intramolecular hydrogen bond formation is less satisfactory than when the rings are six-membered. From both these considerations it is not surprising that interaction of the hydroxyl hydrogen with halogen in the 2-halo alcohols does not produce any noticeable deviation from the usual behavior in the O–H intensity. This is not to say that there is no interaction in a compound such as 2-chloroethanol. From a study of internal rotation in this compound it has been concluded that a weak interaction does indeed exist.[16] It does not necessarily follow, however, that it amounts to hydrogen bonding in the strict sense.[17,18] Since only five-membered rings can be formed to chlorine by hydrogen-bonding in 1,3-dichloro-2-propanol, it is not clear why the intensity for this compound should be higher than that predicted from the linear relationship, and it remains for the time being an anomalous case.

An interesting application of these considerations is afforded by the results for furfuryl and tetrahydrofurfuryl alcohols (Table I). While it is true that five-membered rings might be formed in these compounds, hydrogen bonding would not be expected to be very strong. In furfuryl alcohol the oxygen atom is rendered less basic by resonance with the remainder of the furan ring, so that the oxygen in tetrahydrofurfuryl alcohol should be better suited for hydrogen bonding than it is in the former compound. If hydrogen bonding were not a consideration, the intensity for the saturated compound would be lower than that for the other, since the saturation of the ring undoubtedly makes it less electron-withdrawing. The fact that the intensity is higher is good evidence that there is some hydrogen bonding in tetrahydrofurfuryl alcohol although it is not possible to say whether there is any in furfuryl alcohol itself, since the value of σ^* for the 2-furan ring is not known.

Applications

A least-squares treatment of the data for the fourteen alcohols which obey the linear relationship in Fig. 1 leads to the following equation for the line: $\sigma^* = 7.88A - 2.52$. Using this equation new values of σ^* can be determined from intensity data when there is only one unknown group in the set R_1, R_2 and R_3. Using the intensity data for the set of three alcohols containing the cyclopropyl group,[2] the value of σ^* for the cyclopropyl group is determined to be $+0.11 \pm 0.03$.[19] The correlation presented here should prove to be useful in diagnostic work involving compounds of uncertain structure. For example, if a compound of known molecular weight contains an O–H group which might be in any one of two or three possible positions, a careful determination of the O–H intensity in carbon tetrachloride solution may permit a decision as to its location.

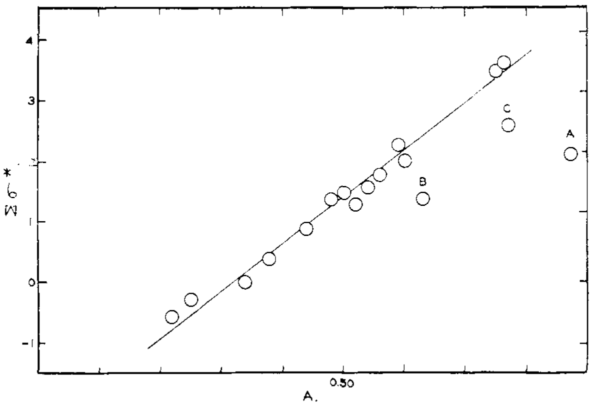

Fig. 1.—Infrared O–H intensity *vs.* sum of the polar substituent constants, σ^*, of the R groups in compounds of the form $R_1R_2R_3C{-}OH$: A, 2-nitro-2-methyl-1-propanol; B, 3-chloro-1-propanol; C, 1,3-dichloro-2-propanol.

Acknowledgments.—The writer wishes to acknowledge the help of Drs. Harold Hart and M. M. Kreevoy, who first pointed out the correlation presented here.

URBANA, ILLINOIS

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[16] S. Mizushima, "Structure of Molecules," Academic Press, Inc., New York, N. Y., 1953, p. 61.

[17] C. A. Coulson, *Research*, **10**, 149 (1957).

[18] C. G. Cannon, *Spectrochim. Acta*, **10**, 341 (1958).

(19) In a previous reference to the correlation reported in this paper,[4] a somewhat different value of σ^* for the cyclopropyl group was obtained. This results from the fact that the data were fewer and the acetylenic compounds were not included in the correlation. The value reported here, although not much different, is considered the more reliable.

[CONTRIBUTION FROM THE DEPARTMENT OF ENGINEERING, UNIVERSITY OF CALIFORNIA]

The Dielectric Constant of *cis*- and *trans*-Decahydronaphthalene and Cyclohexane as a Function of Temperature and Frequency

BY PETER STAUDHAMMER AND WM. F. SEYER

RECEIVED MAY 24, 1958

The dielectric constant of *cis*- and *trans*-decahydronaphthalene as a function of temperature and frequency was measured using highly purified material. The relationship of dielectric constant and temperature were linear in the liquid region between 60 c.p.s. and 4 megacycles. The loss factor was less than 0.0002 in all cases. Re-examination of the discontinuity of the dielectric constant during the freezing process of *trans*-decahydronaphthalene and cyclohexane indicated the presence of several transient solid phases before the stable phase was reached.

Introduction

In a previous publication the dielectric constants of *cis*- and *trans*-decahydronaphthalene as a function of temperature were given.[1] In the course of the measurements certain anomalous behaviors of

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[1] W. F. Seyer and G. M. Barrow, THIS JOURNAL, **70**, 802 (1948).

trans-decahydronaphthalene and cyclohexane were observed during the freezing process. At the time this behavior was thought to be due probably to impurities, hence it was considered worthwhile to repeat the measurements on highly purified materials at different frequencies and temperatures.

Apparatus and Experimental Procedure

The measurement of the dielectric constants was carried out in the cell shown in Fig. 1. The cell consisted of three concentric cylindrical electrodes. The inner and the outer cylinders, which form the walls of the container, were connected to ground at all times, and the center cylinder was energized. Since the center electrode was considerably shorter than the outer ones, the capacitance of the cell was not influenced by anything outside the cell.

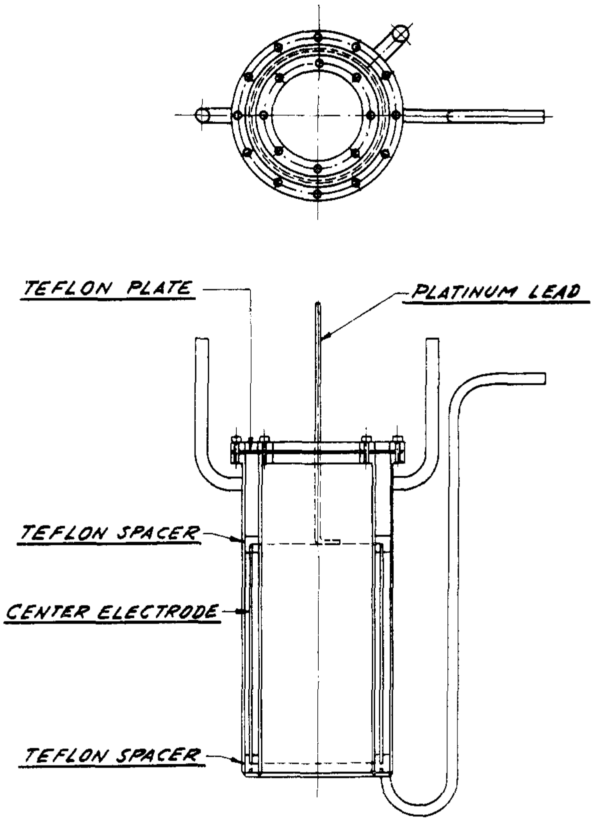

Fig. 1.—Measuring cell.

The walls of the cell and the inner electrode was made of 304 stainless steel tubing. The tubing was machined to such dimensions that the wall thickness of all three cylinders as well as the spacing between them was 1 mm. The volume of liquid required to fit the cell was 41.9 cm. The inner electrode was spaced from the outer ones by means of four small H shaped Teflon spacers at the bottom and at the top, as shown in the figure. Electrical connection to the center cylinder was made by means of a 0.050 in. platinum wire. This wire ran through a Teflon spacer, such that variations in the height of the liquid due to thermal expansion had no effect on the measured capacitance.

The cell was covered at the top with a Teflon gasket, in order to prevent evaporation at high temperatures and condensation at low temperatures. Three stainless steel tubes were connected to the cell for the introduction and withdrawal of the liquids and for the escape of air during filling. The individual stainless steel parts of the cell were soft soldered and then gold plated, such that the liquid inside the cell came into contact with only Teflon and gold. It was felt that with these precautions no chemical reactions took place within the cell. The cell was immersed in a bath whose temperature was regulated to within 0.1°. All temperatures were measured with a Leeds and Northrup resistance thermometer.

As it was planned to study cyclohexane at its freezing point, it was also decided to use it to find the value of the replaceable capacitance. The dielectric constant of cyclohexane has been measured recently by Hartshorn,[2] at the National Physical Laboratory as 2.0250 ± 0.01% at 20°, and the change in dielectric constant with temperature was measured as 0.00155 unit per °C. Measurement of the capacitance of the cell at different temperatures with air and with cyclohexane gave both the replaceable and the non-replaceable capacitance as a function of temperature.

The dielectric constant ϵ_x of any liquid can be found by the formula

$$\epsilon_x = \frac{C_x - C_f}{C_0}$$

where C_0 is the replaceable capacitance, C_f is the non-replaceable capacitance and C_x is the measured capacitance of the cell with the liquid.

The capacitances were measured by the usual substitution method. A General Radio variable capacitance (G R-722D), with full scale of 1100 $\mu\mu$f., was used as the standard. Below 500 kc. a slightly modified shearing bridge was used to detect balance. Provision was made for the measurement of the loss tangent from 0 to 1 in the entire frequency range from 60 c.p.s. to 500 kc. At frequencies higher than 500 kc. a Q-meter was used and the capacitance measurement again was based on the General Radio variable capacitor. At high frequencies a correction due to the inductance of the transmission lines was applied to the measured capacitance.

In the frequency range of 10 to 1000 kc., the capacitance necessary for balance could be read to within 0.05% of full scale. Since the General Radio capacitor was calibrated only to 0.1%, the difference in two readings is accurate to 0.2%. The values of the dielectric constant reported are, therefore, accurate to within 0.2%.

Materials.—The purification of decahydronaphthalene was carried out by fractional distillation followed by fractional crystallization. The freezing point of the *cis* isomer, after 12 successive crystallizations, was found to be −43.15°, while that of the *trans* isomer, after 11 successive crystallizations, was found to be −30.56°.

The freezing points and refractive indices found for the two isomers are compared to values found by other investigations in Table I.

TABLE I

Investigators	Year	F.p., °C. *cis*	F.p., °C. *trans*	n^{20}D *cis*	n^{20}D *trans*
Seyer and Barrow[1]	1948	−43.20	−30.72		
Seyer, Yip and Pyle[3]	1950	−43.27	−30.65		
Mizuhara and Seyer[4]	1953			1.48098	1.46934
This investigation	1957	−43.15	−30.56	1.48097	1.46932

From the time of crystallization to the time they were actually used, both isomers were kept over silica gel, which served to remove any water or other polar substances from the decahydronaphthalene. If any impurities were still left, they had to be non-polar. It is felt that the uncertainty in the dielectric constant due to impurities was much less than 0.1%.

The purification of cyclohexane also was carried out by fractional crystallization. After 13 crystallizations, with a total cumulative time of 275 hours, the final freezing point was found to be 6.51°. Since the cyclohexane was in contact with air during crystallization, the freezing point should be corrected for the concentration of water in the cyclohexane.[5] It has been found by Staudhammer and Seyer[6] that the concentration of water in cyclohexane at its freezing point is approximately 70 parts per million. The depression of the freezing point due to this concentration of

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(2) L. Hartshorn, "Proceedings of the Symposium on Precision Electrical Measurements," Sec. 1, p. 1, National Physical Laboratory, London, Nov. 1954.

(3) W. F. Seyer, S. Yio and G. Pyle, THIS JOURNAL, **72**, 3162 (1950).

(4) S. Mizuhara and W. F. Seyer, *ibid.*, **75**, 3271 (1953).

(5) R. W. Crowe and C. P. Smyth, *ibid.*, **73**, 5409 (1951).

(6) P. Staudhammer and W. F. Seyer, *J. Appl. Phys.*, V. **28**, 405 (1957).

water can be calculated by means of Raoult's law to be 0.02°.

The true freezing point of the final fraction is therefore 6.53°. A similar correction for the freezing point of decahydronaphthalene is not necessary as this compound contains much less water at its freezing point and its heat of fusion is much smaller than that of cyclohexane.

Before use, the cyclohexane was allowed to stand over silica gel, in the hope that any polar compound would be removed. It was felt that in this case also the uncertainty in the dielectric constant due to impurities is less than 0.1%.

Results

The experimental results showed no variation in the dielectric constant of cyclohexane or *cis*- or *trans*-decahydronaphthalene from 60 c.p.s. to 4 megacycles; therefore, only values at 50 kc., where the bridge has its maximum accuracy, are given. The loss factor has been found to be less than 0.0002 at all frequencies and temperatures.

The dielectric constant of liquid *cis*-decahydronaphthalene shows no anomalous behavior at any temperature or frequency in the range from −58 to 93°. It should be noted, however, that some instability in the value of the dielectric constant at 50.1° does occur. The dielectric constant as a function of temperature for *cis*-decahydronaphthalene can be given by

$$\epsilon = 2.211 - 0.00139 \times 10^{-3}t$$

and is shown graphically in Fig. 2. For the *trans* form the following expression applys

$$\epsilon = 2.175 - 0.00136t$$

over a temperature range from −30.0 to 130° (Fig. 3). The molar polarization was found to be remarkably constant for both forms and was calculated to be for the *cis*- 43.61 and for *trans*- 43.98.

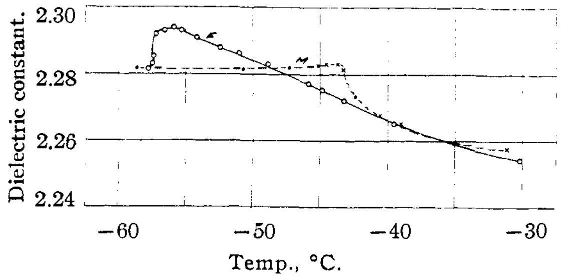

Fig. 2.—Dielectric constant of *trans*-decahydronaphthalene freezing, F and melting, M.

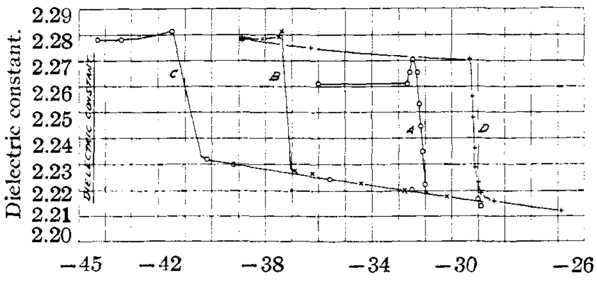

Fig. 3.—Freezing, A, B and C, and melting, D, of *trans*-decahydronaphthalene.

During the freezing process, the dielectric constant of *cis*-decahydronaphthalene exhibits no anomalous behavior but the *trans* form does. As freezing takes place, the dielectric constant first increases and then decreases. The magnitude of the increase, and especially the magnitude of the decrease, are apparently governed by the rate of the freezing process.

In Fig. 3 the data for three representative freezing curves and one melting curve is given. Freezing curve A was seeded slightly below the freezing point. The rates of cooling in the freezing range are 0.039°/min., 0.25°/min. and 0.48°/min. for curves A, B and C, respectively. Curve D represents the melting of the solid obtained in B.

The third hydrocarbon whose dielectric constant was investigated is cyclohexane. Since cyclohexane has been used to calibrate the cell, only measurements during freezing and melting were of any interest.

The behavior of the dielectric constant of cyclohexane at its freezing point is very much like that of *trans*-decahydronaphthalene. During the freezing process, the dielectric constant increases and then decreases. The amount of the decrease after the initial increase depends on the rate of temperature change in the interval in which the decrease takes place. The dielectric constant of the solid assumes any value between 2.0 and 2.1 and is dependent on the rate of cooling after the freezing has taken place.

In Fig. 4 the dielectric constant is given as a function of temperature for a high rate of freezing and a high rate of melting and also for a very low rate of freezing. The freezing curve A was taken at a rate of 2.7° per min., the melting curve B at a rate of 1.8° per min. and the freezing curve C at a rate of 0.01° per min.

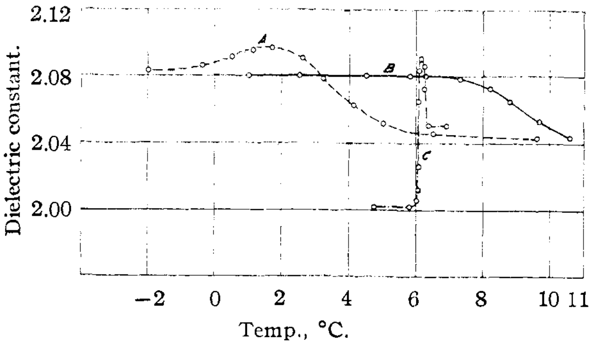

Fig. 4.—Fast freezing, A, fast melting, B, and slow freezing, C, of cyclohexane.

The increase in dielectric constant upon slow melting suggested that a transition may take place below the freezing point. The following experiment was performed in order to check on this.

The temperature of liquid cyclohexane was decreased quickly to 6.1° (the freezing point is 6.5°) and was allowed to remain there for 20 minutes. The dielectric constant quickly increased to 2.103, point P in Fig. 4, and then started to decrease very slowly. Within 20 minutes the dielectric constant had decreased only by 0 002 unit (point Q). The temperature then was quickly lowered to 5.2°, and allowed to stay at this point, R in Fig. 5. With the temperature kept constant, the dielectric constant decreased at a slow rate

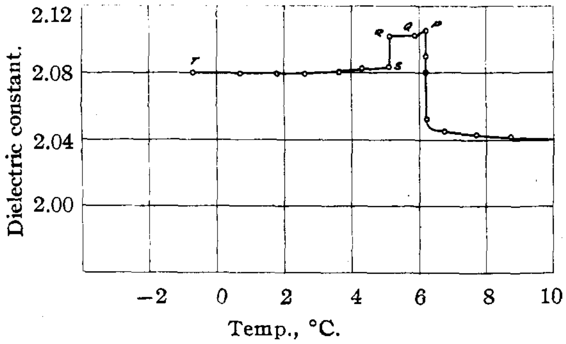

Fig. 5.—Dielectric constant of cyclohexane at the freezing point.

(point R to S). After some decrease had taken place, the temperature was further lowered (point S to T), whereupon the rate of decrease of dielectric constant with time became zero. In successive runs, any value of the dielectric constant between 2.0 and 2.1 could be obtained. The longer the cyclohexane was kept in the range of 5.0 to 6.0° the lower value for the dielectric constant could be obtained. No drift in the dielectric constant over several hours was noted at 3° or below.

Discussion of Results

The disagreement between the values obtained in this investigation and those obtained by Seyer and Barrow[1] is largely due to the fact that the value of the dielectric constant for benzene 2.289 accepted at that time was too high. The present value is given as 2.2836 at 20°. Qualitatively, the behavior of the dielectric constant of the three hydrocarbons has been confirmed during the freezing and melting process. During freezing the value of the dielectric constant for the *cis*-decahydronaphthalene decreases in going from liquid to solid whereas that of the *trans* form rises as does that of cyclohexane (Figs. 6 and 7).

It has been drawn to our attention that Smyth and Crowe could find no anomalous behavior of cyclohexane during the freezing process.[5] Since the m.p. in both cases was 6.5, the divergence in the results may be due to the rate of cooling employed or possibly due to the presence of minute impurities. Thus it has been shown that there is a large increase in the electrical conductivity of cyclohexane during the freezing process with traces of water present.

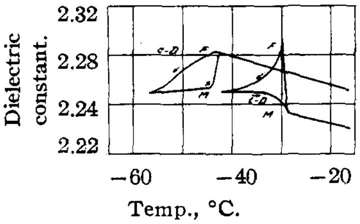

Fig. 6.—Freezing, F, and melting M, of *cis*- and *trans*-decahydronaphthalene after Seyer and Barrow.

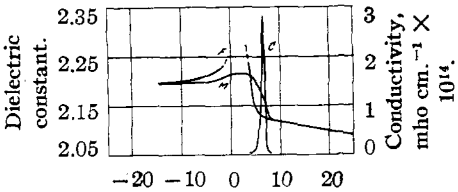

Fig. 7.—Dielectric constant of cyclohexane during freezing, F, and melting, M, after Seyer and Barrow and conductivity of cyclohexane C with excess of water during freezing after Staudhammer and Seyer.

In conclusion, we wish to acknowledge the financial assistance of the Paper-Mate Company of the Gillette Corporation.

LOS ANGELES 24, CALIFORNIA

[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY OF RUTGERS, THE STATE UNIVERSITY]

A Simple Interpretation of Donnan Equilibria Obtained with Long Chain Polyphosphates[1]

BY ULRICH P. STRAUSS AND PAUL ANDER

RECEIVED JUNE 2, 1958

The distribution of electrolyte across a semi-permeable membrane has been measured carefully for long-chain polyphosphates in aqueous solutions of lithium, sodium, potassium and tetramethylammonium bromide as a function of both polymer and salt concentrations. The conventional interpretation of the results in terms of an effective degree of ionization i leads to an increase of i with increasing electrolyte concentration. A more satisfactory interpretation is obtained by considering the Donnan equilibrium as arising from the volume excluded to the salt by the polyelectrolyte chain and its cylindrical ionic atmosphere.

The interactions between polyelectrolytes and simple electrolytes have been the subject of many experimental[2-6] and theoretical[7-14] studies. Yet there is still a considerable lack of understanding of

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(1) This investigation was supported by a grant from the United States Atomic Energy Commission under Contract AT(30-1) 1018. The experimental results presented in this paper will be contained in a thesis to be presented by P. Ander to Rutgers University in partial fulfillment of the requirements for the Ph.D. degree. This paper was presented at a Symposium on Electrokinetic and Membrane Phenomena before the Electrochemical Society, New York, N. Y., April 29, 1958.

(2) R. M. Fuoss and U. P. Strauss, *Ann. N. Y. Acad. Sci.*, **51**, 836 (1949).

(3) D. T. F. Pals and J. J. Hermans, *Rec. trav. chim.*, **71**, 433, 458 (1952).

(4) R. Arnold and J. T. G. Overbeek, *ibid.*, **69**, 192 (1950).

(5) A. Oth and P. Doty, *J. Phys. Chem.*, **56**, 43 (1952).

(6) U. P. Strauss, E. H. Smith and P. L. Wineman, THIS JOURNAL, **75**, 3935 (1953).