[Contribution from the Department of Chemistry of Princeton University]

THE DIELECTRIC POLARIZATION OF LIQUIDS. VII. ISOMERIC OCTYL ALCOHOLS AND MOLECULAR ORIENTATION

By C. P. Smyth and W. N. Stoops

Received July 1, 1929 Published November 8, 1929

As the material in the preceding paper of this series showed the exceedingly complicated effect of molecular orientation upon the polarization of primary alcohols, it seemed important to study the variation of this effect with variation in the position of the hydroxyl group in the molecule and with branching of the carbon chain. The preparation of twenty-two isomers of octyl alcohol by Dr. H. B. Glass, Dr. G. B. Malone and Dr. G. L. Dorough working with Prof. E. Emmet Reid of Johns Hopkins University has given an exceptional opportunity for studying the dependence of dielectric behavior upon these factors. The quantities of material available have not been sufficient to permit of measurements in solution except in the cases of octanol-1, which has been treated in the preceding paper, and 2-methylheptanol-3, but preliminary conclusions may be drawn from the behavior of the pure liquids, taken in conjunction with that of the two very different octyl alcohols in solution, and it is expected that more measurements in solution will be possible in the near future.

The measurements were carried out in the manner described in the previous paper, the dielectric constants being determined with a capacity bridge at a wave length of 600 meters. Table I gives the densities, d, and dielectric constants, ϵ, of solutions of 2-methylheptanol-3 in benzene obtained at 10° intervals by graphical interpolation from measurements made at 10 to 20° intervals, and the polarizations, P_2, of the alcohol calculated from them. The polarizations are shown graphically in Figs. 1 and 2. In the pure alcohols at low temperatures, anomalous dispersion and absorption made it necessary to increase the series resistance in the balancing arm of the bridge, which was used to compensate for conductance in the measuring cell. The introduction of large resistances so reduced the accuracy of the dielectric constant measurements that the values at these low temperatures are sometimes given to only one decimal place in Table II, which also gives the value of the compensating resistance R in ohms as a rough indication of the magnitude of the absorption. A resistance of an ohm or less may be regarded as indicative of a negligible effect and it is only when the resistance approaches 10 ohms or more that the absorption may be regarded as considerable. In the case of 2-methylheptanol-2, the compensating resistance increased somewhat at higher temperatures because of slight decomposition and resulting conductance in the liquid. That the effect of this decomposition on the dielectric constant was negligible was shown by the last value obtained for the liquid after cooling down again to 19.1°. The high resistance required for 5-methylheptanol-2 was the result of rapid decomposition of the liquid, which made the values of ϵ very uncertain. Because the effect of molecular orientation, the dielectric constants of several of the alcohols decrease with decreasing temperature instead of increasing in accordance

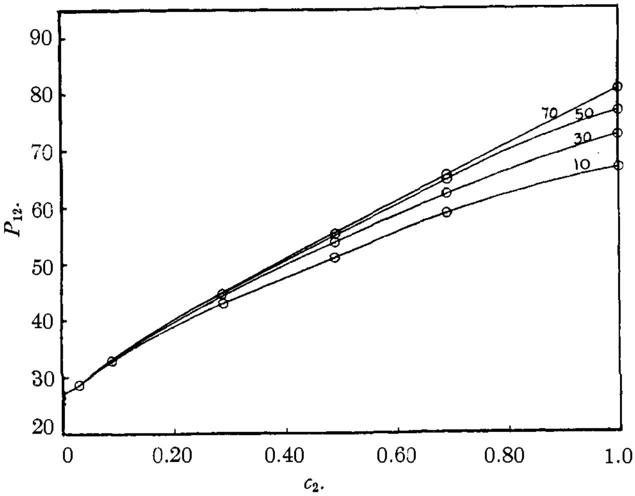

Fig. 1.—Molar polarizations (P_{12}) of benzene-2-methylheptanol-3 mixtures.

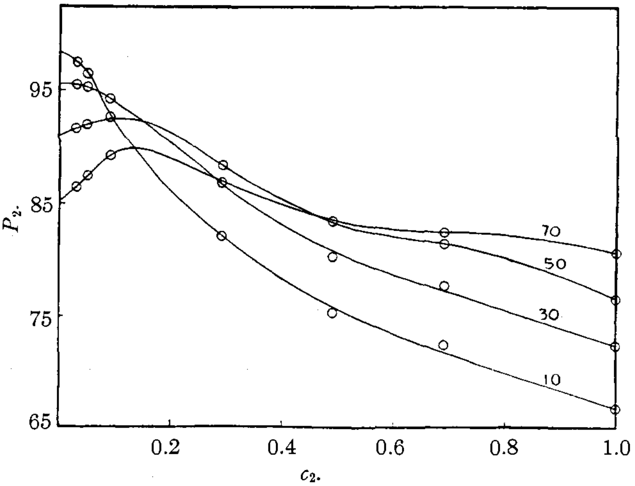

Fig. 2.—Polarizations (P_2) of 2-methylheptanol-3 in solution in benzene.

with the Debye equation, but it is only in a few cases that the measurements have been carried to temperatures at which the anomalous dispersion is sufficient to cause a measurable lowering of dielectric constant with decreasing temperature.

In Table III are given the polarizations of twenty isomeric octyl alcohols which are represented as methylheptanols, the first number at the top of each pair of columns indicating the position of the methyl group and the second that of the hydroxyl. The only methylheptanols omitted are 2-methylheptanol-3, given in Table I, and 5-methylheptanol-2, which decomposed too rapidly in the cell to give reliable results. The densities used in the calculation of the polarizations were obtained by linear extrapolation of the values at 0 and 25° determined by Dr. G. B. Malone. Since the densities of ethyl, *n*-butyl and *n*-octyl alcohols are practically linear functions of temperature below 25°, the use of these extrapolated values should not introduce serious error in the polarizations, which

TABLE I

INTERPOLATED VALUES OF DIELECTRIC CONSTANTS AND DENSITIES OF SOLUTIONS OF 2-METHYLHEPTANOL-3 IN BENZENE AND POLARIZATIONS OF COMPONENTS

Mole fr. $C_8H_{17}OH$ = t, °C.		0.0303	0.0331	0.0398	0.0502	0.0662	0.0889	0.2915	0.4892	0.6915	1.000
		ϵ									
0								2.926	3.077	3.160	3.09
10		2.418	2.428	2.451	2.482	2.530	2.589	2.961	3.154	3.263	3.23
20		2.394	2.402	2.424	2.458	2.506	2.569	2.987	3.214	3.354	3.37
30		2.368	2.376	2.397	2.430	2.479	2.545	2.994	3.253	3.429	3.50
40		2.341	2.350	2.368	2.400	2.448	2.515	2.984	3.280	3.486	3.60
50		2.313	2.322	2.339	2.369	2.415	2.480	2.955	3.274	3.521	3.68
60		2.284	2.295	2.308	2.336	2.380	2.443	2.908	3.242	3.514	3.75
70		2.255	2.267	2.277	2.304	2.345	2.406	2.849	3.192	3.465	
		d									
0								0.8702	0.8585	0.8497	0.8400
10		0.8861	0.8858	0.8846	0.8835	0.8820	0.8791	.8608	.8494	.8411	.8324
20		.8754	.8752	.8740	.8730	.8714	.8687	.8512	.8404	.8323	.8248
30		.8648	.8645	.8633	.8624	.8607	.8581	.8419	.8313	.8236	.8168
40		.8541	.8537	.8527	.8517	.8500	.8475	.8324	.8221	.8150	.8084
50		.8435	.8431	.8422	.8411	.8396	.8372	.8229	.8129	.8063	.7996
60		.8327	.8322	.8315	.8304	.8288	.8266	.8130	.8034	.7984	.7910
70		.8220	.8215	.8206	.8198	.8182	.8160	.8029	.7939	.7885	.7823
	$P_1(C_6H_6)$	$P_2(C_8H_{17}OH)$									
0								79.0	70.2	69.4	63.5
10	26.69	97.6	97.7	97.8	96.4	95.1	92.8	82.1	75.3	72.6	66.7
20	26.72	97.2	96.6	96.8	96.4	95.2	93.7	84.7	78.0	75.2	69.6
30	26.75	95.6	95.3	95.5	95.3	95.0	94.2	86.7	80.2	77.7	72.4
40	26.78	93.4	93.8	93.4	93.6	93.8	93.7	87.9	82.1	79.8	74.6
50	26.78	91.4	92.0	91.6	92.0	92.3	92.5	88.3	83.2	81.5	76.7
60	26.78	88.8	90.5	89.1	89.6	90.3	91.0	87.9	83.6	82.5	78.6
70	26.76	86.4	89.3	86.9	87.6	88.3	89.3	87.0	83.5	82.5	

are probably accurate within 0.5 to 2.0%. For example, the polarization of 2-methylheptanol-3 calculated from the extrapolated density is 78.3 at 60° while that calculated from the interpolation of our own measurements in Table I is 78.6, no difference at all being found at 40°.

TABLE II

DIELECTRIC CONSTANTS AND COMPENSATING RESISTANCES FOR OCTYL ALCOHOLS

t, °C.	ε	*R*
Octanol-1		
−4.4	12.71	4.0
8.6	11.42	2.4
19.1	10.39	1.9
32.1	9.34	1.8
44.6	8.18	1.8
58.2	7.20	1.8
Octanol-4		
−31.1	8.97	28.5
−21.1	7.88	7.4
− 9.6	6.66	1.8
2.5	5.83	0.6
15.6	5.26	.3
27.9	4.91	.2
41.1	4.72	.2
55.2	4.51	.2
4-Methylheptanol-1		
−36.6	7.36	7.3
−36.3	7.49	12.3
−31.2	7.48	7.3
−17.8	6.22	2.6
− 7.0	5.59	1.6
0.0	5.30	0.9
5.3	4.99	.5
17.4	4.63	.4
29.8	4.24	.4
43.7	3.95	.4
59.0	3.73	.4
6-Methylheptanol-2		
−46.0	6.8	63.8
−42.3	9.6	88
−34.2	11.35	12.8
−25.2	10.95	5.2
−16.6	9.87	2.4
− 7.3	8.75	1.2
4.9	7.18	0.7
16.9	6.41	.5
29.0	5.67	.4
41.6	5.10	.4
55.5	4.68	.4
Octanol-2		
−37.9	13.03	19.2
−30.3	14.64	10.0
−21.5	13.61	4.3
− 9.1	11.86	1.6
3.0	10.51	0.8
15.7	8.68	.6
29.8	7.30	.5
43.5	6.28	.4
56.3	5.60	.4
6-Methylheptanol-1		
−45.2	15.13	14.9
−33.5	15.25	5.6
−20.9	14.27	2.4
− 8.1	12.96	1.4
4.4	11.75	1.1
17.1	10.54	1.0
29.4	9.40	1.0
42.2	8.31	1.1
55.0	7.41	1.1
3-Methylheptanol-1		
−32.0	3.239	1.5
−19.6	3.116	0.7
− 7.5	3.022	.5
4.9	2.946	.4
17.1	2.884	.4
29.5	2.827	.3
42.4	2.786	
55.6	2.747	
2-Methylheptanol-1		
−46.2	8.58	21.0
−37.6	9.47	10.7
−28.6	8.85	4.6
−19.2	8.14	2.2
− 7.8	6.96	1.1
5.8	5.89	0.6
19.8	5.16	.5
29.6	4.78	.4
42.0	4.43	.4
54.9	4.15	.4
2-Methylheptanol-4		
−43.7	2.68	5.5
−34.3	2.83	3.9
−24.7	2.91	1.6
−11.4	2.991	0.7
− 1.3	3.081	.5
10.8	3.203	.4
23.1	3.338	.4
35.6	3.469	.4
48.1	3.574	.5
59.5	3.645	.5
2-Methylheptanol-2		
−48.5	3.36	15.5
−41.0	3.55	7.8
−32.6	3.49	2.7
−22.6	3.42	1.1
−13.1	3.38	0.6
− 6.6	3.38	.5
− 0.5	3.39	.5
5.5	3.40	.5
15.0	3.43	.5
28.5	3.47	.7
41.6	3.51	1.2
50.9	3.54	2.1
60.3	3.54	5.2
19.1	3.45	1.0
4-Methylheptanol-2		
−43.3	5.0	79.0
−37.9	5.7	60.9
−33.4	5.6	35.5
−26.6	5.1	13.8
−18.4	4.6	4.3
−10.6	4.22	1.5
− 0.3	3.90	0.8
7.8	3.77	.5
16.8	3.65	.5
25.7	3.59	.5
35.0	3.54	.4
48.0	3.48	.5
60.0	3.36	.5

TABLE II (*Concluded*)

t, °C.	ε	*R*
Octanol-3		
−27.3	10.5	4.9
−19.6	9.83	2.6
− 8.5	9.03	1.4
2.6	8.01	0.9
15.2	7.26	.8
27.9	6.65	.8
42.5	6.06	.8
54.0	5.68	.7
3-Methylheptanol-2		
−44.4	10.8	2.1
−32.8	9.9	1.2
−20.6	9.17	1.0
− 8.1	8.52	1.0
4.6	7.94	1.1
16.4	7.47	1.1
29.0	7.00	1.2
42.0	6.60	1.2
55.6	6.21	1.2
5-Methylheptanol-1		
−38.1	12.67	10.0
−28.3	11.79	4.4
−19.2	10.98	2.4
− 6.6	9.69	1.4
5.0	8.65	1.1
17.2	7.68	1.0
29.6	6.79	1.0
42.8	5.96	0.9
55.0	5.37	0.9
5-Methylheptanol-3		
−42.7	8.58	1.0
−32.5	8.04	0.7
−20.0	7.48	.7
− 8.1	7.01	.7
4.2	6.60	.8
17.7	6.20	.8
30.6	5.85	.9
42.2	5.57	.9
56.5	5.25	.9

t, °C.	ε	*R*
3-Methylheptanol-3		
−41.7	3.60	5.0
−30.8	3.58	1.5
−19.4	3.57	0.7
− 7.5	3.593	.5
0.6	3.624	.5
7.0	3.657	.4
13.5	3.694	.4
22.2	3.755	.4
31.3	3.796	.4
41.3	3.843	.5
50.8	3.878	.5
59.9	3.894	.5
3-Methylheptanol-4		
−43.1	10.37	0.9
−38.1	10.10	.7
−30.3	9.63	.6
−22.2	9.20	.5
−13.7	8.79	.5
− 4.1	8.30	.5
5.0	7.91	.5
16.8	7.46	.5
29.2	7.04	.5
41.5	6.66	.5
56.5	6.21	.6
22.5	7.25	.6
4-Methylheptanol-4		
−43.8	2.528	1.0
−38.2	2.531	0.6
−30.7	2.550	.4
−22.0	2.557	.4
−13.7	2.611	.3
− 1.1	2.688	.3
11.5	2.790	.3
23.0	2.902	.3
35.4	3.037	.3
48.2	3.167	.4
54.1	3.221	.4
60.4	3.270	.4

t, °C.	ε	*R*
2-Methylheptanol-3		
−41.4	2.70	3.0
−34.0	2.76	1.7
−24.7	2.83	0.8
−12.4	2.953	.5
− 1.2	3.087	.4
10.8	3.245	.4
23.6	3.418	.4
35.3	3.554	.4
47.8	3.669	.4
60.4	3.754	.4
4-Methylheptanol-3		
−52.5	7.11	1.1
−43.2	7.04	0.7
−30.8	6.60	.5
−19.0	6.22	.5
− 8.3	5.90	.4
4.7	5.59	.4
17.2	5.31	.3
29.6	5.05	.3
42.3	4.80	.3
55.6	4.61	.3
5-Methylheptanol-2		
−43.0	10.6	14.5
−31.8	9.6	13.7
−18.1	8.6	16.3
− 6.8	8.0	19.4
5.3	7.5	23.1
6-Methylheptanol-3		
−42.6	8.76	3.8
−32.0	7.79	1.7
−19.4	7.13	1.0
− 7.3	6.53	0.6
5.3	6.12	.5
17.4	5.56	.4
29.8	5.18	.4
29.5	5.27	.4
42.6	4.95	.4
55.5	4.67	.4

When the polarizations, P_{12}, of the mixtures of 2-methylheptanol-3 in benzene are plotted against c_2, the mole fractions of the alcohol, the curves obtained (Fig. 1) show so little deviation from the theoretical linearity as to suggest that molecular orientation in the mixtures is slight. When P_2, the polarization of the alcohol, is plotted similarly against c_2, curves are obtained (Fig. 2) which, if only one or two concentrations

TABLE III

POLARIZATIONS OF THE METHYLHEPTANOLS

t, °C	7-1	7-2	7-3	7-4	6-1	5-1	4-1
−50						121	
−40		118.2			124.8	121	104
−30		124.4	115.2	109.6	125.3	120	105
−20		123.1	114.3	105.8	124.7	118	99
−10	123.7	121.4	112.7	101.2	123.8	116	95
0	122.5	118.7	110.0	97.5	122.9	114	93
10	121.0	115.3	108.1	93.6	121.3	111	90
20	119.3	111.9	105.7	91.6	119.8	108	86.7
30	117.3	108.4	104.2	90.5	117.4	106	84.1
40	115.1	104.4	100.8	89.3	115.1	102	82.1
50	112.5	101.0	100.1	88.9	111.8	99	81.9
60	109.4	97.7	99.7	88.6	109.8	95	79.2

t, °C.	3-1	2-1	6-2	4-2	3-2	2-2	6-3
−50	69.6				115		
−40	68.4	113	118	93	114	69.8	111
−30	66.9	113	119	92	112	69.3	110
−20	65.9	110	117	86	111	69.0	108
−10	64.9	106	114	81	110	69.1	106
0	64.2	102	110	78.3	109.4	70.0	104
10	63.6	97	106	76.6	108.4	71.1	102
20	63.2	94.2	102	75.6	107.4	72.1	101
30	62.9	91.1	99	75.4	106.4	73.5	99
40	62.8	88.6	95	75.3	104.3	74.8	97
50	62.8	86.7	93	75.2	104.5	75.9	96
60	62.8	85.1	91	74.1	103.5	76.7	95

t, °C.	5-3	4-3	3-3	2-3	4-4	3-4	2-4
−50		103	68.2	52.4	49.9		
−40	106	102	68.6	54.3	50.4	111	56.9
−30	105	101	69.1	56.3	51.1	110	58.8
−20	104	100	69.5	59.1	52.5	109	60.6
−10	103	99	70.3	61.1	54.0	108	62.5
0	102	98	71.6	63.5	56.0	107	64.5
10	101	97	73.0	66.7	58.2	106	67.0
20	100	95.6	74.6	69.6	60.6	105	69.4
30	99	94.7	76.2	72.4	63.1	104	71.9
40	98	94.0	77.5	74.6	65.7	104	74.0
50	97	93	78.9	76.5	68.4	103	76.0
60	96	91	79.9	78.3	70.7	102	77.8

and one temperature had been measured in the dilute region, would have been extrapolated to $c_2 = 0$ in a shape resembling the P_2–c_2 curves given by ethyl bromide or ethyl iodide, the polarization increasing more and more rapidly up to infinite dilution. Moreover, the value of the moment calculated from the value of P_∞ by subtracting the molar refraction, MR_D, would not have been seriously in error. However, the determination of a number of points in the dilute region makes it clear that the curves possess a maximum or, at least, a tendency toward one, which is much less prominent than in the curves for the primary alcohols in the preceding paper. The curves in the dilute region given on a larger scale in Fig. 3 are linear at the higher temperatures. The values of P_∞ obtained as their intercepts at $c_2 = 0$ are given in Table IV and used to calculate the values of the moment μ shown in the last column. The slight decrease in $(P_\infty - MR_D)T$ and μ with rising temperature may indicate that the effect of orientation is not wholly eliminated by the extrapolation, but the mean value 1.62×10^{-18} is certainly not far from correct.

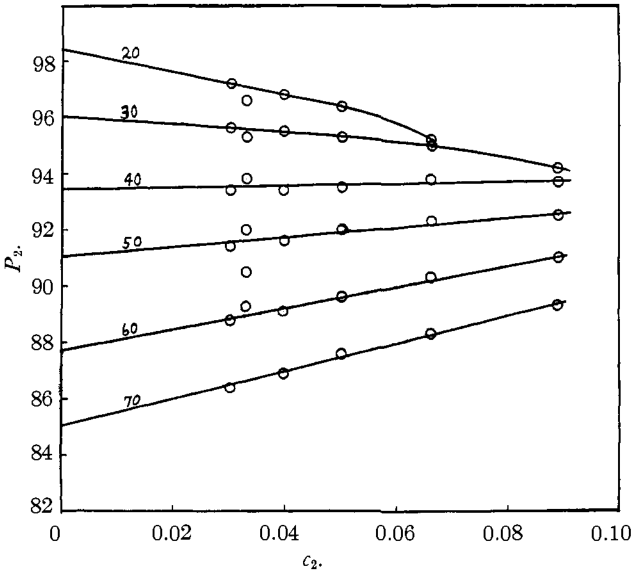

Fig. 3.—Polarizations (P_2) of 2-methylheptanol-3 in benzene solution.

TABLE IV

ELECTRIC MOMENT OF 2-METHYLHEPTANOL-3 CALCULATED AT DIFFERENT TEMPERATURES (MR_D = 40.5)

T, °A.	P_∞	$(P_\infty - MR_D)T$	$\mu \times 10^{18}$
293	98.4	16900	1.66
303	96.0	16800	1.65
313	93.5	16600	1.64
323	91.0	16300	1.62
333	87.7	15700	1.60
343	85.0	15300	1.57
		Mean =	1.62

The moment of 2-methylheptanol-3 appears to be slightly lower than that of octanol-1, although the difference may be the result of error caused by molecular orientation. It has been shown that the electric doublet in the alcohol molecules lies at the hydroxyl group and really consists of two doublets, the resultant of which gives the observed moment.[1] This, taken in conjunction with the fact that the moments of the primary alcohols are practically independent of the length of the carbon chain, at least, up to eight carbon atoms, leads one to expect the differences in moment among the octyl alcohols to be small, as in the case of the two just considered. The dielectric constants at 20° of the nine isomeric heptanes, which have no moments, differ from 1.93 by no more than 0.015 and their polarizations, which consist of P_E plus a very small P_A, differ from 34.50 by no more than 0.26.[2] The molar refractions, MR_{D} of the twenty-two isomeric octyl alcohols determined by Dr. H. B. Glass differ from 40.90 by no more than 1.30. As the polarization is made up of P_M, the contribution of the moment, P_E, the electronic contribution, which differs from MR_{D} by hardly one unit, and the small P_A, the polarizations of the different isomers should be nearly the same in the absence of molecular orientation. From these values of the moment and the refraction, the polarization at 25° is calculated to be approximately 100 and the dielectric constant, 5.4. Marked deviations from these values are to be attributed to the effect of molecular orientation.

The orienting effect of the molecules of a liquid upon one another must depend not only on the size of their doublets, but also upon the location of the doublet or doublets in the molecule, and upon the mere geometrical shape of the molecule. There are two possible simple orientations which two doublets in adjacent molecules may be expected to adopt relative to one another. The negative end of one doublet may attract the positive end of the other so that the axes of the two doublets fall in line and the two support one another. This will be referred to as an orientation of the first type. The two molecules may associate to act as one, but, if they do not, they should still attract one another and tend to orient more or less with respect to one another so that, when a field is applied externally to measure the dielectric constant, the orientation would be greater than that calculated, and the polarization would be abnormally higher. The shape of the molecules would commonly prevent an exact lining up of the doublets and their axes would, consequently, make an angle of somewhat less than 180° with one another. As this angle decreases, the polarization diminishes and the common effect of orientation is to decrease the polarization instead of increasing it. When the angle between the axes becomes zero, that is, when the doublets are parallel and pointing in opposite directions, the moments cancel one another and the doublet contribution to the polarization becomes zero. This position of

[1] Smyth, This Journal, **46,** 2151 (1924).

[2] Smyth and Stoops, *ibid.*, **50,** 1883 (1928).

the doublets, which will be referred to as the second type of orientation, would result in a polarization for a polar substance differing little from its molar refraction. More than two molecules may line up if the first type of orientation prevails and one may imagine a high polarization built up in this way. The stability of the orientation of one molecule relative to another must depend to some extent upon the forces exerted upon it by the other neighboring molecules. It appears probable, therefore, that, when there is not much difference between the energies of two different orientations, one orientation may change to the other as the mean distance between the dipole molecules changes. Thus, when a polar liquid is dissolved in a non-polar, the orientation of the polar molecules relative to one another may change from one type to another with change in concentration. Of course, when the polar molecules are in very dilute solution and, on the average, far away from one another, they should assume a random orientation unless they actually associate to form a definite complex molecule which is not much dissociated even in the dilute solution, as appears to be the case with acetic acid in benzene solution. Change in temperature also might affect the type of orientation.

The interaction of the dipoles in the majority of liquids decreases the polarization in the manner of the first type of orientation, but hydroxyl doublets lie close to the surface of the molecule and produce a strong localized external field. Molecules of the formula ROH may hypothetically be fitted together in such a way as to arrange the doublets according to either type of orientation. The structure of the associated alcohol molecules proposed by Sidgwick[3] would correspond to the first type, but, on paper at least, a double molecule corresponding to the second type may be equally easily obtained. The somewhat hazardous juggling of these formulas on paper has been treated briefly by one of the authors in a paper to appear shortly.

The variation of the polarization of the alcohols with concentration and temperature is so complicated that the correctness of a detailed explanation in terms of orientation cannot be assured, but there are certain obvious facts upon which a possible explanation may be founded. An orientation of the first type must occur to some extent in order to cause the maximum observed in the P_2–c_2 curves. The approximate conformity of the polarizations in the very dilute benzene solutions to the Debye equation and the excellent agreement of the moments obtained from them with the values obtained for several of the alcohols in the vapor state show that in these solutions the alcohol molecules must be nearly all single and oriented practically at random. The approach to the correct values of P_∞ in the heptane solutions at the highest temperatures indi-

---

[3] Sidgwick, "The Electronic Theory of Valency," Oxford University Press, Oxford, **1927**, p. 134.

cates an existence mainly as single molecules oriented at random in the most dilute solutions at high temperatures in heptane, which, with its lower dielectric constant, has less dissociating power than benzene. With increasing concentration in the very dilute solutions, these single dipole molecules acting upon one another appear to bring about an orientation of the second type, by which the polarization is decreased, as in the case of ethyl iodide and ethyl bromide. As this effect is increased by decreasing temperature, it is so strong even in the very dilute heptane solutions of the primary alcohols as to make the extrapolated values, P_∞, decrease with decreasing temperature instead of increasing as required by the Debye equation. At the same time, however, molecules are coming together and orienting according to the first type, probably forming aggregates and tending to increase the polarization. At the low temperatures in heptane this effect more than counterbalances the decrease in polarization with increasing concentration in the very dilute solutions, which has just been discussed; at the high temperatures in benzene it does so as well, since here the effect of the single molecules upon one another is small. At the lower temperatures in benzene and the higher in heptane, this latter effect for a short range of concentration more than counterbalances the increase in polarization caused by the formation of the aggregates. Since the formation of aggregates must be greater the lower the temperature, the rate of increase of the polarization with concentration is also greater the lower the temperature and the maximum reached is higher. As the concentration of these aggregates increases, they may act upon one another as the single molecules are supposed to do in the very dilute solutions. This effect opposes the increase in polarization due to the formation of more aggregates with increasing concentration and becomes stronger and stronger so that the polarization passes through a maximum and decreases. The effect is greater the lower the temperature, with the result that the decrease in polarization is greater, the curves intersect, and the polarization of the pure liquid is lower at the lower temperatures in the case of ethyl alcohol. In the case of butyl alcohol, in which the longer carbon chain produces a greater mean separation of the doublets, the polarization of the pure liquid decreases with temperature only at the lower temperatures, and in *n*-octyl alcohol, where the separation or insulation of the doublets is still greater, it increases with decreasing temperature down to the region of anomalous dispersion. The interaction of the molecular aggregates in producing an effect equivalent to that of the second type of orientation may be treated in terms of the potential energy of the system. The increase of orientation of the first type with increasing concentration should increase the field surrounding the dipole molecules and thus increase the potential energy. If this increase in potential energy is sufficiently great, the resulting instability may cause a change to orientation of the second type with resulting decrease in polarization.

In 2-methylheptanol-3 the hydroxyl doublet is near the middle of a branched carbon chain, which should partially screen it, reduce the external field due to it, and so lessen the chances for orientation of the first type. In the dilute solutions in benzene at high temperatures, the formation of aggregates is sufficient to increase the polarization with increasing concentration over a short range, but, at lower temperatures and at higher concentrations, the orientation of the second type predominates over the rather weak tendency to form aggregates with orientation of the first type. The polarization therefore decreases with decreasing temperature and increasing concentration. So great is the effect that not only the polarization but also the dielectric constant increases with rising temperature, and this is found to be true of all the tertiary and several of the secondary octyl alcohols measured.

In the majority of cases where an abnormally high dielectric constant indicates that the alcohol molecules are probably forming aggregates in an orientation of the first type, the x-ray diffraction measurements of Professor G. W. Stewart, who has very kindly made his results available to us, point to the existence of double molecules, while the x-rays indicate single molecules in the majority of cases in which the low dielectric constant is attributed to the interaction of single molecules in an orientation of the second type. There are exceptions, however, as is true also of the anomalous dispersion and absorption.

The tendency toward anomalous dispersion and absorption is greater in those alcohols which are indicated by high dielectric constants as forming molecular aggregates with orientation of the first type, which would be expected from the dependence of the dispersion and absorption upon the cube of the molecular radius. It is a striking fact that, of the ten methylheptanols which show little or no absorption at the temperatures investigated, eight have either the methyl or the hydroxyl on the third carbon, and the only alcohol with the third carbon occupied by methyl or hydroxyl to show absorption is octanol-3, in which it is less pronounced than in any of the other three octanols. All of these alcohols which show little or no tendency toward dispersion and absorption are indicated by the x-ray measurements as existing as single molecules. 2-Methylheptanol-2 has a low dielectric constant, which at low temperatures above the region of anomalous dispersion decreases with rising temperature and then increases, indicating an orientation of the second type. However, the x-rays indicate existence in double molecules and, in conformity with this, it shows a marked tendency toward anomalous dispersion and absorption. It seems probable, therefore, that the molecules of this substance tend to double up in an orientation of the second type, in which the dipoles oppose one another. It is obvious that our ignorance of the details of the molecular shapes renders impossible the accurate prediction of properties which must be strongly influenced by them, but it appears to be possible to explain, in qualitative fashion, the complex dielectric behavior of the alcohols on the basis of simple and not unreasonable assumptions.

Summary

The dielectric constants of twenty-two isomeric octyl alcohols have been measured over a wide range of temperature and an indication of their tendency toward anomalous dispersion and absorption for a wave length of 600 meters has been obtained.

Solutions of 2-methylheptanol-3 in benzene have been measured in order to obtain the electric moment of the molecule, which is close to that of *n*-octyl alcohol and the lower alcohols.

The great differences among the dielectric constants of the isomers are attributed to the effects of molecular orientation, which causes the dielectric constants of the tertiary methylheptanols and two of the secondary to increase with rising temperature instead of decreasing in the normal manner.

The explanation of the values of the dielectric constants in terms of molecular orientation is consistent with the observed tendencies toward anomalous dispersion and absorption and with the results of the x-ray diffraction measurements of Stewart.

PRINCETON, NEW JERSEY

[CONTRIBUTION NO. 610 FROM THE DEPARTMENT OF CHEMISTRY, COLUMBIA UNIVERSITY]

CHEMICAL KINETICS IN HIGHLY DILUTE SOLUTION. BROMO-ACETATE AND THIOSULFATE IONS IN THE PRESENCE OF SODIUM ION AT 25°

BY VICTOR K. LA MER[1]

RECEIVED AUGUST 20, 1929 PUBLISHED NOVEMBER 8, 1929

It has been shown by Slator[2], as well as others,[3] that reactions of the type

$$BrCH_2COO^- + S_2O_3^{--} \longrightarrow S_2O_3CH_2COO^{--} + Br^- \qquad (1)$$

in which a halogen is replaced by thiosulfate are bimolecular and singularly free from side reactions. Since thiosulfate can be determined with great precision and comparative ease, reactions of this type are particularly well adapted for testing quantitatively, theories of salts catalysis, since the reaction rate can be followed very accurately in the region of high

[1] Paper presented at the Minneapolis Meeting of the American Chemical Society, September, 1929.

[2] Slator, *J. Chem. Soc.*, **87**, 485 (1905), and earlier papers.

[3] Krapivin, *Z. physik. Chem.*, **82**, 439 (1913); see also *J. Chim. Phys.*, **10**, No. 2, 289 (1912), for data on the chloro-acetate reaction.