with rising temperature in a number of liquid paraffins is due to decrease in intermolecular action.

The zero moment found for the benzene molecule agrees with the less accurate results of the measurements upon the liquid and with the symmetrical structure of the molecule. The zero moment found for propane is consistent with the absence of moment in the higher members of the series and shows that any polarity in the C–C bonds, electrical dissymmetry caused by repulsion in the molecule or difference in electronegativity between the hydrogens on the secondary and those on the primary carbons is too small for detection by means of the electric moment.

The small moments found for toluene and propylene are of the same magnitude as those which might arise from inductive effects in the molecules.

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The Possibility of Dipole Rotation in Certain Crystalline Solids

BY S. E. KAMERLING AND C. P. SMYTH

This paper presents the results of an investigation undertaken with the object of studying a possible contribution to the dielectric constants of certain substances through the rotation of a polar group in a molecule fixed in a crystal lattice or through the rotation of the entire molecule in the lattice, the latter possibility having been suggested by the results of Errera.[1,2] When the molecules of a substance are so fixed in the solid state that any dipoles contained by them are unable to orient at all in an externally applied electric field, the dielectric polarization of the substance consists only of the so-called optical part, $P_E + P_A$, which should be virtually independent of temperature and of frequency within the range ordinarily used in dielectric constant measurements. Any considerable variation of polarization with temperature or frequency should, therefore, be evidence of dipole orientation, that is, of rotation of polar groups or molecules in the solid. In the present measurements, a certain number of molecules are placed between the plates of a condenser by filling the condenser with liquid, which is then frozen. Consequently, as the temperature is lowered, the number of molecules between the plates is not appreciably altered by the changing density of the solid and the apparent value observed for the dielectric constant should not alter with the density. Although this apparent value of the dielectric constant evidently differs by a small but increasing amount from the true value as the temperature falls below the freezing point, it makes an excellent substitute for the polarization, which

[1] Errera, *J. phys. radium*, [6] **5**, 304 (1924).

[2] Smyth, "Dielectric Constant and Molecular Structure," The Chemical Catalog Company, Inc., New York, 1931, p. 38.

is hard to obtain because of the difficulty of measuring the densities of the low melting solids as well as the true dielectric constants.

Apparatus

The apparatus used in measuring the dielectric constants was the capacity bridge employed in a previously described investigation,[3] which was actually carried out after the measurements of the present paper. Current of a pure sine wave form and of frequencies from 200 to 50,000 cycles was supplied to the bridge from an 8A Western Electric oscillator. At the higher frequencies, a six-tube amplifier with a detector and a multimeter as null instrument was used with the bridge, while, at lower frequencies, a two stage transformer-coupled audio frequency amplifier was employed. A resistance in series with the condenser in each of the two capacity arms of the bridge served to balance any conductance in the other capacity arm. As the only appreciable conductance occurred in the measuring condenser, the series resistance in the opposite arm provided a means of calculating the phase angle of this condenser.[4] In the present work, however, only qualitative use has been made of this resistance. When it was large, a considerable error was introduced into the results by the capacities of the coils of the non-inductively wound decade box used as the series resistance.

The other apparatus and methods were similar to those described in previous papers from this Laboratory except in the modification of the measuring condenser and its use. A platinum resistance thermometer cased in glass was inserted inside the innermost of the three concentric gold-plated cylinders of the condenser. Before solidification of the liquid in the condenser, dissolved gas was commonly pumped off as far as possible with a water pump. In spite of this, the occurrence of gas pockets and cracks in the solid tended to lower the value observed for the dielectric constant. The solid was melted and slowly frozen again from the bottom up after the cell had been tapped to drive off gas bubbles. This process was repeated several times until an approximately constant value was reached for the dielectric constant, which was then measured at different temperatures below the melting point and at different frequencies. A 10 or 12% increase in the observed value might be brought about by these successive freezings. The dielectric constant observed was evidently a minimum value, but the values observed for a given solid were fairly accurate relative to one another, except at the lowest frequencies where it was difficult to balance the bridge.

Preparation of Materials

***n*-Heptyl bromide** was obtained as in earlier work.[5]

Anisole.—Kahlbaum anisole was dried with calcium chloride and fractionally distilled. The middle fraction boiling at 153.9–154.1° (769 mm.) was used; n_D^{20} 1.51732; d_4^{20} 0.9951.

Phenol.—Merck "Reagent" phenol was melted and fractionated. The fraction boiling at 181.6° (756 mm.) was used.

Benzoyl Chloride.—Eastman Kodak Company benzoyl chloride was fractionally distilled. The middle portion was again distilled, the fraction boiling constantly at 197.9° being used; n_D^{20} 1.55354; m. p. -0.6°.

Experimental Results

The apparent values determined for the dielectric constants ϵ at the temperatures t and at various frequencies from 50 to 0.2 kilocycles are given

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(3) Smyth and Kamerling, THIS JOURNAL, **53**, 2988 (1931).

(4) See Hague, "Alternating Current Bridge Methods," Sir Isaac Pitman and Sons, Ltd., London, 1923, p. 196.

(5) Smyth and Rogers, THIS JOURNAL, **52**, 2227 (1930).

in Table I. In Table II the rounded values of ϵ at 50 k. c. and the densities obtained from various sources are used to calculate approximate values of the molar polarization, $P = \frac{\epsilon - 1}{\epsilon + 2} \cdot \frac{M}{d}$. The values of the atomic polarization P_A are obtained by subtracting from P the values of the electronic polarization P_E obtained by the extrapolation to infinite wave length of data on refraction taken directly from or calculated from material in Landolt–Börnstein (5th edition).[6]

TABLE I

DIELECTRIC CONSTANTS OF SOLIDS

n-Heptyl Bromide (m. p. − 60°)

t, °C.	50	30	10	5	1	0.2 k. c.
−64.0	2.82	2.82	2.83			
−62.3	..	..	..	No change		

Hydroquinone Dimethyl Ether (m. p. 55.2°)

t, °C.	50	30	10	5	1	0.2 k. c.
−91.0		2.80			2.81	
−30.8	2.81	2.81	2.81		2.81	
−14.8	2.81	2.81	2.82		2.82	2.82
1.6		2.82	2.82		2.82	2.82
29.2	2.82	2.82	2.82	2.82	2.83	2.83
36.3	2.82	2.82	2.82	2.82	2.83	2.83

Anisole (m. p. −37.8°)

t, °C.	50	30	20	10	5	1
−56.3	2.88	2.88		2.88		2.92

No change on cooling 10°

Phenol (m. p. 42.5°)

t, °C.	50	30	10	5	1	0.2 k. c.
−22.3	2.77	2.77		2.77	2.78	2.80
− 4.9	2.79	2.80	2.80	2.80	2.83	2.85
− 5.7	2.81	2.82	2.82	2.83	2.86	2.92
22.9	2.84	2.85	2.86	2.88	2.94	2.98
34	2.89	2.90	2.96	2.96	3.00	3.05

Benzoyl Chloride (m. p. −0.6°)

t, °C.	50	30	10	5	1	0.2 k. c.
−51.1	2.96	2.97	2.98	2.99	3.03	3.14
−31.7	3.02	3.04		3.10	3.14	
−20.3	3.09	3.12	3.12	3.22	3.29	
−10.4	3.33	3.44	3.55	3.64	4.0	

TABLE II

POLARIZATION OF THE SOLIDS

	ϵ	d	P	P_E	P_A
n-$C_7H_{15}Br$	2.8	1.23[a]	55	41.2	14
p-$C_6H_4(OCH_3)_2$	2.8	1.13[b]	46	40.8	5
C_6H_5OH	2.8	1.07[c]	33	27.5	5.5

[a] Extrapolated from the densities of the liquid,[5] probably correct to better than 10%. [b] The average of five determinations with a pycnometer. [c] "International Critical Tables," Vol. I, p. 199.

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[6] *Cf.* Ref. 2, p. 23.

Discussion of Results

A rough attempt has been made to calculate P_A for heptyl bromide because of the surprisingly high value, 15.5, found for it by Smyth and Rogers by means of the variation of the polarization with temperature in solution.[5] The value in Table II is in excellent agreement with that given by the solution measurements, but, if the density of the solid were 10% higher, as is not impossible, the value of P_A given by the solid would drop to 8. The values of P_A for the other substances are of the magnitude usually found for polar molecules of fair size.[7]

The values in Table I show positively that heptyl bromide, hydroquinone dimethyl ether, and anisole give no dipole orientation in the alternating electric field in the ranges of temperature and frequency used. This means not only that the large polar molecules do not turn as a whole in the field but also that the polar CH_3—O group, which might be mobile about its bond to the ring, is not turned by the field. The results on phenol and benzoyl chloride are inconclusive. The dielectric constants increase somewhat with rising temperature and decreasing frequency of the field in the manner that might be expected if an occasional molecule or polar group attached to the ring were able to turn in the field. However, the same effects could arise from the displacement in the field of small amounts of ions, which would be more important as the melting point was approached and the frequency lowered. As phenol and benzoyl chloride are difficult substances to obtain in a very pure state, it appears probable that the small variation of dielectric constant observed is due to the presence of impurities rather than to any motion of the large molecules as a whole or of their polar groups.

Summary

A low frequency capacity bridge is used to measure the dielectric constants of certain crystalline solids over a range of temperature from the melting point down and at frequencies from 200 to 50,000 cycles. Heptyl bromide, hydroquinone dimethyl ether and anisole show no turning of the molecules or of their polar groups in the externally applied field, while, in phenol and benzoyl chloride, effects which might indicate such turning are attributed to the presence of small quantities of impurities. The atomic polarizations of three of these substances are calculated.

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[7] Ref. 2, p. 164.