).

[19] L. E. O. Fischer, *Bull. soc. chim. Belg.*, **49**, 129 (1940).

[20] "Handbook of Chemistry and Physics," Chemical Rubber Publishing Co., Cleveland, Ohio, 1947.

[21] C. P. Smyth and C. S. Hitchcock, THIS JOURNAL, **54**, 4631 (1932); **55**, 1830 (1933).

[22] J. D. Hoffman and C. P. Smyth, *ibid.*, **71**, 431 (1949).

[23] W. Kauzmann, *Chem. Revs.*, **43**, 219 (1948).

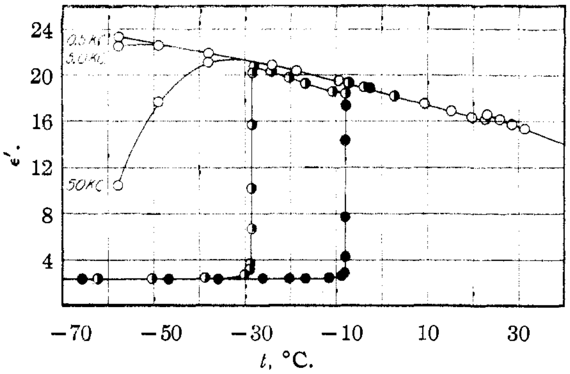

Fig. 1.—Temperature dependence of the dielectric constant of cyclohexanol. Hollow circles are for cooling, half-filled circles for warming immediately after cooling, and filled circles for warming after 10 hr. at −196°.

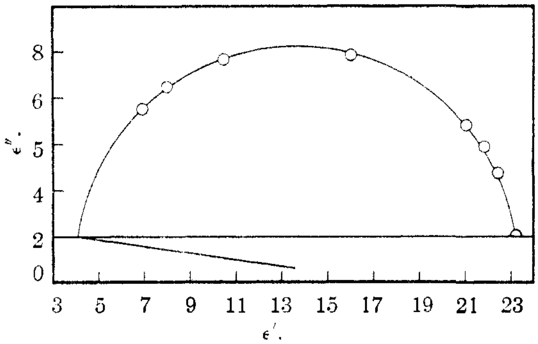

Fig. 2.—Semicircular arc plot for solid cyclohexanol at −57.7°.

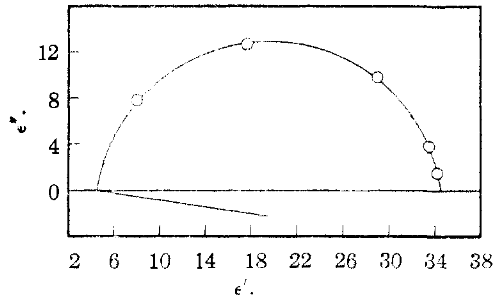

Fig. 3.—Semicircular arc plot for solid cyclopentanol at −70°. Data are those of White and Bishop.[13]

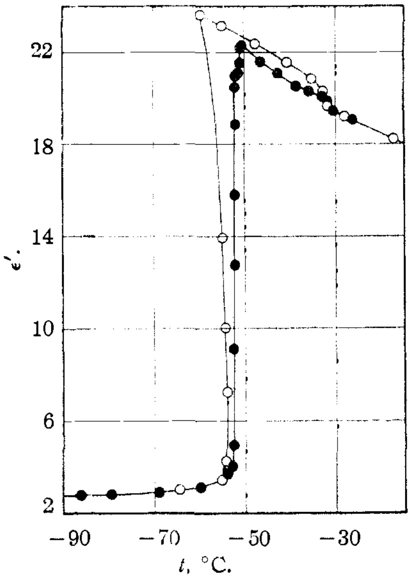

Fig. 4.—Temperature dependence of the dielectric constant of cyclohexanone at 50 kc. Hollow circles are for cooling and filled circles for warming.

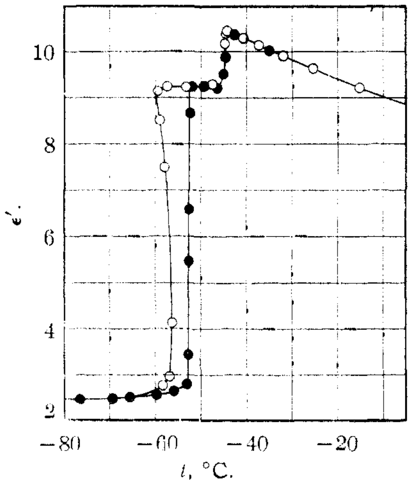

Fig. 5.—Temperature dependence of the dielectric constant of chlorocyclohexane. Hollow circles are for cooling and filled circles for warming.

In Fig. 1 is plotted the dielectric constant of cyclohexanol as a function of increasing and decreasing temperature. Upon solidification, a small but very reproducible decrease was observed, in contrast to the absence of any discontinuity previously reported. With further cooling, the behavior was found to be identical with that reported by White and Morgan. In the present investigation, the transformation from the supercooled high temperature form to the low temperature form usually took place near −57°. However, since this was not a reproducible transformation, its course has not been plotted in Fig. 1. Upon warming immediately after the transformation was complete, the dielectric constant remained essentially constant up to a sharp rotational transition at −28.5°. This evidently corresponds to the transition found by White and Morgan since it occurs at approximately the same temperature. Although the dielectric constant just above the transition point was nearly the same as that obtained on cooling through the same temperature region, it began to drop below the cooling curve as warming was continued. This immediately suggested that this phase was metastable and that the dielectric constant in this region was time dependent. At −7.8°, another sharp rise in dielectric constant was observed, this rise returning the values again to the cooling curve.

Assuming that the phase existing between −28.5 and −7.8° was metastable, the next step in the investigation was to try to remove the transition at −28.5° entirely by varying the thermal history of the sample. To do this, the sample was allowed to remain at −196° for about 12 hours before measurements were made with increasing temperature.

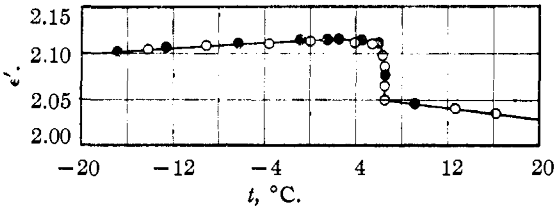

Fig. 6.—Temperature dependence of the dielectric constant of cyclohexane near its melting point. Hollow circles are for cooling and filled circles for warming.

As seen in Fig. 1, this treatment completely eliminated the lower transition, the dielectric constant retaining its low value until the upper transition temperature was reached at −7.8°. Since Kelley's heat capacity measurements were made by initially cooling the sample to very low temperatures, it is believed that the upper transition reported here corresponds to the transition he found at −10°.

From the findings discussed above, it must be concluded that cyclohexanol is trimorphic instead of dimorphic, possessing a high temperature form (I) and two low temperature forms (II and III). On cooling form I transforms to metastable form II, which is a non-rotator. If form II is warmed immediately after its formation, it transforms directly to form I at −28.5°. However, since form I is unstable below −7.8°, it slowly transforms to form III, the only thermodynamically stable low temperature form. When form II is cooled to very low temperatures and allowed to stand for a considerable length of time, it also transforms slowly to form III. Subsequent warming results in a sharp transition from form III to form I at −7.8°. In a sense, this phenomenon can be compared with the double melting observed for *n*-heptyl and *n*-nonyl bromides.[24]

By careful manipulation, it was possible to study the dielectric relaxation behavior of cyclohexanol in the supercooled high temperature form at −57.7°. The results are listed in Table III.

TABLE III

DIELECTRIC CONSTANTS AND LOSSES FOR SOLID CYCLOHEXANOL AT −57.7°

| $f$(kc.) | $\epsilon'$ | $\epsilon''$ |
|---|---|---|
| 0.5 | 23.20 | 0.00 |
| 5.0 | 22.45 | 2.71 |
| 7.5 | 21.82 | 3.89 |
| 10.0 | 21.05 | 4.85 |
| 25.0 | 15.97 | 7.84 |
| 50.0 | 10.48 | 7.65 |
| 75.0 | 8.00 | 6.49 |
| 100.0 | 6.93 | 5.51 |

When the data are plotted according to the method of Cole and Cole[25] (Fig. 2), the experimental points fit well on the arc of a circle whose center is depressed only slightly below the $\epsilon'$-axis. It must, therefore, be concluded that the orientation process is accompanied by a small distribution of relaxation times ($\alpha = 0.09$). For purposes of comparison, dielectric constant and loss data for solid cyclopentanol at −70°, taken from the literature,[13] are plotted in the complex plane in Fig. 3. The results are seen to be quite similar to those obtained for solid cyclohexanol, the distribution of relaxation times being essentially the same ($\alpha = 0.09$). By extrapolation of these plots, the values of $\epsilon_\infty$ were found to be 4.4 for cyclopentanol and 4.2 for cyclohexanol. These values are much higher than either the square of the corresponding refractive indices or the dielectric constants of the low temperature forms of these compounds. This phenomenon is probably the result of librational freedom of the molecules about positions of minimum potential energy in the expanded lattice of the high temperature forms, giving rise to an additional contribution to the atomic polarization. On the other hand, the stronger binding forces which undoubtedly exist in the denser low temperature forms probably restrict this librational freedom to a large extent.

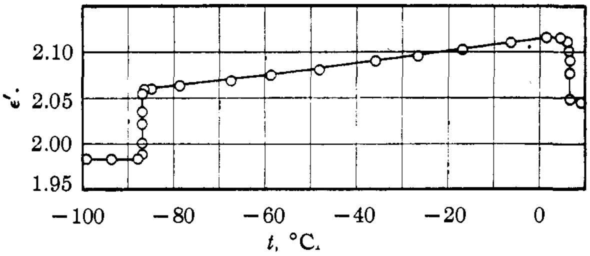

Fig. 7.—Variation of the dielectric constant of cyclohexane with increasing temperature showing transition and melting points.

It might be suggested that the high polarization found in the high temperature forms of these solid alcohols is due only to orientation of the hydroxyl groups, the hydrocarbon parts of the molecules remaining rigidly fixed in the lattice. It is also conceivable that a proton transfer mechanism, similar to that suggested for ice,[26] and for solid long-chain alcohols,[27] could account for the behavior. However, if either of these two mechanisms were occurring, one would not expect a significant difference in the relaxation times for the process in the two compounds. It was found that the relaxation time for cyclohexanol was considerably longer than that for cyclopentanol at a given temperature. For example, $\tau = {}^1/_{2\pi f_m}$ for cyclopentanol at −57.5° is $1.59 \times 10^{-6}$ second while that for cyclohexanol at the same temperature is $4.55 \times 10^{-6}$. This difference, and the abnormally low heats and entropies of fusion[9,28] of these compounds lead one to believe that the entire molecule is free to orient in the lattice.

White and Bishop[13] have investigated the dielectric properties of a number of non-aromatic ring compounds in the solid state. Included in this group were cyclohexanone and chlorocyclohexane. Rather high dielectric constants observed for some distance below their freezing points suggested molecular freedom in the crystal lattice. However, since the polymorphic, and likewise the dielectric,

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[24] R. W. Crowe and C. P. Smyth, THIS JOURNAL, **72**, 1098 (1950).

[25] K. S. Cole and R. H. Cole, *J. Chem. Phys.*, **9**, 341 (1941).

[26] M. L. Huggins, *J. Phys. Chem.*, **40**, 723 (1936).

[27] J. D. Hoffman and C. P. Smyth, THIS JOURNAL, **71**, 431 (1949).

[28] J. Hirschfelder, D. Stevenson and H. Eyring, *J. Chem. Phys.*, **5**, 896 (1937).

behavior of the closely related cyclohexanol was found in the present investigation to depend upon its previous thermal treatment, it seemed advisable to reinvestigate these substances in a like manner.

The dielectric behavior of cyclohexanone is shown graphically in Fig. 4. With the exception of the freezing temperature, the results obtained on cooling are close to those obtained by White and Bishop down to about −60°. Although these authors did not discuss the behavior of this substance, their data indicate that the form obtained upon solidification could be supercooled, as in cyclohexanol, with anomalous dispersion at very low temperatures. Upon subsequent warming of the sample, they found that a transformation to the low temperature form with low dielectric constant had taken place. The transition from this to the high temperature form appeared to be very gradual, occurring between −62 and −53°. In the present investigation, cooling of the high temperature form to −60° invariably resulted in its rapid transition to the low temperature form, the energy involved causing a slight rise in temperature as the dielectric constant decreased. Upon subsequent warming, the transition appeared sharply at −52.5°. Other investigators have reported −49.7°[12] and −53°[19] for this temperature. It can be seen in Fig. 4, however, that a further increase in dielectric constant is apparent at about −51°, this increase appearing in every run. The phenomenon suggests a possible second transition in this region, and may account partially for the rather wide range of temperatures reported by White and Bishop for the transition. However, the low freezing point reported by these authors (−40°) suggests that impurities were present, which could easily account for the behavior. The critical frequency for the orientation process in this compound is evidently much higher, that is, the relaxation time is much shorter than that for cyclohexanol, probably due to the absence of hydrogen bonding in the former.

White and Bishop have reported that the rotational transition in chlorocyclohexane is monotropic, appearing only on cooling. This, of course, suggests a possible second low temperature form, similar to that found in solid cyclohexanol. The dielectric behavior of this compound, as observed in the present investigation, is shown graphically in Fig. 5. On solidification, a small drop in dielectric constant, similar to that reported in the previous work, was observed. On further cooling, the dielectric constant remained essentially constant down to a temperature of −60°, where transformation to the low temperature form began. On subsequent warming, the transition appeared sharply and reproducibly at −52.5°. Even prolonged treatment at low temperatures did not eliminate it. It must, therefore, be concluded that the transition is enantiotropic and not monotropic.

Heat capacity measurements upon solid cyclohexane by Parks, Huffman and Thomas[29] have definitely established the existence of two crystalline forms of this compound, with a sharp enantiotropic transition from one to the other at −87.3°. Since cyclohexane possesses no permanent dipole moment, it is impossible to determine from dielectric constant measurements whether or not its molecules are capable of orientation in an alternating electric field in the solid state. However, the similarity of the thermodynamic properties, crystal structure and glassy appearance of its high temperature form to those of the closely related derivatives discussed above suggests that molecular rotation is possible in this form.

Seyer and Barrow[30] have investigated the freezing and melting process of cyclohexane by dielectric constant measurements. They found that, during the freezing process, its dielectric constant became so large that the reading was completely off the dial scale of the precision condenser. Several degrees below the freezing point, the dielectric constant decreased again and assumed an almost constant value somewhat higher than that reported for the liquid. Upon subsequent warming, the sharp peak did not appear and the sample melted at a temperature somewhat higher than the freezing point. Although the normal increase in density accompanying solidification would be expected to result in a corresponding increase in dielectric constant, a high value such as that observed by the previous investigators at the freezing point is unusual for a nonpolar compound. The dielectric behavior of cyclohexane near its melting point, as observed in the present investigation, is shown in Fig. 6. At the freezing point (6.5°), the dielectric constant increased sharply from a value of 2.047 to 2.113, followed by a gradual decrease as the temperature was lowered. The sharp peak reported by Seyer and Barrow could not be found. In order to obtain reproducible values in the solid, however, it was necessary to freeze and remelt the sample several times, this procedure tending to expel dissolved gases whose separation during the freezing process resulted in void formation. The data plotted in Fig. 6 are for a sample which froze into an almost transparent mass with no visible cracks or voids. As can be seen, the dielectric behavior was, within experimental error, reproducible upon warming, the melting point being extremely sharp as it should be for a pure compound.

The variation of the dielectric constant of cyclohexane over a wide temperature range is shown in Fig. 7. Here the transition and melting points are clearly indicated by sharp breaks in the curve. The gradual decrease in dielectric constant with decrease in temperature from the freezing point to the transition point (−86.9°), as well as the low value assumed below the transition point, are of interest. Once the solidification process is complete, the amount of polarizable material between the condenser plates cannot change appreciably with decrease in temperature, even though the density of the sample undoubtedly increases under these conditions. One would expect, therefore, that, if the sum of the electronic and atomic polarizations remained constant throughout the temperature range investigated, there should be no signifi-

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[29] G. S. Parks, H. M. Huffman and S. B. Thomas, THIS JOURNAL, **52**, 1032 (1930).

[30] W. F. Seyer and G. M. Barrow, *ibid.*, **70**, 802 (1948).

cant change in dielectric constant once solidification has taken place. The increase in density accompanying solidification of this compound has been found by direct means[31] to be 5.2%, while that calculated here from the change in dielectric constant at the freezing point is 4.2%. Considering the fact that complete filling of the cell with solid is difficult, this agreement may be considered satisfactory. It is impossible,, however, to account for the gradual decrease in dielectric constant with decrease in temperature, as well as the sharp decrease below the transition point, unless it is assumed that a decrease in polarization is involved. It may be that the force fields in the crystals increase the binding forces on the electrons so as to decrease the molecular polarizabilities, the effect becoming more pronounced as the distance between neighboring molecules decreases (increase in density). This could account for the gradual decrease in dielectric constant with decrease in temperature down to the transition point. Since the number of molecules between the condenser plates remains approximately constant, the increase in density which, presumably, accompanies the transition to the low temperature form can, by the same argument, cause the observed drop in dielectric constant at this point. Measurements upon solid carbon tetrachloride, carried out recently in this Laboratory,[32] have indicated similar behavior for the substance.

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(31) L. Rotinjanz and N. Nagornow, *Z. physik. Chem.*, **A169**, 20 (1934).

(32) A. DiGiacomo, unpublished measurements.

PRINCETON, NEW JERSEY RECEIVED MAY 16, 1951

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF WASHINGTON]

# Studies on Sulfonates. XI. Electrical Conductances of Aqueous Solutions of Some Magnesium $n$-Alkane Sulfonates[1]

BY A. L. M. LELONG, H. V. TARTAR, E. C. LINGAFELTER, J. K. O'LOANE AND R. D. CADLE

Magnesium hexane, octane, decane and dodecane sulfonates have been prepared, and the conductances of their aqueous solutions measured at 25 and 40° for the C$_6$ salt; at 25 and 60° for C$_8$; and at 60 and 80° for the C$_{10}$ and C$_{12}$ salts. The critical concentrations for micelle formation are given, for the C$_{12}$, C$_{10}$ and C$_8$ magnesium salts, as shown by conductance data; for the C$_6$ magnesium salt and C$_6$ and C$_8$ sodium salts, as determined by the pinacyanol dye method. The values of the heat of micelle formation over the range 60–80° have been calculated for the C$_{10}$ and C$_{12}$ magnesium salts. The variation of the critical concentrations for micelle formation (cmc) with carbon chain length has been discussed. The change with carbon chain length of the slope of the $\Lambda$ *vs.* $\sqrt{Nv}$ curves immediately above the critical concentrations has been shown to be a function of $\sqrt{\text{cmc}}$. The Krafft points of magnesium octane, decane and dodecane sulfonates have been determined.

The results herein reported are a continuation of earlier work in this Laboratory, on the properties of paraffin chain salts. The previous investigations have dealt with aqueous solutions of uni-univalent electrolytes. This report is concerned with some properties of magnesium alkane sulfonates (salts of the 2–1 type), with particular reference to their conductance and behavior toward micelle formation. The hydrocarbon chains are unbranched in all cases. For simplicity the prefix $n$-(normal) will be omitted from the names of the alcohols, bromides and salts.

## Experimental

**Preparation of Salts.**—Octyl and decyl bromides were prepared from the corresponding alcohols by the method of Kamm and Marvel.[2] The octyl alcohol was purchased from the Eastman Kodak Company. Decyl alcohol was obtained from repeated fractionation of lorol. Hexyl and dodecyl bromide were from the Eastman Kodak Company and Halogen Chemicals Inc., respectively. The bromides were further purified by fractionation under reduced pressure: the hexyl and decyl bromides in an efficient Widmer column 61 cm. long; the octyl and dodecyl bromides in a column 1.2 meters in length and filled with small glass helices, which gave a performance equivalent to 19 theoretical plates. The bromides prepared during the latter part of the work (hexyl, octyl and dodecyl) were more carefully checked for boiling point and refractive index.

The uncorrected boiling points and corresponding pressures were: decyl alcohol, 119° (10 mm.); the bromides: hexyl, 87.8–88.8° (90 mm.); octyl, 97.0° (20 mm.); dodecyl, 160–161° (25 mm.). The refractive indices of three of the bromides were determined at 25°; the data (including those of other investigators) were as follows: hexyl, 1.4451, 1.4452[3]; octyl, 1.4504, 1.4503[3]; dodecyl, 1.4562, 1.4563.[4]

Sodium alkane sulfonates were prepared by the Strecker reaction: the hexane, octane and dodecane salts by the method of Houlton and Tartar,[5] the decane salt by treating the bromide with sodium sulfite in an autoclave at 150–200°, and recrystallizing several times from alcohol.

Magnesium hexane, octane and dodecane sulfonates were prepared by obtaining the sulfonic acids from the sodium salts: hexane and octane by the method of Zuffanti[6]; dodecane by the method of Reychler,[7] and neutralizing the acid with magnesium oxide or hydroxide, the excess of which was separated by centrifugation. Magnesium decane sulfonate was prepared from the sodium salt by double decomposition with magnesium chloride. The salts were all recrystallized from water, except the hexane sulfonate, which was recrystallized from alcohol.

The criterion for purity used in the recrystallizations was the absence of chloride ion, and negligible amount of sodium, as evidenced by the flame test. This degree of purity was generally reached after five recrystallizations. It was found that filtrations through a büchner funnel are greatly improved by the use of a covering of rubber dam, which reduces the formation of foams occurring when air is sucked through the wet precipitate.

The magnesium salts were dried in a vacuum oven at 130° and analyzed for magnesium; the hexane sulfonate, by the method of Fleck and Ward,[8] the octane and dodecane sul-

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(1) For detailed tables of data order Document 3302 from American Documentation Institute, 1719 N Street, N. W., Washington 6, D. C., remitting $1.00 for microfilm (images 1 inch high on standard 35 mm. motion picture film) or $1.00 for photocopies (6 × 8 inches) readable without optical aid.

(2) Kamm and Marvel, "Organic Syntheses," Coll. Vol. I, 2nd Ed., John Wiley and Sons, Inc., New York, N. Y., 1941, p. 25.

(3) Ellis and Reid, THIS JOURNAL, **54**, 1674 (1932).

(4) Heston, Hennelly and Smyth, *ibid.*, **72**, 2071 (1950).

(5) Houlton and Tartar, *ibid.*, **60**, 544 (1938).

(6) Zuffanti, *ibid.*, **62**, 1044 (1940).

(7) Reychler, *Kolloid-Z.*, **13**, 277 (1913).

(8) Fleck and Ward, *Analyst*, **58**, 388 (1933).