

Spurious effects of impurities are unlikely in view of the care that was taken and the use of a dropping electrode with a continuously renewed surface.

### Other Possible Cases of Local Field Effect

This study dealt with the case in which the discharged species is attracted in the diffuse double layer and the absolute value of the ionic valence ( $|z|$ ) of the discharged ion is larger or equal to that of the ion of the indifferent electrolyte which is attracted in the diffuse double layer. Other possible cases should be considered, e.g.: (a) attraction of the discharged species but with  $|z|$  for the discharged species smaller than for the ion of the indifferent electrolyte being attracted in the diffuse double layer; (b) repulsion of the discharge species with  $|z|$  larger for the discharged species than for the ion of the indifferent electrolyte being attracted in or repelled from the diffuse double layer; and (c) repulsion of a discharged species having a  $|z|$  smaller than the ion of the indifferent electrolyte (attraction in or repulsion from the diffuse double layer). Some evidence of a local field effect for case *a* may possibly be found by comparison of the effect of KCl on H<sup>+</sup> discharge on mercury, as studied by Bagotskii and Yablokova,<sup>4b,16</sup> with the effect of LaCl<sub>3</sub> on this reaction, as investigated by Levina and Sarinsky.<sup>4b,17</sup> The agreement between theory and experiment was very good for KCl but poorer for LaCl<sub>3</sub>. Further work on some of the above cases is now under way.

### Conclusion

Results for the discharge of Ga<sup>+3</sup> in presence of Na<sup>+</sup>, Mg<sup>+2</sup> or Al<sup>+3</sup> suggest that the double layer

(16) V. S. Bagotskii and I. E. Yablokova, *Zhur. fiz. Khim.*, **23**, 413 (1949).

(17) S. Levina and V. Sarinsky, *Acta Physicochim. U.S.S.S.*, **7**, 485 (1937).

correction in electrode kinetics may fail in the absence of specific adsorption in the following case: the ion being discharged is attracted in the diffuse double layer; and the ion of the indifferent electrolyte, which is attracted in the diffuse double layer, has an ionic valence of the same sign as the discharged species but of different value. This failure is attributed to the local field effect *though other causes of departure from theory such as difference in solvation, etc., are not ruled out.*<sup>18</sup> The local field effect results from the *discrete* nature of ions in the plane of closest approach and recalls, though the problem is not the same, the effect of the discrete nature of specifically adsorbed ions<sup>19-21</sup> How general the local field effect is remains to be determined by further work.

**Acknowledgments.**—This investigation was supported in part by the National Science Foundation. One of us (A.K.S.) is indebted to the International Coöperation Administration, Washington, D. C., for a fellowship which made possible his stay in this Laboratory.

(18) Cf., e.g., the difference on the effect of alkali metals in the reduction of peroxydisulfate studied by Frumkin and co-workers; see A. N. Frumkin, *Z. Elektrochem.*, **59**, 807 (1955).

(19) (a) O. A. Esin and B. F. Markov, *Acta Physicochim., U.S.S.R.*, **10**, 353 (1939); (b) O. A. Esin and V. Shikov, *Zhur. fiz. Khim.*, **17**, 236 (1943).

(20) B. V. Ershler, *ibid.*, **20**, 679 (1946).

(21) (a) D. C. Grahame, *Z. Elektrochem.*, **62**, 264 (1958); *J. Am. Chem. Soc.*, **80**, 4201 (1958). (b) See ref. 2 for a review.

[CONTRIBUTION FROM THE COLLEGE OF CHEMISTRY AND PHYSICS OF THE PENNSYLVANIA STATE UNIVERSITY, UNIVERSITY PARK, PENNSYLVANIA]

## Conductance of Solutions of Water, Acetic Anhydride and Acetyl Chloride in Acetic Acid

BY THOMAS B. HOOVER<sup>1</sup> AND A. WITT HUTCHISON

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The electrical conductances of solutions of water, acetic anhydride and acetyl chloride in acetic acid have been measured at 25°. The solvent employed was purified by careful fractional distillation and samples exhibiting specific conductances in the range of 2.4 to 3.0 × 10<sup>-9</sup> mho were consistently obtained. The results showed water to be an exceedingly weak electrolyte in acetic acid; the specific conductance of a 0.1 molal solution was only a little more than twice that of the solvent itself. With increasing concentrations of water, the conductance increased more rapidly. Acetic anhydride increased the conductance of the solvent similarly in dilute solutions. Acetyl chloride solutions were much more conducting and resembled solutions of hydrogen chloride in this solvent. A few measurements were made of the conductance of acetic anhydride and of dilute solutions of acetic acid in this liquid.

### Introduction

The objective of the investigation was to contribute to the knowledge of the electrolytic dissociation of solutes which have little ionic character, in a solvent where short range interionic attractions are an additional factor. The two-stage nature of the dissociation of ionogens in acetic acid (or solvents of similarly low dielectric constant) has been discussed in detail by Kolthoff and Bruckenstein.<sup>2</sup> These authors consider first, the primary ionization of the solute, involving the transformation of a partially covalent bond to a purely electrostatic attraction in the ion pair, and second,

the dissociation of the ion pair to free ions subject only to long range interactions.

Several investigations<sup>3</sup> have been made of the conductance behavior of the binary system water-acetic acid but, in general, these did not provide measurements in dilute solutions. Kolthoff and Willman<sup>3a</sup> reported consistent conductance measurements of solutions of water extending to concentrations as low as 0.02 molal in connection with an investigation of the effect of water on the conductance of other electrolytes in acetic acid. They

(1) Abstracted from a thesis by Thomas B. Hoover presented to the Graduate School in partial fulfillment of the requirements for the Ph.D. degree, June, 1960.

(2) I. M. Kolthoff and S. Bruckenstein, *J. Am. Chem. Soc.*, **78**, 1 (1956).

(3) (a) I. M. Kolthoff and A. Willman, *ibid.*, **56**, 1007 (1934). (b) W. R. Bousfield and T. M. Lowry, *J. Chem. Soc.*, **99**, 1432 (1911); W. C. Eichelberger and V. K. LaMer, *J. Am. Chem. Soc.*, **55**, 3635 (1933); A. A. Glagoleva, *Zhur. Obshchei Khim.*, **18**, 1005 (1948); A. N. Campbell and E. M. Kartzmark, *Can. J. Research*, **28B**, 43 (1950). (c) T. S. Brun, *Univ. i Bergen Årbok 1952, Naturvitenskap. Rekke No. 12*, 1 (1953).

did not attempt to interpret the results of the measurements of the simple water solutions. Brun<sup>3c</sup> endeavored to measure the conductance of low concentrations of water in acetic acid of high purity but the internal consistency of the results was poor.

Brun also measured the conductances of solutions of especially purified acetic anhydride in acetic acid. He concluded that the acetic anhydride in very dilute solutions was no more ionized than the solvent. In more concentrated solutions the conductance increased but the results were poorly reproducible. The only other conductometric study of this system which has been reported is that of Trifonov and Cherbov<sup>4</sup> who investigated the entire binary system. These authors used acetic anhydride of such high specific conductance that, according to Brun, their data merely represent the dilution of the impurities in the anhydride.

Hall and Voge<sup>5</sup> observed that the addition of acetic anhydride to a solution of sulfuric acid in acetic acid increased the specific conductance by much more than a simple additive effect. The same result was confirmed by us<sup>6</sup> in the conductometric technique for titrating water in acetic acid solutions, where an excess of acetic anhydride was found to increase the conductance of the sulfuric acid catalyst to the same extent, on a molar basis, as water. Thus acetic anhydride, in analogy to water, may function as a weak base in acetic acid systems.<sup>7</sup>

The only record which has been found of previous conductance measurements on solutions of acetyl chloride in acetic acid is the report of Usanovich and Vasil'eva.<sup>8</sup> The original paper has not been obtained for study but, since the investigation covered the complete binary system, it is unlikely that data were obtained for very dilute solutions.

### Experimental

**Conductivity Apparatus.**—The fully shielded conductivity bridge used was based on the design of Luder.<sup>9</sup> The audio oscillator was the Hewlett-Packard Model 200AB and a Hewlett-Packard Model 415A Standing Wave Meter was employed as the amplifier-detector. The use of this instrument in conductance work has not been described previously. In the present study it has proved to show high gain with exceptional stability and freedom from interference. Frequency control was obtained by means of interchangeable narrow band pass filters in the detector circuit. Values of 500, 1000 and 2000 c.p.s. were used in this work.

The conductance cell was a modified erlenmeyer design with a 500-ml. round bottom flask as mixing chamber and a connecting electrode chamber. The electrodes were concentric cylinders of bright platinum foil, providing a constant of 0.00584. Calibration was performed with solutions of potassium acetate in acetic acid by intercomparison with two other cells which were referred to the potassium chloride standards of Jones and Bradshaw through the equation of Lind, Zwolenik and Fuoss.<sup>10</sup> The thermostat was a 5-quart

kerosine bath set in a larger water-bath and controlled at  $24.94 \pm 0.01^\circ$ .

**Materials.**—Acetic acid with specific conductances in the range  $2.4$  to  $3.0 \times 10^{-9}$  mho was obtained by careful fractional distillation of reagent grade glacial acetic acid at atmospheric pressure. Prior treatment with an oxidizing agent<sup>8a,11</sup> did not give a product of any lower specific conductance.

Triply distilled water with a specific conductance of  $0.8$  to  $1 \times 10^{-6}$  mho was used as a solute.

Acetic anhydride of reproducible quality could not be obtained by the procedures employed in this work. These included distillation at reduced pressure, under nitrogen, and from various bases such as quinoline, potassium acetate and silver acetate. The material of lowest specific conductance ( $2.9 \times 10^{-8}$  mho) was prepared by distillation from synthetic quinoline (1% of the total charge) at 75 mm. pressure. Only Brun<sup>3c</sup> has reported a lower specific conductance ( $0.5 \times 10^{-8}$ ), obtained by refluxing the material through his cell for several days. A dielectric constant of  $22.5 \pm 0.2$  was measured on a sample of acetic anhydride having a specific conductance of  $9.3 \times 10^{-8}$  mho. Tedder<sup>12</sup> has reported a dielectric constant of 21 at the same temperature ( $25^\circ$ ).

Acetyl chloride was twice distilled from quinoline at atmospheric pressure. The product was collected in Pyrex ampules which were sealed under vacuum.

**Conductance Measurements.**—Transfers of solvent or solution to and from the cell were made under an atmosphere of dry nitrogen since experience demonstrated that protection from atmospheric contamination was essential. At the start of each run the cell was rinsed with changes of solvent until no further reduction in conductance was observed. The quantity of solvent taken was determined by weighing the filled cell. Solutes, either pure or in stock solution, were added by weight from hypodermic syringes of 1- to 10-ml. capacity. In most cases a 24-gage stainless steel needle was used with the syringe and the tip of the needle was sealed by insertion in a small piece of Kel-F elastomer to prevent any loss during weighing. Because of the corrosive nature of acetyl chloride this substance was added from an all-glass syringe.

Bridge measurements were made with the ratio arms in normal and reversed positions at each of the three frequencies. The extrapolation of resistance to infinite frequency was made as a quadratic function of  $f^{-1/2}$  as proposed by Nichol and Fuoss.<sup>13</sup> The correction rarely amounted to more than 1% of the resistance measured at 2000 c.p.s. and differed only a few tenths of a per cent. from a linear extrapolation against  $f^{-1/2}$  from the measured values at 500 and 2000 c.p.s.

**Dielectric Constant Measurements.**—Dielectric constant determinations were made with the same cell and bridge as for the conductance measurements. The difference method suggested by Smyth<sup>14</sup> was followed. The cell was calibrated at  $25^\circ$  with benzene, acetic acid and nitrobenzene using dielectric constant values of 2.274, 6.24 and 34.22, respectively.<sup>15</sup> The extrapolated vacuum capacitance of the cell was 15.7 pf. as compared with 13.6 pf. calculated from the conductance constant.

### Results

**Water in Acetic Acid.**—The data obtained for the conductances of solutions of water in acetic acid are shown in Fig. 1. An examination shows that the data obtained in the present study are in excellent agreement with the results reported by Kolthoff and Willman.<sup>3a</sup> The values of Brun<sup>3c</sup> and a single result of Campbell and Kartzmark<sup>3b</sup> in

(4) N. A. Trifonov and S. I. Cherbov, *Bull. inst. recherches biol. Perm.*, **6**, 259 (1929); *C. A.*, **23**, 4608 (1929). Quoted by Brun.<sup>3c</sup>  
 (5) N. F. Hall and H. H. Voge, *J. Am. Chem. Soc.*, **55**, 239 (1933).  
 (6) T. B. Hoover and A. W. Hutchison, *Anal. Chem.*, **29**, 518 (1957).  
 (7) For alternative hypotheses see J. Russell and A. E. Cameron, *J. Am. Chem. Soc.*, **60**, 1345 (1938); H. A. E. Mackenzie, *J. S. African Chem. Inst. [N.S.]*, **3**, 1 (1950).  
 (8) M. Usanovich and L. N. Vasil'eva, *Zhur. Obshchei Khim.*, **16**, 1202 (1946); *C.A.*, **41**, 2976 (1947).  
 (9) W. F. Luder, *J. Am. Chem. Soc.*, **62**, 89 (1940).  
 (10) J. E. Lind, Jr., J. J. Zwolenik and R. M. Fuoss, *ibid.*, **81**, 1557 (1959).

(11) K. J. P. Orton and A. E. Bradfield, *J. Chem. Soc.*, 960 (1924); A. W. Hutchison and G. C. Chandler, *J. Am. Chem. Soc.*, **53**, 2881 (1931); W. C. Eichelberger and V. K. LaMer, *ibid.*, **55**, 3633 (1933).  
 (12) J. M. Tedder, *J. Chem. Soc.*, 2646 (1954).  
 (13) J. C. Nichol and R. M. Fuoss, *J. Phys. Chem.*, **58**, 696 (1954).  
 (14) C. P. Smyth, "Dielectric Behavior and Structure," McGraw-Hill Book Co., New York, N. Y., 1955, p. 212.  
 (15) A. A. Maryott and E. R. Smith, "Table of Dielectric Constants of Pure Liquids," National Bureau of Standards Circular No. 514, 1951; J. Timmermans, A. M. Piette and R. Phillippe, *Bull. soc. chim Belges*, **64**, 5 (1955).

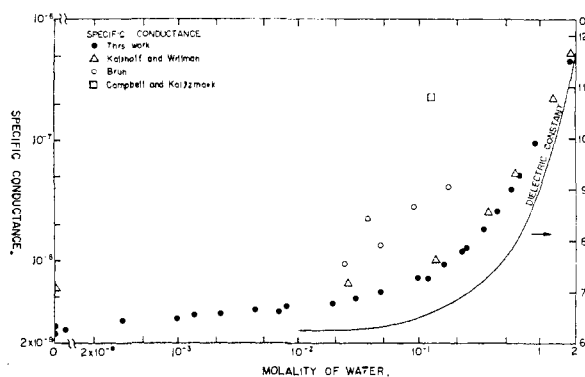
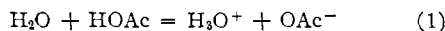


Fig. 1.—Specific conductance and dielectric constant of solutions of water in acetic acid.

the range of concentrations examined in the present work are also shown in the figure.

The outstanding feature of the conductance data for this system is that they indicate water to be an extremely weak electrolyte. It is necessary to go to concentrations as high as 0.05 *m* in order to double the specific conductance of the solvent. Thus, the ionization of dilute solutions of water cannot be discussed apart from the ionization of the acetic acid.

In view of the well established basic character of water relative to acetic acid the obvious mode of ionization is



This is formally the same process as for the ionization of acetic acid in aqueous solutions.

Water is much too weak an electrolyte in this solvent to permit reliable estimates of both the limiting equivalent conductance,  $\Lambda^0$ , and the dissociation constant,  $K$ , to be obtained by extrapolation of the conductance data according to the Fuoss-Shedlovsky conductance equations.<sup>16</sup> However, the data can be interpreted with the use of a value for  $K$  obtained independently by Bruckenstein and Kolthoff<sup>17</sup> from potentiometric and spectrophotometric measurements.

Since the solvent conductance correction is relatively very large, we have followed the procedure of Shedlovsky and Kay<sup>18</sup> in determining empirically a solvent term to be subtracted from the measured specific conductance in the equation

$$L - L_0 = \frac{\Lambda^0 K^{1/2} c^{1/2}}{S f_{\pm}} \left[ 1 - \frac{\Lambda^* S}{\Lambda^0} \right]^{1/2} \quad (2)$$

The symbols have the significance ascribed by the original authors. It is to be noted that  $L$  is a thousand times  $\bar{L}$ , the measured specific conductance. The term in brackets is an approximation to  $(1 - x)^{1/2}$  where  $x$  is the degree of ionization. Over the entire concentration range covered by this investigation the term does not differ appreciably from unity and it has been omitted from subsequent equations. Several factors relating to medium effects were taken into account, however, in order to represent the data for the whole concentration range. First, the activity coefficient

(16) R. M. Fuoss and T. Shedlovsky, *J. Am. Chem. Soc.*, **71**, 1490 (1949).

(17) S. Bruckenstein and I. M. Kolthoff, *ibid.*, **79**, 5915 (1957).

(18) T. Shedlovsky and R. L. Kay, *J. Phys. Chem.*, **60**, 151 (1956).

of the undissociated solute,  $f_u$ , was included explicitly in the expression for the apparent over-all dissociation constant,  $K$ . Second, the effect of the varying viscosity of the solution was allowed for approximately by replacing  $\Lambda^0$  by  $\Lambda^0 \eta^0 / \eta$ , where  $\eta^0$  is the viscosity of acetic acid and  $\eta$  is the viscosity of the solution of concentration  $c$ . The major medium effect, however, is that of dielectric constant. According to Denison and Ramsey<sup>19</sup>

$$-\log K_d = \frac{\epsilon^2}{2.303 a D k T} \quad (3)$$

for a uni-univalent electrolyte. In equation 3  $K_d$  is the dissociation constant for ion pairs,  $\epsilon$  is the electronic charge,  $a$  is the distance of closest approach of the ions,  $D$  is the dielectric constant,  $k$  is the Boltzmann constant and  $T$  is absolute temperature. If, then, the variation in  $K$  of equation 2 with changing medium be ascribed entirely to the effect of the changing dielectric constant on  $K_d$  according to equation 3 the following substitution may be made.

$$K^{1/2} = (K^0)^{1/2} 10^B \quad (4)$$

where

$$B = \frac{3.628 \times 10^4}{dT} \left( \frac{1}{D^0} - \frac{1}{D} \right) \quad (5)$$

after substituting values of the universal constants and expressing  $\bar{a}$  in ångström units. Parameters with superscript zeros refer to the infinitely dilute solution. This step carries the implication that  $K$  is proportional to  $K_d$ . As Kolthoff and Bruckenstein<sup>2</sup> have shown that  $K$  is well represented by the product of  $K_d$  and the dissociation constant  $K_i$  for the equilibrium between the neutral molecule and ion pair, our treatment is equivalent to assuming that  $K_i$  is independent of dielectric constant. With these modifications equation 2 becomes

$$L - L_0 = \Lambda^0 (K^0)^{1/2} \left[ \frac{\eta^0 f_u^{1/2}}{\eta S f_{\pm}} 10^B \times c^{1/2} \right] \quad (6)$$

It is to be noted that  $K^0$  includes not only the limiting value of the ion pair dissociation constant in the pure solvent but also any non-electrostatic dissociation,  $K_i$ . When  $\bar{a}$  is properly chosen by trial and error, a plot of  $L$  versus the bracketed term is linear, with intercept  $L_0$  and slope  $\Lambda_0 (K^0)^{1/2}$ . In applying equation 6 a trial value of  $\Lambda^0$  was obtained by plotting  $L$  against  $c^{1/2}$  and taking the limiting slope at low concentrations as an initial estimate of  $\Lambda^0 (K^0)^{1/2}$ .  $K^0$ , as determined by Bruckenstein and Kolthoff<sup>17</sup> has the value of  $2.95 \times 10^{-18}$ . With the resulting provisional value of  $\Lambda^0$ ,  $S$  and  $f_{\pm}$  were calculated for each experimental point and the plot according to equation 6 gave an improved estimate of  $\Lambda^0$ . Recalculation with the second trial value of  $\Lambda^0$  did not produce any further change. The final values are shown in Figs. 2 and 3. A choice of  $\bar{a}$  equal to 5 Å. gave a satisfactorily linear plot. Points for the dilute solutions are shown on a larger scale in Fig. 2. The straight line in both Figs. 2 and 3 represents the least squares fit of all the points since there was no significant difference between the two runs. The line has an intercept,  $L_0$ , of  $0.33 \times 10^{-6}$  and a slope of  $7.87 \times 10^{-6}$ , corresponding to  $\Lambda^0$  of 14.5.

(19) J. T. Denison and J. B. Ramsey, *J. Am. Chem. Soc.*, **77**, 2615 (1955).

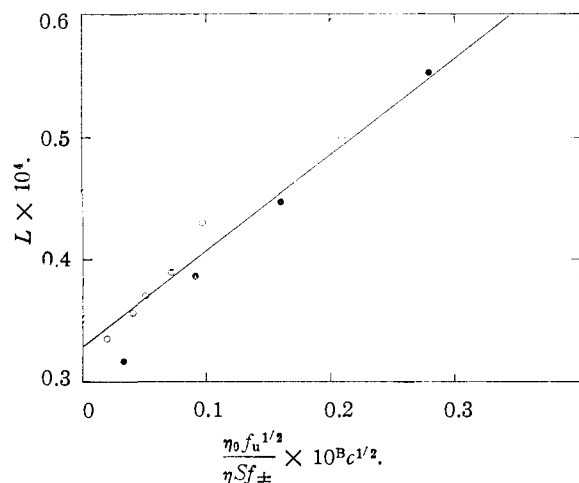


Fig. 2.—O, Run 30; ●, Run 32.

In the above calculations values of  $f_u$  were computed from the empirical equation of Hansen, Miller and Christian<sup>20</sup> and converted to the molar concentration scale with reference state corresponding to infinite dilution in acetic acid. Densities of the water-acetic acid solutions were taken from the International Critical Tables<sup>21</sup> and viscosities were interpolated from the results of Bingham, White, Thomas and Caldwell.<sup>22</sup> Dielectric constants were measured during the course of this investigation and can be represented by the equation

$$D = 6.24 + 2.74m_{H_2O} \quad (7)$$

in which  $m_{H_2O}$  is the molal concentration of water. Table I presents values of the parameters which were used in equation 6 at even values of concentration.

TABLE I  
 $K = 2.95 \times 10^{-18}$ ,  $d = 5.0 \text{ \AA}$ .

$m$	$10^2 \eta$	$f_u$	$f_{\pm}$	$pK_d$	$\frac{\eta_0 f_u^{1/2}}{\eta S f_{\pm}} 10^B \times c^{1/2}$
0.001	1.150	1.000	0.999	7.79	0.033
.010	1.152	0.997	.991	7.76	.106
.100	1.174	.973	.976	7.46	.466
1.000	1.360	.779	.923	5.42	12.372
2.000	1.525	.645	.865	4.15	63.487

The result that  $L^0$  is slightly greater than the measured solvent conductance and that  $L$  is essentially linear in  $c^{1/2}$  at low concentrations is quite unexpected. If the ionization follows equation 1 an appreciable common ion effect from the autoprotolysis of the solvent would be expected since the respective ionization constants differ by only a hundred-fold.<sup>17,23</sup>

Trial calculations with assumed values of the limiting molar conductances of water and solvent in the range of 10 to 50 indicated that there should be a depression of the conductance well beyond the experimental error and having a maximum effect at a concentration of approximately 0.01  $m$ .

(20) R. S. Hansen, F. A. Miller and S. D. Christian, *J. Phys. Chem.*, **59**, 391 (1955).

(21) "International Critical Tables," Vol. III, McGraw-Hill Book Co., New York, N. Y., 1926, p. 123.

(22) E. C. Bingham, G. F. White, A. Thomas and J. L. Caldwell, *Z. physik. Chem.*, **83**, 641 (1913).

(23) S. Bruckenstein and I. M. Kolthoff, *J. Am. Chem. Soc.*, **78**, 2974 (1956).

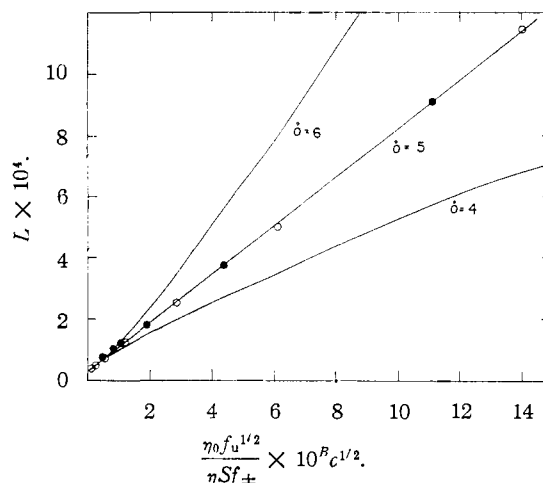


Fig. 3.—O, Run 30; ●, Run 32.

An alternative explanation which was considered is based on the hypothesis that water does not form any ions in this solvent but contributes to the ionization of acetic acid by displacing the monomer-dimer equilibrium in the direction of increasing the monomer concentration. A  $\Lambda^0$  of 37 for acetic acid, derived from the lowest measured specific conductance of  $2.2 \times 10^{-9}$  mho, and the molecular equilibrium constants deduced by Kipling<sup>24</sup> from density measurements lead to an apparent ionization constant for water which agrees within a factor of three with the value of Bruckenstein and Kolthoff.<sup>17</sup> The equilibria involved in this treatment, however, imply a more complex relationship between specific conductance and concentration of water than the one-half power of concentration. Whatever the mechanism of ionization in the dilute solutions, the Denison and Ramsey<sup>19</sup> theory of ion pair dissociation seems adequate to represent the changes in conductance in the more concentrated solutions.

Values of the equivalent conductance of the solutions were calculated without applying any solvent correction. When a plot was made of the logarithm of these values *vs.*  $\log m$  a linear relation was found up to concentrations approaching 0.1  $m$ . The slope of this curve was about  $-0.88$ . At higher concentrations the curve passed through a minimum (at approximately  $m = 0.2$ ).

**Acetic Anhydride in Acetic Acid.**—The data presented in Fig. 4 serve to establish an upper limit for conductance due to acetic anhydride and provide at least circumstantial evidence of the results to be expected under ideal conditions. The initial steep portions of the curves for Runs 17 and 33 correspond to the addition of solute as a dilute stock solution in acetic acid. The subsequent portions of these runs and all of Run 38 were made by adding undiluted acetic anhydride to the cell. It is apparent that the stock solutions must have been contaminated in some manner. The vertical solid arrows in Fig. 4 represent additions of water to the systems. Initial measurements indicated that the conductances due to water and to acetic anhydride were strictly additive. After standing for a

(24) J. J. Kipling, *J. Chem. Soc.*, 2858 (1952).

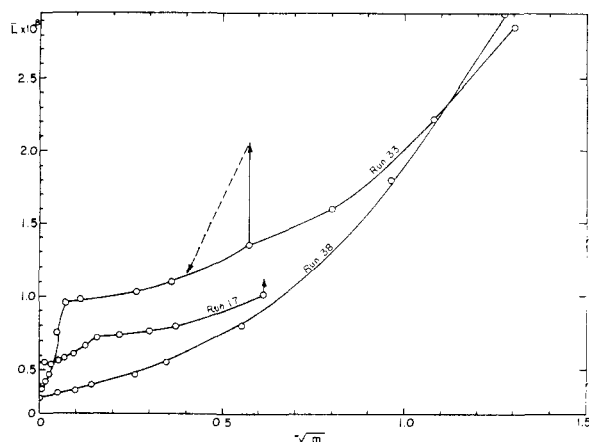


Fig. 4.—Specific conductance *vs.* square root of molality of acetic anhydride in acetic acid solutions.

week at room temperature the specific conductances decreased to steady values corresponding very closely to the stoichiometric reaction of water and anhydride as shown by the broken arrow. These experiments provide phenomenological evidence of conductance changes due to acetic anhydride itself rather than to any contaminants. By the same reasoning the high conductance of the solvent used in Run 17 is not ascribable to water since a week elapsed after the addition corresponding to  $\sqrt{m} = 0.094$  without a significant break appearing in the curve.

The data for solutions of acetic anhydride do not warrant an attempt at a detailed analysis on account of the evidences of contamination. As will be seen by reference to Fig. 4 the smallest slope of the plots of specific conductance *vs.* the square root of molality of anhydride occurs for the additions of undiluted solute in Run 17. Unfortunately the solvent used in this run had a relatively high conductance and the stock solution used for the lower concentrations apparently introduced additional contaminant. If it be assumed that the unidentified impurities make only an additive contribution to the specific conductance then the smallest slope of  $\bar{L}$  *vs.*  $\sqrt{m}$  sets an upper limit to the contribution from the acetic anhydride. In this way it is concluded from the data of Run 17 that

$$K(\Lambda_A^0)^2 \leq 1 \times 10^{-11}$$

The corresponding value for water is  $6.19 \times 10^{-11}$ . Thus, acetic anhydride is a weaker electrolyte than water if  $\Lambda_A^0$  and  $\Lambda_W^0$  are similar in magnitude.

**Acetic Acid in Acetic Anhydride.**—One run was made of acetic acid solute in acetic anhydride solvent. Data are shown in Fig. 5. The acetic anhydride was the same as used in Run 38, having a specific conductance of  $9.33 \times 10^{-8}$  mho and the acetic acid had a specific conductance of  $2.14 \times 10^{-9}$  niho. Because of the presumed impurities in the acetic anhydride, a duplicate run was not attempted and no great importance is attached to the data for this system.

This experiment was made in order to gain some information about the ionization of acetic acid as a solute in a medium not too dissimilar from its own bulk properties. The plot of specific conductance

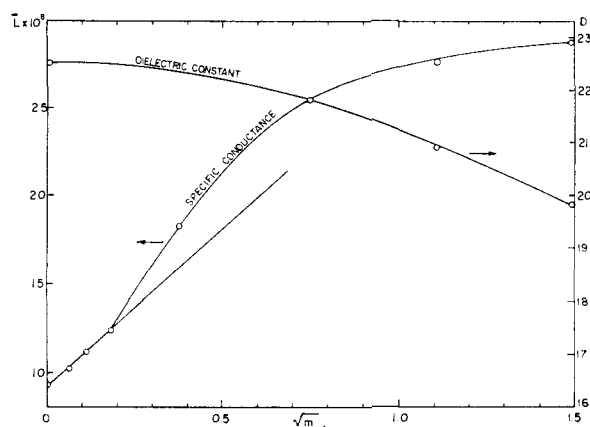


Fig. 5.—Specific conductance and dielectric constant *vs.* square root of molality of acetic acid in acetic anhydride solutions.

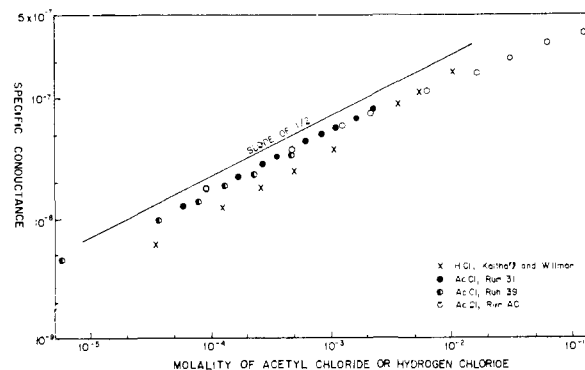


Fig. 6.—Specific conductance of solutions of acetyl chloride and of hydrogen chloride in acetic acid.

*vs.* square root of molality is linear for the three lowest concentrations and has a slope corresponding to

$$K(\Lambda^0)^2 = 4 \times 10^{-8}$$

On the assumption that the only cause for a difference between the dissociation constants of acetic acid in the pure state and as a dilute solution in acetic anhydride is the difference in dielectric constants, the corresponding value in acetic acid of the product  $K(\Lambda^0)^2$  can be calculated from the ratio of  $K_d$ 's according to equation 3. When an "*a*" of 5 Å. is used the expected value of  $K(\Lambda^0)^2$  at a dielectric constant of 6.24 (acetic acid) becomes  $9.3 \times 10^{-14}$ . A value of  $2.9 \times 10^{-13}$ , differing by a factor of 3, is calculated from the lowest measured specific conductance of pure acetic acid.<sup>25</sup>

**Acetyl Chloride in Acetic Acid.**—The first runs made with acetyl chloride were poorly reproducible, and the conductances of individual solutions tended to drift to higher values with passing time so that a characteristic value could not be determined precisely. It was evident, however, that acetyl chloride is a much stronger electrolyte than water or acetic anhydride. Subsequently more reliable data were obtained in three runs and these results are presented in Fig. 6. The points are

(25) In this comparison between different media *K* is not the ion product constant for acetic acid used earlier but is that constant divided by the molality of acetic acid.

seen to be on a nearly straight line with a slope of approximately 0.5. This suggests that the Ostwald dilution relation is obeyed and that the solute is behaving as a weak electrolyte. The data of Kolthoff and Willman<sup>3a</sup> for hydrogen chloride have been represented on the same figure to permit a comparison. It is interesting to note that the data for acetyl chloride are very similar, except that the conductances are somewhat higher in the dilute solution region.

After the last solution ( $m = 2.19 \times 10^{-3}$ ) of Run 31 was measured, water was added to correspond to a concentration of  $1.6 \times 10^{-2} m$ , thus in large excess. The first reading made three minutes after adding the water showed an increase in the conductance from  $8.12 \times 10^{-3}$  to  $10.2 \times$

$10^{-3}$ . The conductance was  $10.1 \times 10^{-3}$  after twenty additional minutes had passed and remained essentially unaltered on standing overnight. This indicated that the hydrolysis reaction must have been substantially complete in the first three minutes.

The possibility has been considered that instead of acetyl chloride the products of a solvolytic reaction (acetic anhydride and hydrogen chloride) were actually being observed. No information bearing directly and decisively on this point has been found. We believe that the comparative stability of these solutions when rigorous precautions were taken to avoid traces of moisture or hydrogen chloride is indicative of the absence of a solvolytic reaction.

[CONTRIBUTION FROM THE WHITMORE CHEMICAL LABORATORY, THE PENNSYLVANIA STATE UNIVERSITY, UNIVERSITY PARK, PENNSYLVANIA]

## Intramolecular Twisting Effects in *o,o'*-Alkyl Substituted Anisole Spectra<sup>1</sup>

BY LOIS J. FROLEN AND LIONEL GOODMAN

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The  ${}^1L_b \rightarrow {}^1A(2600 \text{ \AA.})$ ,  ${}^1L_a \rightarrow {}^1A(2100 \text{ \AA.})$  and the  ${}^1B_a, {}^1B_b \rightarrow {}^1A(1800 \text{ \AA.})$   $\pi \rightarrow \pi^*$  absorption bands were measured for a series of *o*, and *o,o'*-alkyl substituted anisoles. The triplet  $\rightarrow$  singlet emission spectra for this series as well as the corresponding *N,N*-dimethylanilines at 77°K. in 1:6 methylcyclohexane-isopentane solvent are also reported. It is shown that the "classical" case of the spectra of *o* and *o,o'*-substituted *N,N*-dimethylanilines, representing the effect of twisting of a  $\pi$ -orbital into a  $\sigma$ -orbital on the benzene analog bands, is anomalous due to interaction between benzene analog and charge transfer states. The anisoles are shown to represent the "normal" case of intramolecular twisting effects on the  $\pi \rightarrow \pi^*$  spectra (resulting from the absence of appreciable BA-CT interaction).

### Introduction

In this paper we are concerned with a comparison of the steric effects of *o* and *o,o'*-alkyl substitution on dimethylaniline and anisole spectra. Such a comparison is of interest since the 2500 Å. band in dimethylaniline is primarily charge transfer<sup>2</sup> (CT) yielding the opportunity for appreciable interaction between the CT and benzene analog (BA) states. In anisole, no low-lying CT band is observed, consistent with the higher electronegativity of oxygen. Inasmuch as CT configurations arising from excitation of the methoxy-oxygen,  $\pi$ -electrons should be at much higher energies than the BA configurations, opportunity for any appreciable BA-CT interaction is precluded.

**Spectra.**—We have carefully examined the three benzene analog bands ( ${}^1L_b \leftarrow {}^1A(2600 \text{ \AA.})$ ,  ${}^1L_a \leftarrow {}^1A(2100 \text{ \AA.})$  and  ${}^1B_a, {}^1B_b \leftarrow {}^1A(1800 \text{ \AA.})$ ) for a series of substituted anisoles obtaining  $\nu_{\infty}$  and  $\nu_{\max}$  in the vapor phase and oscillator strengths in hydrocarbon solutions. Previous measurements on substituted anisole spectra have been obtained by Burawoy and Chamberlain<sup>3</sup> and Dearden and Forbes.<sup>4</sup> Burawoy and Chamberlain examined the  ${}^1L_b \leftarrow {}^1A$  bands in polar solvents. Dearden and

Forbes measured extinction coefficients and the values of  $\lambda_{\max}$  for the  ${}^1L_b \leftarrow {}^1A$  and  ${}^1L_a \leftarrow {}^1A$  bands. The experimental data on the *o*-alkyl substituted anisoles as obtained from references 3 and 4 and from our own work are shown in Fig. 1.<sup>5</sup> The trends in the corrected (see footnote c to Table I) observed transition energies and observed intensities are illustrated in Figs. 2a and 3a, respectively. There can be little doubt that the observed intensity and frequency changes may be attributed primarily to intramolecular twisting perturbations since *m* or *p*-substitutions have relatively small effects.<sup>3</sup>

The four molecules appearing in Table I are designated in order of probable increasing twist angle. Since the effective "size" of the methoxy group as computed from van der Waals radii is approximately the same as that computed in the same way for the *N,N*-dimethylamino group (planar 120° configuration), the ordering of steric effects is probably the same in both series of compounds.

The trends in transition energies and intensities for substituted *N,N*-dimethylanilines (DMA) are taken from (I) and are reproduced in Figs. 2b and 3b, respectively.

Comparison of the trends of the anisole and dimethylaniline transition energies shows that the  ${}^1L_b \leftarrow {}^1A(2600 \text{ \AA.})$  band undergoes similar behavior

(1) This research was supported by a grant from the National Science Foundation.

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(4) J. C. Dearden and W. F. Forbes, *Can. J. Chem.*, **37**, 1305 (1959). The extinction coefficient for 2,6-dimethylanisole appears to be in error.

(5) All compounds and solvents were subjected to repeated purification until a constant extinction coefficient was obtained. The  ${}^1L_a \leftarrow {}^1A$  and  ${}^1B_a, {}^1B_b \leftarrow {}^1A$  bands were measured with a Cary Model 13 Recording Spectrophotometer and the  ${}^1L_b \leftarrow {}^1A$  band was measured with a Beckman Model DU Spectrophotometer with a recording attachment made by Warren Electronics, Inc.