

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF PRINCETON UNIVERSITY]

THE DIELECTRIC POLARIZATION OF LIQUIDS. VIII. ACETIC AND BUTYRIC ACIDS

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RECEIVED JANUARY 11, 1930

PUBLISHED MAY 8, 1930

The fatty acids have been so extensively investigated from many points of view that their dielectric behavior should be of unusual interest. Solutions of acetic acid in benzene and in ether were studied some years ago by Dr. S. O. Morgan and one of the writers, but, as the results were peculiar and as some doubt arose as to the purity of the acetic acid which had been employed, no use was made of the data. The measurements have been repeated with carefully purified acetic acid over a wider range of temperature and extended to butyric acid. The apparatus, with which the dielectric constant was determined at a wave length of 600 meters, has been described previously.¹

Preparation of Materials

Benzene.—Benzene was purified in the usual manner, being finally dried and distilled over sodium; b. p. 80.1°; n_D^{20} 1.50135.

Ether.—U. S. P. ether was shaken several times with a strong sodium chloride solution containing a little sodium hydroxide, washed with water, dried over calcium chloride and distilled; b. p. 35.1°; d_4^{20} 0.7137.

Acetic Acid.—Merck's C. P. glacial acetic acid was crystallized twelve times, the final melting point being 16.6° and the refractive index n_D^{20} 1.37175. This sample was fractionally distilled; b. p. 117.8°; d_4^{20} 1.0491; n_D^{20} 1.37175.

Butyric Acid.—*n*-Butyric acid obtained from the Eastman Kodak Company was fractionally distilled, the fraction boiling between 163.2 and 163.4° being taken for the measurements; d_4^{20} 0.9591.

Experimental Results

For the acetic acid solutions and the pure substance the dielectric constants ϵ were measured at temperature intervals of approximately 10° and the densities d at intervals of about 15°. The values given for them in Table I were obtained by graphical interpolation. The butyric acid measurements were made at three fixed temperatures, which make interpolation unnecessary. The polarizations, P_2 , of the acids were calculated by means of the equations

$$P_{12} = \frac{\epsilon - 1}{\epsilon + 2} \times \frac{c_1 M_1 + c_2 M_2}{d} \quad \text{and} \quad P_2 = \frac{P_{12} - P_1}{c_2} + P_1$$

in which P_{12} is the polarization of the mixture, and c_1 and c_2 , M_1 and M_2 , and P_1 and P_2 are, respectively, the mole fractions, molecular weights, and polarizations of the individual components.

In the case of pure acetic acid slightly supercooled to 16.4°, a resistance

¹ Smyth, Morgan and Boyce, THIS JOURNAL, 50, 1536 (1928); Smyth and Morgan, *ibid.*, 50, 1547 (1928).

TABLE I
DIELECTRIC CONSTANTS AND DENSITIES OF SOLUTIONS AND POLARIZATIONS OF ACIDS
Benzene-Acetic Acid

Mole fr. CH ₃ COOH <i>t</i> , °C.	= 0	0.0978	0.2305	0.4372	0.6134	0.7912	1.000		
0	2.336	2.375	2.464	2.706	3.113	3.956			
10	2.315	2.358	2.449	2.700	3.118	3.981	6.074		
20	2.295	2.340	2.434	2.693	3.124	4.007	6.13		
30	2.274	2.322	2.418	2.687	3.130	4.032	6.20		
40	2.253	2.303	2.403	2.679	3.133	4.052	6.27		
50	2.232	2.285	2.388	2.672	3.132	4.067	6.36		
60	2.210	2.266	2.372	2.663	3.129	4.078	6.47		
70	2.188	2.246	2.357	2.655	3.126	4.084	6.60		
<i>d</i>									
0	0.8986	0.9100	0.9222	0.9484	0.9760	1.0134			
10	.8896	.8989	.9113	.9369	.9645	1.0020	1.0607		
20	.8786	.8879	.9006	.9257	.9532	0.9904	1.0491		
30	.8682	.8768	.8901	.9144	.9418	.9788	1.0376		
40	.8574	.8657	.8796	.9032	.9307	.9675	1.0264		
50	.8466	.8546	.8688	.8920	.9193	.9562	1.0153		
60	.8357	.8436	.8582	.8810	.9078	.9448	1.0039		
70	.8246	.8327	.8475	.8698	.8964	.9333	0.9923		
<i>P_∞</i>									
0	21.3	22.6	24.7	26.9	29.4	32.4			
10	22.4	23.8	25.3	27.5	30.0	33.1	35.6		
20	22.8	24.2	25.7	28.1	30.6	33.7	35.9		
30	23.1	24.5	26.2	28.7	31.3	34.3	36.7		
40	23.7	25.5	26.6	29.2	31.9	35.0	37.3		
50	24.2	26.1	27.2	29.8	32.5	35.5	37.9		
60	24.8	26.8	27.6	30.4	33.0	36.1	38.6		
70	25.5	27.7	28.2	31.0	33.6	36.7	39.4		
Ether-Acetic Acid									
	0	0.0339	0.0673	0.1039	0.1269	0.3549	0.5233	0.7198	1.000
0	4.746	4.817	4.869	4.966	5.015	5.489	5.793	6.28	
10	4.499	4.608	4.671	4.749	4.797	5.275	5.606	6.12	6.07
20	4.296	4.402	4.462	4.542	4.593	5.072	5.428	5.97	6.13
30	4.113	4.197	4.276	4.348	4.406	4.880	5.268	5.81	6.20
<i>d</i>									
0	0.7370	0.7364	0.7532	0.7619	0.7669	0.8259	0.8731	0.9450	
10	.7254	.7276	.7414	.7504	.7556	.8146	.8628	.9342	1.0607
20	.7137	.7189	.7295	.7387	.7442	.8032	.8526	.9234	1.0491
30	.7021	.7102	.7176	.7271	.7328	.7918	.8424	.9126	1.0376
<i>P_∞</i>									
0	64.0	57.3	57.3	45.6	44.9	41.0	39.5	38.6	
10	62.7	55.7	55.0	43.2	43.0	40.5	39.3	38.6	35.6
20	61.7	54.5	55.2	43.6	43.3	40.8	39.7	38.2	35.9
30	59.7	52.3	52.8	40.6	41.3	40.4	39.6	38.9	36.7

TABLE I (Concluded)

Benzene-Butyric Acid

Mole fr. $C_3H_7COOH = 0$	0.0379	0.0640	0.0894	0.1875	0.4729	0.7183	1.000	
$t, ^\circ C.$								
10	2.315	2.301	2.333	2.342	2.388	2.542	2.932	
40	2.253	2.266	2.280	2.290	2.340	2.519	3.001	
70	2.188	2.203	2.219	2.231	2.291	2.500	3.074	
	d							
10	0.8896	0.8916	0.8933	0.8939	0.9026	0.9254	0.9703	
40	.8574	.8595	.8616	.8636	.8713	.8933	.9389	
70	.8246	.8270	.8292	.8313	.8388	.8634	.9119	
	P_∞	P_{12}						
10	31.4	31.2	32.4	33.0	33.5	34.7	34.6	35.6
40	33.1	33.7	34.5	34.3	34.8	36.3	36.6	37.5
70	33.9	34.5	35.8	35.6	36.6	37.9	38.4	39.5

of 3.6 ohms had to be inserted in series with the condenser in the opposite arm of the bridge to balance the small conductance of the liquid. At 85.1° the dielectric constant was 7.11 and the compensating resistance 41.5 ohms, and at 100.0° ϵ was 8.05 and the resistance 60.0 ohms. For the benzene solution containing a mole fraction 0.7912 of acetic acid, the resistance required at room temperature was negligible, but rose to 6.6 ohms at 90.6° . In the less concentrated solutions the conductance was negligibly small. In the ether solutions the conductances were small, as the temperature of measurement was not above 30° , but were detectable at concentrations of acid down to mole fraction 0.3549.

Discussion of Results

The acetic acid data in Table I do not agree precisely with the earlier unpublished values, but the small differences observed are no greater than might be expected in view of the difference in the material used and are insufficient to affect the conclusions to be drawn. When these earlier measurements were made upon acetic acid, the increase in the dielectric constant of the pure liquid with rising temperature was thought to be the first observed case of such a phenomenon, although it was known that the polarization of pure ethyl bromide increased with rising temperature. Since these first measurements were made, similar behavior has been observed for a number of secondary and tertiary octyl alcohols.² As the dielectric constants of the dilute benzene solutions decrease in the normal manner with rising temperature, there is an intermediate region of concentration within which the temperature coefficient of the dielectric constant is very small. Thus, the solution containing 0.6134 mole fraction of acetic acid shows a slight increase in ϵ with rising temperature up to 40° followed by an even more gradual decrease. The values of P_{12} which

² Smyth and Stoops, *THIS JOURNAL*, 51, 3330 (1929).

are not shown in Table I increase with temperature throughout the entire range of concentration, although the increase is very slight in the dilute solutions where the effect of the almost constant polarization, P_1 , of the benzene predominates. As the polarization P_2 of the acetic acid in the dilute solutions is lower than that of benzene, the $P_{12}-c_2$ curves pass through a flat minimum in a region where there is little change of P_{12} with concentration.

The reason for this peculiar behavior is to be sought in the strong molecular association which is known to occur in acetic acid. Freezing point and partition coefficient measurements show that the apparent molecular weight of acetic acid in dilute solution in benzene is close to 120, the weight which it would have if polymerized into double molecules.³ X-ray investigations indicate that the molecules of the higher fatty acids in the solid state are paired⁴ end to end with their carboxyl groups in contact and a similar conclusion has recently been drawn for the liquid.⁵ Such a pairing should bring the electric moments of the single molecules into opposition with resultant partial or complete cancellation of one another's effects. It is easy to picture the acetic acid in dilute solution in benzene as consisting largely of these double molecules possessing little or no electric moment. The concentration of single molecules is so low in the solutions here measured that extrapolation of the P_2 values to $c_2 = 0$ gives not the polarization of the molecules existing singly but rather their polarization when paired in the double molecules. Since these values of P_∞ increase with rising temperature, presumably because of increasing dissociation into single molecules, it is evident that they are not wholly free from the effect of the small number of single molecules present. It may be concluded, however, that the polarization of the molecules in this complex state is not far from 20. The molar refraction of acetic acid for the sodium D line is 13.0.⁶ The difference between this and 20 is little, if any, larger than the value which the atomic polarization P_A might be expected to have. Consequently, the dipole contribution to the polarization, P_M , must be close to zero, if not actually zero, the electric moments of the single acetic acid molecules being practically canceled in the complex molecules. This conclusion is in agreement with results privately communicated some years ago by Dr. L. Ebert, who obtained 18.85 as the value of P_∞ for acetic acid in benzene and 19.4 for the molar polarization of the solid measured at 0° with a wave length of 5 meters. As there is no dipole contribution to the polarization of the solid measured under

³ Beckmann, *Z. physik. Chem.*, **22**, 610 (1897); Herz and Fischer, *Ber.*, **38**, 1138 (1905); Trautz and Moschel, *Z. anorg. allgem. Chem.*, **155**, 13 (1926).

⁴ Müller, *J. Chem. Soc.*, **123**, 2043 (1923); Müller and Shearer, *ibid.*, **123**, 3156 (1923); Trillat, *Ann. phys.*, **6**, 5 (1926).

⁵ Morrow, *Phys. Rev.*, **31**, 10 (1928).

⁶ Landolt-Börnstein-Roth, "Tabellen," 5th ed.

these conditions, it is evident that P_∞ is made up of the electronic and atomic polarizations only, that is, $P_\infty = P_E + P_A$ and $P_M = 0$, which is equivalent to saying that the molecular complexes in the dilute benzene solutions possess no electric moment.

Apparently, when the concentration increases, these complexes, in spite of their lack of electric moment, affect one another sufficiently to cause increase of polarization. It seems possible that the higher dielectric constants of the more concentrated solutions may further the dissociation of the complexes into single molecules and so increase the polarization. The fact that the polarization increases with rising temperature would seem to support the attribution of the increase to the separation of single molecules rather than to the formation of a different type of complex. The absence of electric moment in the complexes in the dilute solutions and the closeness of the apparent molecular weight to that of a double molecule point to a polymerization to double molecules in which the carboxyl groups are in contact as indicated by the x-ray results. However, the mere assumption of the existence of single and double molecules without effect upon one another is inadequate to explain the observed phenomena. The freezing point measurements of Trautz and Moschel³ give an apparent molecular weight of 117.5 for acetic acid when the mole fraction in the benzene solution is 0.0288, increasing to 124.9 when the mole fraction is 0.0650. This and similar results may indicate the formation of definite complexes containing more than two molecules, but it appears possible to explain the observed phenomena in terms of single and double molecules and strong intermolecular forces.

In the hope of reducing the intermolecular forces and the extent of the association, a solvent of higher dielectric constant than benzene was sought. Ether was adopted as being the only liquid of higher constant which, when dissolved in non-polar solvents, showed a polarization independent of concentration. Unfortunately, however, ether may form an addition compound with acetic acid and thus complicate the situation. The polarization of the acetic acid, P_2 , calculated on the assumption that the polarization of the ether, P_1 , is unaffected by the presence of the acid, shows a normal behavior, although the values for the dilute solutions contain errors larger than usual because of loss of ether by volatilization. The P_{12-c_2} curve passes through a flat maximum in the region of high dilution where the apparent polarization of the acetic acid is higher than that of the ether. The value of P_M is calculated by subtracting from P_∞ the approximate value 20 found for $P_E + P_A$ and, from P_M , the electric moment 1.40×10^{-18} is obtained for the single acetic acid molecule. This value cannot be regarded as certain since it may be really the moment of an addition compound of acetic acid and ether, but there is some evidence in its favor.

In order to investigate the question of a definite equilibrium between single and double acetic acid molecules in ether solution, Mr. C. H. Lindsley has measured the distribution of acetic acid between water and ether at 25° over a range of concentration of 0.086 to 1.644 moles of acetic acid per liter of ether, a range within which lie the four most dilute solutions in Table I. The most constant value of the distribution coefficient was obtained when an equilibrium between single and double molecules was assumed. If a is the total number of moles per liter of acetic acid, all the acid being calculated as having molecular weight 60.04, and x is the concentration of single molecules, the equilibrium constant $K = x^2/(a - x)$. The mean value obtained for K was 2.7.

Since it has been shown that the double molecules have practically no moment and do not, therefore, contribute to the orientation polarization P_M and, since it has been assumed that the P_∞ obtained from the ether solutions is the polarization of the single molecules, the value of P_M observed at any concentration should be the orientation polarization for the single molecules $P_{M\infty}$ multiplied by the fraction of the acetic acid which is present as single molecules, that is, $P_M = (x/a)P_{M\infty}$. The values of P have been obtained by interpolation at 25° and those of P_M by subtracting from them $P_E + P_A = 20$. From the value $P_{M\infty} = 41$ thus obtained, the values of P_M have been calculated by means of K and the values of a and x calculated from it. The difference between the observed and calculated values of P_M is large at $c_2 = 0.1039$ and $c_2 = 0.1269$, but for the other solutions and the pure acid the average difference is only 1.9.

Since the value of K determined in the distribution measurements may be affected by the water with which the ether layer is saturated and since it may be different in the concentrated solutions and the pure acid from what it is in the dilute solutions, too much significance should not be attached to the agreement between the observed and calculated values of P_M . It may be said, however, that the entire behavior of acetic acid which has been described is consistent with the theory of its existence in single and double molecules, the force fields of which may affect one another and cause further abnormalities. As the moment of acetic acid might be expected to be not very different from that of methyl acetate, for which Williams⁷ has found a value of 1.67×10^{-18} , the value 1.4×10^{-18} seems reasonable, but it must be borne in mind that there is a possibility that this is really the moment of an addition compound of acetic acid and ether.

The behavior of butyric acid is very similar to that of acetic. The dielectric constants of the pure liquid and the most concentrated solution increase with rising temperature. The dielectric constant is lowered

⁷ Williams, *Physik. Z.*, **29**, 174 (1928).

by the lengthened hydrocarbon chain, which reduces the number of dipoles in unit volume so that pure butyric acid behaves much like a benzene solution containing 0.6 to 0.7 mole fraction of acetic acid. The two methylene groups which differentiate butyric from acetic acid have a combined refraction for the sodium D line of 9.2, which is their contribution to P_E for the compound. This is very nearly the difference between the values of P_∞ for the two substances. The larger proportion of hydrocarbon in the butyric acid molecule lessens the rate of increase of the polarization with decrease in the concentration of benzene in the mixture so that pure butyric acid happens to have the same polarization as acetic.

The close resemblance of butyric acid to acetic is what would be expected from freezing point and partition coefficient measurements and the indication of double molecules by x-ray studies. The single butyric acid molecules must have approximately the same moment as those of acetic acid and form similar complexes in which the carboxyl groups are in contact with one another, canceling their moments.⁸

Summary

The dielectric constants and densities of solutions of acetic and butyric acids have been measured at different temperatures, and the data have been used to calculate the polarizations of the substances.

The dielectric constants of the pure acids behave abnormally in that they increase with rising temperature instead of decreasing.

The results are shown to be consistent with the theory of the existence of the acids in single and double molecules, the latter of which have little or no electric moment. It must be supposed, however, that the molecular force fields may affect one another and cause further abnormalities.

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⁸ Since the submission of the manuscript of this paper for publication, Dr. C. T. Zahn has communicated to the authors a value 1.4×10^{-18} for the moment of acetic acid measured as vapor at high temperatures and low pressures where it must have existed as single molecules. This may be regarded as excellent confirmation of the value for what was thought to be the single acetic acid molecule in ether solution. Wolf, in a paper just published [*Physik. Z.*, 31, 227 (1930)], obtains a value of 0.74×10^{-18} for acetic acid from measurements in benzene solution at 22°, a value of 0.68×10^{-18} for butyric acid and 0.63×10^{-18} for both propionic and isovaleric acid. In calculating these results he used an estimated value of P_A equal to 15% of the molar refraction, which the evidence cited above shows to be much too small in the case of acetic acid. If $P - P_E$ in our results is used to calculate the moments of acetic and butyric acid, the values obtained are close to those calculated by Wolf. As it has been shown that $P - P_E$ consists mainly of the atomic polarization P_A for molecular complexes, the values calculated for moments from these differences and attributed to single molecules would seem to have little significance. These results also cast doubt upon the moment assigned to the carboxyl group in aromatic compounds from measurements upon the strongly associated benzoic acid in benzene solution [Williams, *Chem. Rev.*, 6, 589 (1929)].