Molecular Rotation in Solid Aliphatic Alcohols

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

A previous investigation has given indications of the occurrence of dipole rotation in solid methyl alcohol.[1] This paper presents the results of measurements of the dielectric constants of methyl, tertiary butyl and n-octyl alcohols from liquid air temperatures to the melting points. The apparatus and technique employed were essentially the same as that described in earlier papers from this Laboratory,[2] the same bridge being used.

Purification

Methyl Alcohol.—C. P. synthetic methyl alcohol was refluxed over lime for several hours and fractionally distilled. The middle fraction was then fractionally distilled from shiny magnesium ribbon, b. p. 64.74 ± 0.05°.

Tertiary Butyl Alcohol.—An Eastman Kodak Co. product was washed with a saturated solution of sodium bisulfite, the alcoholic layer decanted and refluxed for several hours with 10% sodium hydroxide solution. The alcohol was distilled off and dried with sodium sulfate and potassium carbonate and then refluxed over lime for several hours before distilling. The lime treatment was repeated, after which the distillate stood over calcium turnings for two days before distilling. The final fractional distillation was made from tartaric acid; b. p. 82.3°. The distillate was then recrystallized from its own melt four times; m. p. 24.8°.

Octanol-1.—The material was part of a sample employed in a previous determination of dipole moment.[3]

Experimental Results

The dielectric constants ε and the specific conductances k (ohm^{-1} 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. Many determinations at intermediate temperatures and frequencies are omitted for the sake of brevity. Unless otherwise indicated, the values were obtained with rising temperature. The values for methyl alcohol could not be extended to higher temperatures because increasing conductance made the bridge measurements too inaccurate.

Discussion of Results

The melting point found for methyl alcohol, 175.4°K., is sharp and is in very good agreement with the value 175.3°K. given in "International Critical Tables" but indicates a less pure sample

(1) Smyth and Hitchcock, THIS JOURNAL, **56**, 1084 (1934).
(2) Smyth and Hitchcock, *ibid.*, **54**, 4631 (1932); **55**, 1830 (1933).
(3) Smyth and Stoops, *ibid.*, **51**, 3312 (1929).

TABLE I

DIELECTRIC CONSTANTS AND SPECIFIC CONDUCTANCES

Methyl Alcohol (m. p. 175.4°K.)

Kc.....	50	5	0.5	50	5	0.5
T, °K.	ε			$k \times 10^9$		
108.4	3.22	3.28	3.36	0.96	0.17	0.02
126.6	3.38	3.52	3.66	2.27	.30	.04
138.0	3.54	3.76	3.92	3.61	.40	.04
154.9	3.68	3.93	5.07	3.60	1.78	1.12
156.5	3.73	4.10	5.65	5.00	2.85	1.82
157.3	3.78	4.21	6.01	6.31	3.59	2.35
158.2	3.81	4.37	6.50	7.74	4.65	3.14
159.0		4.46			5.55	
159.4		4.56			6.20	
159.9		4.66			7.01	
159.9		5.65			5.64	
160.0		5.97			5.04	
161.0		7.03			3.47	
163.2	6.46	7.50	10.82	13.0	4.23	1.48
169.0	6.88	9.00		27.7	9.16	
171.6		10.82			16.6	
173.8		15.43			50.2	
(Falling temperature)						
166.2		8.15			6.06	
157.5		6.95			3.21	
150.8		6.46			0.88	
138.8		6.35			.19	
132.9		5.59			.28	

Tertiary Butyl Alcohol (m. p. 297.9°K.)

T, °K.	50	5	0.5	50	5	0.5
94.3	2.23	2.22	2.20	0.17	<0.01	<0.01
99.7	2.24	2.24	2.19	.17	< .01	< .01
111.5	2.24	2.24	2.20	.18	< .01	< .01
120.5	2.24	2.24	2.20	.17	< .01	< .01
131.0	2.24	2.24	2.21	.17	< .01	< .01
140.0	2.24	2.25	2.22	.17	< .01	< .01
143.2	2.25	2.25	2.22	.17	< .01	< .01
152.6	2.26	2.26	2.22	.18	< .01	< .01
162.1	2.26	2.26	2.23	.18	< .01	< .01
179.9	2.27	2.27	2.24	.18	< .01	< .01
196.4	2.28	2.28	2.25	.17	.02	< .01
213.7	2.30	2.30	2.28	.17	.02	.02
228.6	2.32	2.31	2.29	.17	.02	.02
234.8	2.32	2.32	2.29	.18	.02	.02
251.5	2.35	2.36	2.35	.18	.04	.02
257.9	2.40	2.42	2.50	.81	.15	.04
272.9	2.53	2.70	3.23	2.88	1.04	.52
287.9	2.74	3.04	3.86	4.01	1.53	.67
(after 24 hours)						
292.2	2.53	2.66	3.03	2.23	0.72	0.32
295.3	2.69	2.96	3.68	2.83	1.52	.71
297.4	3.50	4.12	5.43	6.08	5.52	3.78
Liquid						
299.2		12.12			26.6	
301.9		11.92			29.6	

TABLE I (Concluded)

Octanol-1 (m. p. 256.8°K.)

Kc.	50	5	0.5	50	5	0.5
T, °K.	ϵ			$k \times 10^9$		
87.3	2.32	2.32	2.25	0.67	<0.03	<0.03
102.6	2.32	2.32	2.25	.70	< .03	< .03
118.8	2.33	2.32	2.26	.67	< .03	< .03
128.8	2.33	2.33	2.29	.67	< .03	< .03
159.1	2.34	2.36	2.33	.67	.03	< .03
179.1	2.35	2.38	2.42	.93	.06	< .03
208.0	2.36	2.47	2.60	1.22	.15	< .03
249.2	2.71	3.06	4.50	3.71	.97	.32
251.3	2.77	3.25	5.70	4.11	1.41	.53
253.7	3.03	4.15	9.13	6.49	3.28	1.50
254.6	3.63	5.38	11.7	10.0	6.63	4.07
255.5	5.55	7.47	12.3	17.2	14.9	13.7
256.0	6.58	8.70		21.8	19.9	
256.6	9.63	11.79		32.3	34.6	
		Liquid				
258.9	12.97	13.0	13.1	48.5	48.1	51.1
260.9	12.71	12.82	13.1	54.6	53.1	57.5
262.0	12.66	12.80	13.1	58.2	56.0	56.9
269.1	11.93	12.22	12.7	78.2	76.0	77.4
272.6	11.60	11.87	12.3	92.5	89.6	90.5
287.1	10.34	10.57	11.0	127	124	125
296.3	9.47	9.58	10.1	140	139	141
		Solid Cooling				
252.5	4.08	4.80	5.4	8.48	2.43	0.24
222.1	2.36	2.46	2.48	1.63	0.09	< .03
203.8	2.30	2.36	2.36	1.05	.06	< .03
		Warming				
210.9	2.30	2.39	2.40	1.05	.09	< .03
217.0	2.32	2.42	2.44	1.25	.09	< .03
224.2	2.34	2.45	2.52	1.40	.12	< .03
230.5	2.36	2.50	2.62	1.63	.15	.03
237.2	2.41	2.56	2.78	1.92	.25	.06
243.6	2.46	2.66	3.17	2.30	.35	.12
249.7	2.56	2.89	4.20	3.07	.70	.18
252.5	2.68	3.18	4.33	3.78	1.05	.24

than that for which Timmermans and Hennaut-Roland[4] report 176.1°K. It is to be regretted that the difficulty of purification has prevented the removal of the last traces of impurity, which have some effect upon the results in the neighborhood of the melting point. The dielectric constant curve in Fig. 1 for a frequency of 5 kilocycles shows a transition at 159.9°K. with a sharp rise in value with rising temperature. The transition is somewhat obscured by anomalous dispersion both below and above it but for high frequencies the change in the value of the dielectric constant is quite sharp and a time–temperature curve shows a halt at 159.9°K. for a period of between thirty and forty minutes for rising temperature. The apparent conductance at 5 kc.

also shows a maximum at this temperature. This is 0.8° higher than that previously reported but differs by only 0.1° from the transition temperature found for another sample and lies between the values found from specific heat measurements, 157.4°K. by Kelley[5] and 161.1°K. by Parks.[6] Falling temperature gives a very much delayed transition, for with decreasing temperature the high temperature form has been observed as far down as 133°K., whereas with rising temperature a lag of more than 0.1° has never been detected.

The solid, in spite of every effort to purify it, contains a small amount of impurity, presumably water, as shown by the slightly low melting point and the slight premelting indicated by a time–temperature curve taken over the melting range. As the eutectic point of the methyl alcohol–water system is about 134°K.,[7] a minute trace of liquid would remain down to this temperature, which is just about where the cooling dielectric constant curve dips downward toward the rising temperature curve. This apparent hysteresis loop, which, unfortunately, was not completed experimentally, is not unlike that found for phenol containing a trace of water. It may arise from the presence of a minute quantity of liquid, which would raise the dielectric constant, or it may be due merely to an unusually large lag in the transition, supercooling undoubtedly occurring. Probably, both factors contribute to the seeming discrepancies and the changes of dielectric constant and conductance with time observed here and in the earlier work. The considerable variation of the dielectric constant and the conductance with frequency is doubtless contributed to by the liquid, but the uniform rise of dielectric constant with temperature below and above the eutectic point of the methyl alcohol–water system, the difference between it and the much lower values, almost constant in this region, found for t-butyl and octyl alcohols, and the sharp rise at the transition followed by a further rapid increase as the temperature rises toward the melting point indicate a very small amount of rotation at low temperature, increasing with temperature and rising sharply at the transition, which loosens the structure. Even above the transition, rotation encounters a resistance which diminishes with rising temperature and causes the dielectric constant to be higher at lower frequencies. The approxi-

(4) Timmermans and Hennaut-Roland, J. chim. phys., 27, 401 (1929).

(5) Kelley, THIS JOURNAL, 51, 180 (1929).

(6) Parks, ibid., 47, 338 (1925).

(7) Baumé and Borowski, J. chim. phys., 12, 276 (1914).

mate value calculated for the polarization at 108.4°K. is 13.8 as compared to a molecular refraction 8.23 for the D sodium line while at 173.8° it is 27.4, values indicative of rotation, as the difference 5.6 between the polarization at the low temperature and the refraction seems too high to arise entirely from the atomic polarization of so small a molecule.
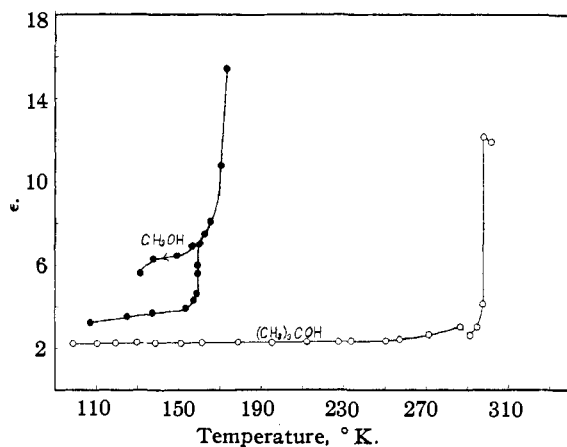

Fig. 1.—Variation with temperature of the dielectric constants (5 kc.) of methyl and *t*-butyl alcohol.

The dielectric constant of solid *t*-butyl alcohol at 5 kc. (Fig. 1) is as low as that of liquid benzene and other non-polar substances, showing the absence of any freedom of the dipole in the molecule to rotate. The small rise in the dielectric constant and the considerable rise in the conductance as the melting point is approached is the normally observed behavior, and is, presumably, due to the presence of traces of impurities which cause very small quantities of liquid to form in this region of temperature. The small break in the curve at 287.9°K. is the effect of twenty-four hours' standing between measurements, which is apt to cause a setting of the structure and reduction of molecular freedom. The increase of dielectric constant with decrease in frequency is reduced by this setting and the apparent conductance is cut in half. In the case of *n*-octyl alcohol, the resolidified sample gave a slightly lower dielectric constant depending less on frequency and a lower conductance except at the first temperature measured after solidification. The dielectric behavior of *n*-octyl alcohol (Fig. 2) is practically identical with that of *t*-butyl, the curves being hardly distinguishable at the lower temperatures. A slight rise with some dependence upon frequency develops near the melting point, probably due mainly to the presence of minute quan-

tities of liquid, but possibly due in part to an occasional molecular rotation with loosening of the structure just below the melting point. In general, however, there is obviously no appreciable amount of rotation of the molecule as a whole or of the hydroxyl group in the molecule in either of these two alcohols in the solid state.

Dielectric constant measurements on phenol[2] and specific heat measurements on many alcohols have failed to show rotation. It is evident, therefore, that the rotation in solid methyl alcohol must be a rotation of the entire molecule rather than of the hydroxyl group within the molecule, since the latter could occur equally well in the other alcohols. As rotation of the methyl alcohol molecule around its C–O axis should involve little change in the space occupied by the molecule, such rotation would probably not be blocked by the surrounding molecules. The main hindrance would be the strong intermolecular attraction probably expressing itself in the formation of a hydrogen bond between molecules such as seems to exist in ice.[8] The opportunity for such bond formation is not as good as in ice and, even in ice, the dielectric constant gives evidence of some molecular rotation. The anomalous dispersion in ice is much stronger than in solid methyl alcohol, probably because of the
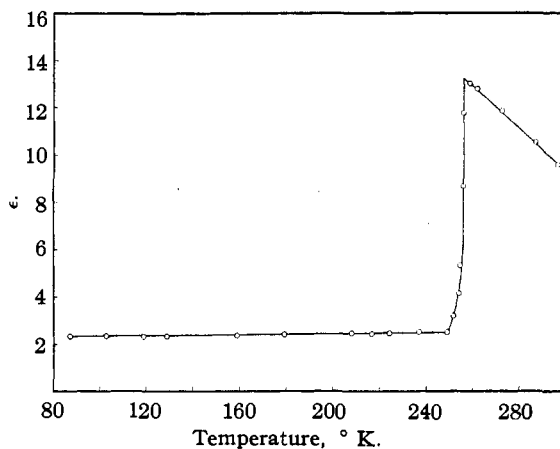

Fig. 2.—Variation with temperature of the dielectric constant (5 kc.) of octanol-1.

stronger internal field of the crystal. Because of the presence of the methyl group in the molecule, the freezing point of methyl alcohol is much lower than that of water and molecular rotation can occur in the solid at a low temperature with higher frequencies than in ice.

(8) Pauling, THIS JOURNAL, **57**, 268 (1935).

Although the molecule of *t*-butyl alcohol is not very far from spherical in shape, reasonably close packing of the molecules, such as would naturally occur in the crystal lattice, would probably cause the rotation of a molecule to be blocked by its neighbors. In the crystal of *n*-octyl alcohol, the molecules probably lie as extended zig-zag chains parallel to one another. As many cases are known in which carbon chains parallel to one another in a solid rotate about their long axes,[9] there would seem to be a possibility of rotation of this type here, which is evidently not realized. Bernal has found by x-ray analysis[10] that *n*-dodecyl alcohol shows a transition from a monoclinic to a hexagonal crystal at 289°K. with molecular rotation setting in around the axis of the carbonchain. It is probable that the higher temperature attainable before melting gives the energy

(9) Müller, *Nature*, **129**, 436 (1932): Southard. Milner and Hendricks. *J. Chem. Phys.*, **1**, 95 (1933).
(10) Bernal. *Nature*, **129**, 870 (1932).

necessary to overcome the resistance to rotation, lacking in the *n*-octyl alcohol, which melted 32° below this transition temperature.

Summary

The dielectric constants of solid methyl, *t*-butyl and *n*-octyl alcohols have been measured from liquid air temperatures up to the melting point in order to investigate the question of dipole rotation in the solid state. The high dielectric constant of methyl alcohol just below the melting point, dropping to a low value at a transition temperature 159.9°K., gives evidence of dipole rotation in this region. The absence of dipole rotation in solid *t*-butyl and *n*-octyl alcohols and the failure of specific heat measurements to show transitions in many other alcohols, indicate that the hydroxyl group does not rotate inside the molecule, but that the entire methyl alcohol molecule rotates above the transition point.

The Magnetic Rotation of Lanthanum and Neodymium Chlorides in Aqueous Solution

BY CHARLES M. MASON, ROGER D. GRAY AND GRACE L. ERNST

The magnetic rotation of the plane of polarized light is particularly interesting in the case of the rare earths. The chemical properties of these substances in aqueous solutions are so nearly identical that it is only by physical measurements of this type that any differentiation of properties can be made.

In this work the Verdet constants of aqueous solutions of lanthanum and neodymium chlorides have been measured over a temperature interval of from 10 to 50°. The concentration of the solutions was varied from zero (water) to 3.7 molal for the lanthanum chloride and 0.5 molal for the neodymium chloride. For comparison the Verdet constants were determined for aluminum chloride solutions from zero to 2.8 molal over the same temperature range.

Experimental Details

The rotations were measured with a Franz Schmidt and Haensch Model 55 "Landolt" half shade polarimeter, which could be read to hundredths of a degree.

The two light sources used were a mercury "Lab-Arc" with Corning filters G-555-Q and G-35-Y to transmit λ 5460.7 Å. and a sodium "Lab-Arc." This latter was used without filters since the accuracy attained in setting the polarimeter without any filters more than offset any error due to wave lengths other than the principal doublet λ 5893 Å.

The solution, the rotation of which was to be measured, was placed in a water-jacketed cell of Pyrex glass. This was equipped with optical windows of the same, fused on to the ends. The cell, which is shown in Fig. 1, was provided with an entrance through which a calibrated thermometer could be placed in the solution while the rotation was measured.

The magnetic field was provided by a coil of fourteen layers of No. 20 B. and S. cotton and enamel covered copper wire. The total number of turns was 2,059 and the length of the coil was 23.57 cm. The inside diameter was 2.84 cm. and the outside diameter 6.70 cm. The length of the light path through the solution was 21.74 cm. From these data the field strength, H, of the coil at any point along the axis is easily calculated. The product of the effective field strength times the length of the light path in the cell was determined by integration. The value of this integral was found to be 2218.2 gausscm. per ampere of current through the coil. This value, when used to calculate the Verdet constants for water and carbon bisulfide, checked the standard values[1] within 0.5%. This is a good check when we consider the irregularities of the coil winding as shown by an examination of Fig. 1.

(1) "International Critical Tables," McGraw-Hill Book Co., Inc., New York, Vol. VI, 1926, p. 425.