[CONTRIBUTION FROM THE FRICK CHEMICAL LABORATORY OF PRINCETON UNIVERSITY]

Non-Rotation of Molecules in a Number of Solids

BY S. A. McNEIGHT AND C. P. SMYTH

This paper presents the negative results of investigation through dielectric constant measurements on a number of solids in which the size and shape of the molecule or the properties of the substance indicated the possibility of molecular rotation. The apparatus and method employed was essentially the same as that described in earlier papers.[1] The work on benzophenone was carried out by Dr. W. S. Walls.

Purification

Methylamine.—This was prepared by the action of a concentrated potassium hydroxide solution on Merck C. P. methylamine hydrochloride, dried by passing over fused potassium hydroxide, condensed by a carbon dioxide–acetone slush and fractionally distilled, the middle third being collected directly in the dielectric constant cell. Evaporation of the last third of the material at about 183°K. left no residue, m. p. 179.7°K.

Ethyl Ether.—The material used was part of a sample carefully purified for freezing point measurements.[2]

Acetone.—C. P. acetone was dried by standing over fused calcium chloride for some weeks with a subsequent fractional distillation from a fresh supply of calcium chloride; m. p. 178.2°K.; b. p. 329.3°K.

Benzophenone.—Material from the Florasinth Laboratories, Inc., was dissolved in a small amount of benzene and filtered. The benzene was distilled off and the residue fractionally crystallized ten times; m. p. 321.2°K. A portion of the original material was fractionally distilled under reduced pressure and a sample boiling from 457.6 to 458.1°K. was collected and measured. This material showed such dispersion of the dielectric constant that the sample purified by fractional crystallization was used for the measurements reported in Table I.

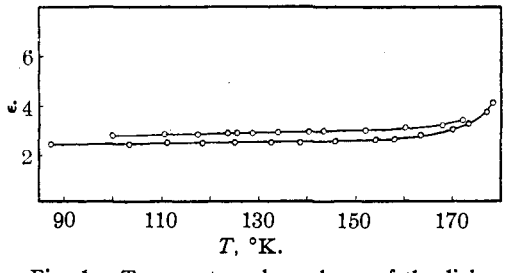

Fig. 1.—Temperature dependence of the dielectric constants (at 50 kc.) of acetone and methylamine; upper curve, acetone; lower curve, methylamine.

Succinic Acid.—C. P. succinic acid was recrystallized from water three times; m. p. 455.9°K. The material on which measurements were made probably contained appreciable amounts of succinic anhydride since melting was necessary in order to fill the condenser and a melting point determination made at the conclusion of the measurements gave 453.6°K.

Experimental Results

The dielectric constants ϵ and the specific conductances $k(\text{ohm}^{-1}\,\text{cm}^{-1})$ are given in Table I, the absolute temperatures being given in the first column and the frequencies in kilocycles across the top of each group of data. Unless otherwise indicated, the values were obtained with rising temperature. As the material in each case is frozen between the fixed plates of the measuring condenser, the value found for the dielectric constant does not change because of change in the number of molecules per cc. with temperature. For an approximate calculation of the polarization of the solid at any temperature, the density at the melting point is the one to be used. Many values of the dielectric constant at intermediate frequencies and temperatures have been omitted for the sake of brevity. As no appreciable dependence upon frequency was observed for ether, its dielectric constant values are given only at 5 kc. and its specific conductances, 0.02×10^{-9} for the solid and 0.04×10^{-9} for the liquid at 5 kc., are omitted.

Discussion of Results

As methyl alcohol has been found to show rotation with some difficulty above a transition point, methylamine, which has a melting point 4° higher, a dipole moment 1.23 instead of 1.68×10^{-18} and a molecule rather similar in shape and size, might also be expected to show molecular rotation. Figure 1 shows that the dielectric constant rises rapidly above 160°K., the rapidity increasing with increasing temperature and decreasing frequency. The first part of the rise appears like the curves for ice, in which the molecules evidently turn with difficulty, but the very steep rise as the melting point is approached and the great increase in conductance as compared to a maximum in the conductance curve shown by ice and by methyl alcohol show that this rise in dielectric constant is not due to the setting in of molecular rotation in the solid but is caused by impurities, which give rise

(1) Smyth and Hitchcock, THIS JOURNAL, **54**, 4631 (1932); **55**, 1830 (1933).

(2) Huettig and Smyth, *ibid.*, **57**, 1523 (1935).

TABLE I

DIELECTRIC CONSTANTS AND SPECIFIC CONDUCTANCES

Methylamine (m. p. 179.7°K.)

Kc T, °K.	50	5 ϵ	0.5	50	5 $k \times 10^9$	0.5
87.6	2.47	2.46	2.42	0.58	0.01	0.01
91.8	2.48	2.46	2.40	.58	.01	.01
103.7	2.48	2.46	2.41	.67	.01	.01
111.3	2.50	2.48	2.42	.67	.01	.01
118.6	2.52	2.48	2.44	.67	.01	.01
125.3	2.52	2.49	2.46	.67	.03	.01
132.9	2.55	2.52	2.48	.76	.03	.01
138.6	2.56	2.53	2.53	.76	.03	.03
145.8	2.57	2.59	2.84	.93	.21	.09
150.0	2.58	2.64	3.16	1.30	.35	.15
154.4	2.60	2.78	3.68	1.91	.61	.21
158.1	2.66	3.01	4.56	3.17	1.06	.35
163.4	2.83	3.60	5.91	6.41	2.18	.91
170.1	3.05	4.14	7.37	9.46	3.22	1.50
173.4	3.22	4.47	7.68	11.0	3.76	1.93
177.2	3.78	5.21	9.22	15.9	4.84	2.14
178.4	4.12	6.62	12.6	20.3	9.25	8.04
179.0		9.17			23.0	

Ethyl Ether (m. p. 156.8°; f. p. 149.8°K.)

Kc.....5 T, °K.		Kc.....5 T, °K.		Kc.....5 T, °K.	
Cooling		Warming			
173.0	9.04	145.0	2.28	167.8	9.49
169.9	9.55	147.8	2.28	172.2	9.05
164.1	9.91	148.7	2.29	198.3	7.25
161.4	10.17	149.3	2.30	205.9	6.87
160.1	10.32	149.5	2.30	213.0	6.55
156.4	10.72	149.7	2.30	223.1	6.13
154.3	11.02	150.0	2.30	232.3	5.80
153.2	11.21	150.2	2.30	243.9	5.45
151.5	11.36	151.6	2.31	250.7	5.26
150.8	11.47	152.5	2.33	263.4	4.96
150.1	11.55	153.6	2.35	272.6	4.75
149.3	11.64	155.6	2.43	287.2	4.42
148.7	11.73	155.9	2.46	294.2	4.27
147.6	11.88	156.0	2.52	295.9	4.17
147.0	11.98	156.2	2.58	Refrozen, warming	
146.3	12.07	156.4	2.73	89.9	2.20
145.2	12.22	156.5	2.82	91.6	2.20
149.8	8.02	156.6	3.38	99.5	2.20
149.8	7.71	156.7	4.08	106.2	2.20
149.8	3.20	156.8	6.46	117.0	2.21
Solid		156.9	8.28	128.7	2.30
		157.0	10.02	136.9	2.30
149.8	2.26				
148.6	2.24	Liquid			
146.7	2.22	157.0	10.42		
136.0	2.18	157.2	10.37		

Acetone (m. p. 178.2°K.)

Kc T, °K.	50	5 ϵ	0.5	50	5 $k \times 10^9$	0.5
100.2	2.80	2.82	2.84	0.20	0.02	0.01
103.9	2.80	2.83	2.85	.20	.02	.01
110.7	2.82	2.85	2.86	.20	.02	.01
117.5	2.85	2.88	2.89	.20	.02	.01
123.7	2.87	2.90	2.92	.20	.02	.01
124.9	2.87	2.90	2.93	.24	.02	.01
125.7	2.88	2.90	2.93	.27	.03	.01
126.7	2.88	2.92	2.94	.28	.03	.01
128.8	2.89	2.93	2.97	.29	.04	.01
134.0	2.92	2.99	3.00	.47	.05	.01
140.3	2.99	3.04	3.04	.59	.03	.01
143.3	3.00	3.04	3.06	.48	.03	.01
152.0	3.04	3.08	3.17	.33	.07	.04
160.2	3.10	3.22	3.57	.55	.22	.10
168.0	3.20	3.49	4.59	1.51	.70	.29
172.4	3.39	4.01	5.96	4.11	1.97	1.33

Benzophenone (m. p. 321.2°K.)

Kc T, °K.	70	12	3	0.7	0.3
200.4	3.16	3.15	3.15	3.16	3.15
214.1	3.16	3.15	3.15	3.16	3.15
222.6	3.16	3.15	3.15	3.16	3.15
235.1	3.16	3.15	3.15	3.16	3.15
244.6	3.16	3.15	3.15	3.16	3.16
255.1	3.16	3.15	3.15	3.16	3.16
266.3	3.16	3.15	3.15	3.16	3.15
279.6	3.16	3.15	3.15	3.16	3.16
288.9	3.16	3.15	3.16	3.17	3.17
297.6	3.16	3.16	3.16	3.18	3.19
306.1	3.17	3.16	3.17	3.20	3.23
313.3	3.18	3.17	3.20	3.25	3.31
319.6	3.26	3.27	3.30	3.37	3.42
Liquid					
320.6	11.50	11.51	11.55	11.73	12.01
321.6	11.45	11.47	11.52	11.70	11.98
325.6	11.26	11.28	11.35	11.58	11.85

Succinic Acid (m. p. 455.9°K.)

Kc T, °K.	5 ϵ	5 $k \times 10^9$	Kc T, °K.	5 ϵ	5 $k \times 10^9$
Cooling					
387.4	5.35	1.27	270.5	2.56	0.03
370.0	2.90	0.24	258.3	2.56	.03
334.1	2.74	.06	247.2	2.54	.03
305.4	2.66	.03	238.1	2.53	.03
298.2	2.64	.03	217.0	2.53	.03
289.6	2.58	.03			
285.2	2.56	.03			
276.9	2.56	.03			
Warming					
223.1	2.52	0.03	260.2	2.36	0.05
228.5	2.51	.03	271.0	2.42	.11
237.3	2.51	.03	271.7	2.43	.12
252.0	2.53	.03	272.3	2.44	.14
Melted and refrozen (m. p. 453.6°K.)			272.6	2.46	.17
			273.1	2.47	.17
100	2.29	0.01	273.2	2.48	.18
112	2.29	.01	273.4	2.49	.19
122.2	2.29	.01			
175.3	2.30	.01			
188.8	2.31	.02			
205.5	2.31	.02			
214.7	2.32	.02			
222.5	2.34	.04			
234.7	2.35	.03			
247.1	2.36	.04			

to traces of liquid and probably ionic displacements. The presence of these impurities is indicated by the fact that the melting point of the sample used was 0.9° lower than that found by Timmermans and Mattaar[3] and lacking in sharpness. The size, shape and dipole moment of the methylamine molecule are such that its rotation in the solid might occur at least as easily as that of the methyl alcohol molecule. As this begins to show limited rotation only 15.5° below its melting point, the rotation of the methylamine molecule might be expected to begin a few degrees below its melting point. However, the uncertainty in the effects of the various factors is more than enough to make possible the postponement of rotation in the solid until a temperature above the melting point is reached. Methylamine resembles ammonia, which shows no molecular rotation in the solid, much as methyl alcohol does water, which turns with difficulty in the solid. The absence of any rotation of the $-NH_2$ group in the molecule is like that in aniline, which shows no molecular or group rotation.[1]

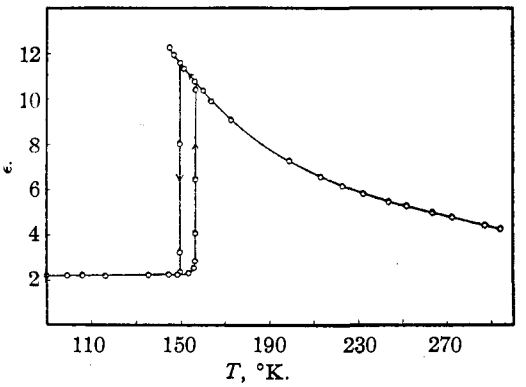

Fig. 2.—Temperature dependence of the dielectric constant (at 5 kc.) of ethyl ether.

It may be concluded from the low dielectric constant values found[4] for solid methyl chloride, bromide and iodide that there is no molecular rotation around any axis perpendicular to the carbon–halogen line, the dielectric constant giving no information as to rotation around the carbon–halogen line, in which the molecular dipole lies. Low dielectric constants found[4] for solid methylene chloride and chloroform show that these molecules do not rotate around any axes perpendicular to their one axis of symmetry. It is probable that all of these molecules are so located in their lattices as to block one another's rotations around axes perpendicular to those in which their dipoles lie, such rotation being presumably much more difficult than rotation of the methylamine molecule around the C–N line or of the methyl alcohol molecule around the C–O line.

The dielectric polarization of ethyl ether in solution and in the pure liquid state shows very little orienting force between the molecules.[5] As the freezing point is 7° lower than the melting point, a change from an unstable to a stable form apparently occurring in the solid, one would anticipate a considerable amount of molecular freedom in the solid. The dielectric constant–temperature curve in Fig. 2 shows clearly the different freezing and melting temperatures and shows equally clearly by its low and almost horizontal position below the freezing point the absence of molecular rotation in the solid. The curves for falling and rising temperature are coincident below the freezing point and show no sign of any transition, therein agreeing with the absence of discontinuity in the temperature–time curves run in this Laboratory.[2] The curve gives no sign of the behavior reported for liquid ether by Mazur,[6] whose measurements showed a rise in dielectric constant from 4.18 at 303.7°K. to a maximum of 12.39 at 167.7°K. followed by a decreasingly rapid decrease with further lowering of temperature, then a slight increase with only a small break downward on freezing. Mazur ascribed this phenomenon to the formation of two liquid phases by the ether, which was supposed to undergo a transition at 167.7°K., but Smits[7] has concluded that Mazur's results are due to the presence of impurities. The material measured in the present work appeared to be very pure, since the melting point was shown by temperature–time curves to be very sharp and in excellent agreement with the carefully determined value of Timmermans and Martin[8] as well as that of Skau.[9] The failure to find the abnormal behavior reported by Mazur for liquid ether parallels a similar failure in the case of nitrobenzene.[1] The specific volume 1.156[10] at 150°K. and the dielectric constant 2.20 from 89.9 to 106.2°K. give a polarization value 24.5, from which subtraction of the electronic

(3) Timmermans and Mattaar, *Bull. soc. chim. Belg.*, **30**, 213 (1921).

(4) Morgan and Lowry, *J. Phys. Chem.*, **34**, 2385 (1930).

(5) Smyth, "Dielectric Constant and Molecular Structure," The Chemical Catalog Co., Inc., New York, 1931, p. 180.

(6) Mazur, *Nature*, **126**, 649 (1930).

(7) Smits, *Z. physik. Chem.*, **A160**, 225 (1932).

(8) Timmermans and Martin, *J. chim. phys.*, **25**, 411 (1928).

(9) Skau, *J. Phys. Chem.*, **37**, 609 (1933).

(10) Isnardi, *Z. Physik*, **9**, 160 (1922).

polarization 22.0[11] gives 2.5 for the atomic polarization in fair agreement with the value 3.3 obtained by Fuchs.

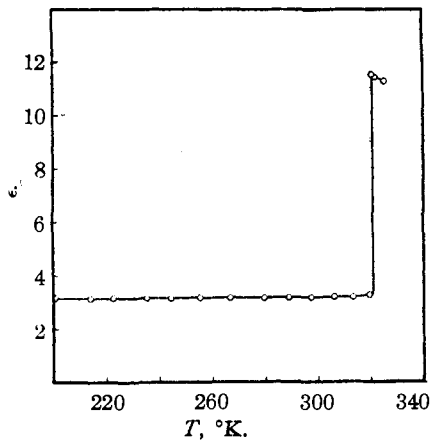

Fig. 3.—Temperature dependence of the dielectric constant (at 70 kc.) of benzophenone.

The considerable departure of the acetone molecule from a spherical or cylindrical shape would lead one to expect no rotation in the solid. This expectation is borne out by the dielectric constant values in Table I and Fig. 1, the rapid increase of both dielectric constant and conductance and their variation with frequency as the region of the melting point is approached being caused by impurities as in the case of methylamine. Special care was taken with the measurements in the neighborhood of 126°K., where a small hump had been found[12] in the specific heat–temperature curve but no irregularity was observed in the dielectric constant–temperature curve at any of the frequencies used. Pauling has suggested[13] that the small hump sometimes observed in specific heat–temperature curves is due to the setting in of rotation of a group within the molecules. Although the dielectric constant values show that the entire molecule does not rotate in the solid, they would not be affected appreciably by rotation of the methyl groups in the molecule, which may be the cause of the hump in the specific heat curve. Use is made of the density 0.9686 of solid acetone at its melting point given by "International Critical Tables" to calculate the polarization of the solid at 100°K. The value 22.7 thus obtained gives an atomic polarization value 7, which is almost certainly too high. The small but not negligible variation of dielectric constant with frequency and temperature even down to 100°K. shows that it has not quite settled down to the value which arises wholly from induced shifts of charge in the molecule.

Although benzophenone exists in an unstable monoclinic form as well as in a stable rhombic, the large size of its molecule and its great departure from spherical shape render molecular rotation even more improbable than in acetone. The absence of molecular rotation is established very clearly by the data in Table I and Fig. 3, which show a dielectric constant value independent of frequency and temperature for temperatures more than 20° below the melting point. The considerable rise on melting is due to the large dipole moment of the molecule.

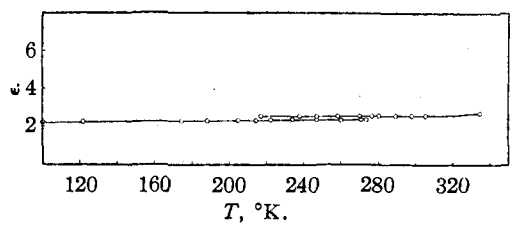

Fig. 4.—Temperature dependence of the dielectric constant (at 5 kc.) of succinic acid; lower curve after remelting and refreezing.

As the variation of the dielectric constant of succinic acid (Fig. 4) apparently was caused by impurities, the values at frequencies other than 5 kc. are omitted from Table I. It was necessary to melt the substance in order to fill the space between the condenser plates which undoubtedly produced appreciable quantities of succinic anhydride as shown by the somewhat lower melting point obtained on a second melting. To investigate the effect of increasing quantities of the anhydride, the dielectric constant–temperature curve for the refrozen sample was obtained but, aside from a decrease in the temperature at which variation with frequency became pronounced, little change was observed. The specific heat–temperature curve of succinic acid[14] shows a hump, with a heat effect of 41 cal. per mole at 272°K. The dielectric constant values give no indication of any effect as they vary slightly but steadily both on heating and cooling through this temperature. It would appear therefore that this effect cannot be due to rotation of the molecule or of any groups within the molecule since such rota-

(11) Fuchs, *Z. Physik*, **63**, 824 (1930).
(12) Kelley, THIS JOURNAL, **51**, 1145 (1929).
(13) Pauling, *Phys. Rev.*, **36**, 430 (1930).
(14) Parks and Huffman, THIS JOURNAL, **52**, 4381 (1930).

tion would cause an increase of the dielectric constant at the temperature of its appearance. Unfortunately it proved impossible, due to the high conductance, to investigate the transition at 310°K. where a transition from a triclinic to a monoclinic form has been observed.[15]

Such variation of dielectric constant and conductance with frequency and temperature as has been found for these substances has been dismissed as not being significant of rotation. The ordinary direct current conductance rises with rising temperature as does that of a liquid and the alternating current conductance increases with increasing frequency.[16] The apparent capacity of a condenser and, hence, the value of the dielectric constant calculated from it, increases with decreasing frequency and resistance.[17] At very high frequencies and resistances the effect upon the apparent capacity is slight or negligible, but at the lower frequencies employed in these measurements and with the lower resistances in the region of the melting point, the effect is considerable. It is well illustrated by the dielectric constant values for liquid benzophenone (Table I), where there can be no question of a true anomalous dispersion. The value for the slightly supercooled liquid increases only 0.01 on lowering the frequency from 70 to 12 kc., but increases 0.50 on further lowering the frequency from 12 to 0.3 kc., more than half of the increase occurring between 0.7 and 0.3 kc. A temperature rise of 5° lowers the resistance and thus increases the effect slightly. As the conductivity of a material of low conductivity is tremendously affected by the presence of minute traces of ionic impurities, the effects under discussion have been attributed mainly to impurities rather than to the properties of the pure substances under examination. Although the effects are undoubtedly due primarily to the conductances of the materials examined, there remains a possibility, particularly in the case of methylamine, that an occasional molecule may have sufficient freedom of rotation to orient in the electric field or that a larger number of molecules executing small rotational oscillations in their lattices may each contribute very slightly to the dielectric constant through a distortion of the oscillation by the field.

(15) La Tour, *Compt. rend.*, **193**, 180 (1931); *Ann. phys.*, **18**, 199 (1932).

(16) *Cf.* Murphy, *Trans. Am. Electrochem. Soc.*, **65**, 133 (1934).

(17) Joffé, "The Physics of Crystals," McGraw-Hill Book Company, Inc., New York, 1928, p. 148.

Summary

The dielectric constants of solid methylamine, ethyl ether, acetone, benzophenone and succinic acid have been measured over a wide range of temperature and frequency to investigate the possibility of rotation of their molecules. Although the molecular shape of methylamine is such that rotation might well occur and although ether shows different freezing and melting points, benzophenone shows polymorphism, and acetone and succinic acid show humps in their specific heat–temperature curves, no molecular rotation has been found in these solids.

The low dielectric constants of solid methyl chloride, bromide and iodide, methylene chloride and chloroform are used to show that, in the solid state, their molecules cannot rotate around any axes perpendicular to the axis of molecular symmetry.

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