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The High Field Conductance of Acetic Acid from 5 to 55° Relative to Hydrochloric Acid

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The high field conductance of acetic acid in aqueous solution in the concentration range near 10^{-4} molar has been determined relative to hydrochloric acid at temperatures from 5 to 55°. The fractional change of conductance is greater at the lower temperatures than at the higher. Because of polarization effects it was found impossible to carry out determinations relative to potassium chloride; these effects seemed to be absent when hydrochloric acid was employed as reference electrolyte. However, it is concluded that polarization is present in equal degree in both the acetic and hydrochloric acid cells under high field measurement conditions employed. This conclusion is based on the departures from linearity of the fractional high field conductance quotient, $\Delta\lambda/\lambda_0$, at high fields and high temperatures.

Although a quarter of a century has passed since Wien[1] announced his discovery that the conductances of electrolytic solutions do not conform to Ohm's law under the influence of high potential gradients, only one set of precise data has been published for an aqueous solution of a weak electrolyte[2] with which it is possible to test the theory of Onsager.[3] In Schiele's paper both the temperature and concentration of the solutions were unspecified. The present paper includes data on the high field conductance of acetic acid in aqueous solution in the concentration range near 10^{-4} molar, relative to hydrochloric acid, at temperatures from 5 to 55°.

Experimental

The experimental procedure was identical with that of Gledhill and Patterson,[4] employing a differential pulse transformer bridge circuit. All measurements were made with four microsecond pulse duration. Preliminary experiments in which potassium chloride was used as reference electrolyte indicated either that polarization was taking place in the acetic acid conductance cell, or that time lags of a duration far greater than might reasonably be expected were involved (see the discussion, below). The reference electrolyte was then changed to hydrochloric acid, whereupon it became possible to carry out the measurements without undue difficulty. Accordingly, other pulse durations were not studied. Acetic acid stock solution was made by dilution of reagent grade glacial acetic acid with carbon dioxide-free water. This stock solution, approximately 0.7 molar, was analyzed by titration against a barium hydroxide solution standardized against potassium acid phthalate. The solutions used in the high field measurements were made by weight dilution in the conductance cell to give a resistance in the order of 1000 ohms at 25°, corresponding to a concentration of $7. \times 10^{-4}$ molar. Hydrochloric acid stock solution, approximately 0.01 molar, was made by dilution of the concentrated acid. The solutions used as references for the high field measurements were made by dilution of this stock solution in the conductance cell to give a resistance 60-70 ohms lower than that of the acetic acid solutions. The concentration of the hydrochloric acid was determined by low field conductance measurement. The temperature control was within 0.015 at 25° and within 0.02° at all other temperatures. All temperatures were measured against a recently calibrated platinum resistance thermometer.

Results

Table I contains the experimental results as well as the relative Wien effects computed from the Onsager theory[3] employing the relation

$$\frac{K(X)}{K(O)} = \mathrm{F}(b) = 1 + b + \frac{b^2}{3} + \frac{b^3}{18} + \frac{b^4}{180} + \frac{b^5}{2700} + \ldots \tag{1}$$

where

$$b = \frac{z_1{}^2 z_2{}^2(\Lambda_1 + \Lambda_2)}{z_2\Lambda_1 + z_1\Lambda_2} \times \frac{|X|\,\epsilon^3}{2Dk^2T^2} \tag{2}$$

(The symbols used throughout this paper are those of Harned and Owen.[5] The symbols are further defined elsewhere.[6] The symbol R_v used in Table I refers to the resistance measured at the field in question.) In Table I, columns 1, 2 and 3 give the experimental data. Columns 4, 5 and 6 give the essential quantities for the Onsager calculation for acetic acid.[3] Columns 7 and 8 are the data for the high field conductance of the reference electrolyte, hydrochloric acid. For this calculation the relation

$$\Lambda = \Lambda^0 - \frac{|e_j|^2\kappa\Lambda^0}{2DkT}\,g(\mathrm{x}) - \frac{96500k|e_j|2\kappa}{6\sqrt{2}\pi\eta 300}\,\mathrm{f}(\mathrm{x}) \tag{3}$$

was employed; these values were subtracted from the computed values for acetic acid so that the theoretical data would be comparable with the relative high field conductances measured. The theoretical relative values of the change of conductance of acetic acid, expressed as per cent., have been corrected further for the weakening of the interionic attraction by the atmosphere by subtraction of the quantity

$$(1 - \gamma_\pm)100 \tag{4}$$

It has been assumed that the hydrogen ion concentration of the acetic acid is approximately the same as that in the hydrochloric acid, and the values of $\gamma_\pm$ employed are those for hydrochloric acid at 10^{-4} molar concentration over the temperature range 5–55°.

Figure 1 is a plot of the data. Only the theoretical curves for 5° and 55° have been drawn on the graph.

Discussion

When attempts were made to determine the high field conductance of acetic acid relative to potassium chloride, two peculiar effects were observed. At fields above approximately 140 kv./cm. at 25°, the balance patterns observed on the oscilloscope became tilted from the normal horizontal position which is a criterion of impedance balance. The tilt suggested a capacitative unbalance, but it was found impossible to restore balance by addition or removal of capacitance across the cells. Further, the experimental percentage increases in conductance of acetic acid were not found to follow

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[1] M. Wien and J. Malsch, *Ann. Physik*, **83**, 305 (1927).

[2] J. Schiele, *ibid.*, **13**, 811 (1932).

[3] L. Onsager, *J. Chem. Phys.*, **2**, 599 (1934).

[4] J. A. Gledhill and A. Patterson, *J. Phys. Chem.*, accepted for publication, December, 1952.

[5] H. S. Harned and B. B. Owen, "The Physical Chemistry of Electrolytic Solutions," Reinhold Publishing Corp., New York, N. Y., 2d ed., 1950, pp. 95–106.

[6] F. E. Bailey and A. Patterson, THIS JOURNAL, **74**, 4426 (1952).

TABLE I

THE HIGH FIELD CONDUCTANCE OF AQUEOUS SOLUTIONS OF ACETIC ACID RELATIVE TO HYDROCHLORIC ACID FROM 5 TO 55°

HAcO, 7.428 × 10^{-4} molar; HCl, 0.975 × 10^{-4} molar; $\Lambda^0 = 297.53$; $\Lambda_{x_0} = 296.53$; $(1 - \gamma_\pm)100 = 1.14$

Experimental Results			Onsager Theory					
Field, kv./cm.	Rv HAcO	$\frac{\Delta\lambda}{\lambda_0}$, %	$K(X)$	$\frac{-K + (K^2 + 4cK)^{1/2}}{2c}$	$\frac{\Delta\lambda}{\lambda_0}$, HAcO theor. %	$\Delta\Lambda x$ HCl	$\frac{\Delta\lambda}{\lambda_0}$, HCl %	$\frac{\Delta\lambda}{\lambda_0}$, rel. %
0	1566.5	0.000	1.700 × 10^{-5}	0.1403	0.000	0.000	0.000	−1.14
30	1550.3	1.045						
50	1531.7	2.272	1.826	.1450	3.358	.484	.163	2.06
70	1513.5	3.502						
90	1496.2	4.699						
99	1487.8	5.290						
108	1481.2	5.759						
118	1474.0	6.275						
0	1568.5							
134	1455.5	7.764						
143	1448.2	8.307						
150			2.097	.1545	10.145	.638	.215	8.79
152	1443.0	8.697						
170	1433.0	9.456						
187	1422.3	10.297						
200			2.242	.1593	13.567	.663	.223	12.20
15°								
HAcO, 7.420 × 10^{-4} molar; HCl, 0.975 × 10^{-4} molar; $\Lambda^0 = 362.16$; $\Lambda_{x_0} = 360.89$; $(1 - \gamma_\pm)100 = 1.10$								
0	1259.5	0.000	1.744 × 10^{-5}	0.1420	0.000	0.000	0.000	−1.10
30	1248.3	0.897						
50	1233.5	2.108	1.870	.1467	3.274	.593	.164	2.01
69	1219.1	3.314						
88	1206.5	4.393						
97	1200.9	4.880						
107	1195.2	5.380						
116	1188.7	5.956						
143	1171.5	7.512						
150			2.140	.1560	9.866	.793	.220	8.55
169	1156.5	8.906						
186	1147.8	9.732						
200			2.285	.1608	13.203	.824	.228	11.88
25°								
HAcO, 7.405 × 10^{-4} molar; HCl, 1.01 × 10^{-4} molar; $\Lambda^0 = 426.20$; $\Lambda_{x_0} = 424.62$; $(1 - \gamma_\pm)100 = 1.09$								
0	1069.7	0.000	1.749 × 10^{-5}	0.1423	0.000	0.000	0.000	−1.09
20	1063.0	.351						
30	1061.6	.768						
50	1051.3	1.755	1.872	0.1469	3.183	.711	.167	1.93
0	1070.7							
80	1032.6	3.690						
90	1027.0	4.255						
100	1021.0	4.868	2.002	0.1515	6.422	.890	.210	5.12
110	1015.7	5.410						
119	1010.7	5.931						
138	1001.6	6.899						
147	997.3	7.365						
150			2.137	0.1561	9.647	.966	.228	8.33
200			2.278	.1607	12.900	1.006	.237	11.57
35°								
HAcO, 7.383 × 10^{-4} molar; HCl, 1.06 × 10^{-4} molar; $\Lambda^0 = 489.11$; $\Lambda_{x_0} = 487.16$; $(1 - \gamma_\pm)100 = 1.14$								
0	939.0	0.000	1.718 × 10^{-5}	0.1414	0.000	0.000	0.000	−1.14
30	931.0	0.859						
50	922.0	1.844	1.837	.1458	3.141	.833	.171	1.83
70	911.3	3.040						
90	901.0	4.218						
120	887.0	5.862						
150	874.0	7.437	2.091	.1547	9.466	1.101	.226	8.10
180	862.7	8.844						
200	856.0	9.696	2.227	.1592	12.664	1.206	.248	11.28

TABLE I (*Continued*)

Field, kv./cm.	R_v HAcO	$\frac{\Delta\lambda}{\lambda_0}$, %	$K(X)$	$\frac{-K + (K^2 + 4cK)^{1/2}}{2c}$	$\frac{\Delta\lambda}{\lambda_0}$, HAcO theor. %	$\Delta\lambda_x$ HCl	$\frac{\Delta\lambda}{\lambda_0}$, HCl %	$\frac{\Delta\lambda}{\lambda_0}$, rel. %
45°								
HAcO, 7.354 × 10^{-4} molar; HCl, 1.02 × 10^{-4} molar; Λ^0 = 550.34; Λ_{x_0} = 548.09; $(1 - \gamma_\pm)100$ = 1.17								
0	850.2	0.000	1.654 × 10^{-5}	0.1391	0.000	0.000	0.000	−1.17
30	842.6	0.896						
50	834.7	1.857	1.766	.1434	3.076	.936	.171	1.74
70	825.2	3.030						
90	817.5	3.994						
120	805.1	5.602						
150	794.5	7.011	2.007	.1521	9.314	1.304	.238	7.91
180	785.7	8.202						
200	780.2	8.972	2.135	.1565	12.461	1.366	.249	11.04
55°								
HAcO, 7.321 × 10^{-4} molar; HCl, 0.989 × 10^{-4} molar; Λ^0 = 609.38; Λ_{x_0} = 606.83; $(1 - \gamma_\pm)100$ = 1.21								
0	787.3	0.000	1.566 × 10^{-5}	0.1359	0.000	0.000	0.000	−1.21
30	781.4	0.755						
50	772.9	1.863	1.671	.1401	3.053	1.036	.171	1.67
70	765.4	2.861						
90	757.4	3.941						
100	753.7	4.458						
110	750.2	4.945						
120	746.8	5.423						
150	736.6	6.883	1.895	.1485	9.217	1.457	.240	7.77
180	728.1	8.131						
200	724.3	8.698	2.014	.1527	12.306	1.526	.251	10.85

the linear slope predicted by the Onsager theory, although in the absence of a true balance pattern the high field conductance measured could be no more than an educated guess.

Bailey, Patterson and Fuoss[7] found such tilted balance patterns to be an indication of time of relaxation effects in polymeric electrolyte solutions, but with acetic acid any predicted times of relaxation would be at least one hundred-fold smaller than the four microsecond pulse duration employed for observation. It was therefore concluded that the problem was one of polarization. Hydrochloric acid was substituted as reference electrolyte, and no difficulty was then found in obtaining meaningful balance patterns by impedance matching. No change of capacitance balance was observed with increasing field. The high field conductance, when plotted as $\Delta\lambda/\lambda_0$ as a function of increasing field, still showed a departure from linearity at fields above about 140 kv./cm. at 25° (see Fig. 1). This departure was negative, and was greater the higher the field and the higher the temperature.

One may conclude, therefore, that the anomalous results found with potassium chloride as reference electrolyte are due to concentration polarization in the acetic acid cell; such polarization is enhanced by the enormous velocities attained by hydrogen ions under the influence of high fields, and thus is more or less characteristic of the hydrogen ion alone. Since the concentration of hydrogen ions is approximately the same in solutions of acetic and hydrochloric acids having the same conductance, the polarization effects should be approximately the same in the two if the effects are due to hydrogen ion alone. Such a situation seems to hold at low and intermediate field strengths.

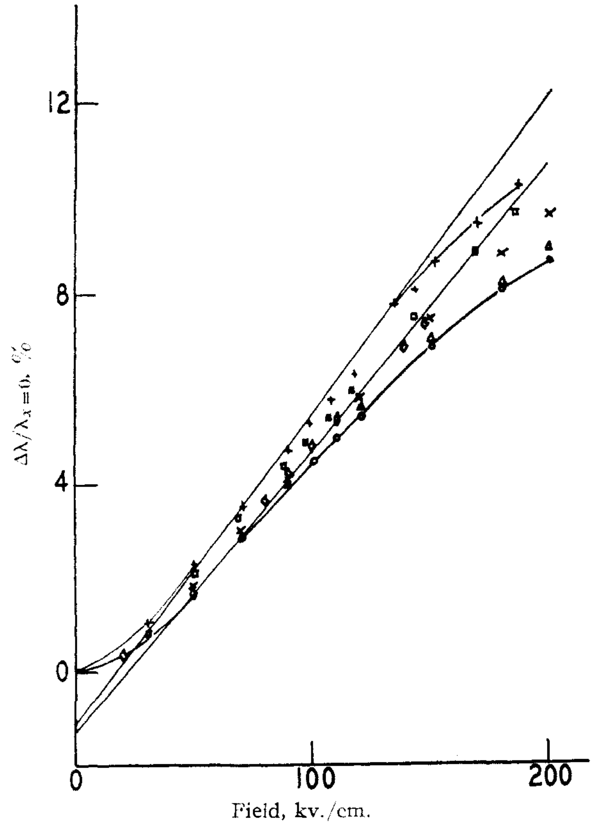

Fig. 1.—The high field conductance of solutions of acetic acid, approximately 7 × 10^{-4} molar, relative to hydrochloric acid: upper straight line, Onsager theory for 5°; lower straight line, Onsager theory for 55°; upper curve, experimental results for 5°; lower curve, experimental results for 55°. Symbols: +, 5°; □, 15°; ◊, 25°; ×, 35°; △, 45°; ○, 55°.

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[7] F. E. Bailey, A. Patterson and R. M. Fuoss, THIS JOURNAL, **74**, 1845 (1952).

Experimentally, the results of polarization seem to disappear when hydrochloric acid is used as reference electrolyte; it is thus proper to conclude that the polarization effects in the two solutions cancel, and that the measurements give rise to the correct *changes* at low and intermediate fields. If, however, concentration polarization is the correct explanation of the observed experimental results, deviations from the predicted Onsager slope would be expected at the highest fields. At high fields, the conductance of hydrochloric acid—a strong electrolyte—is not very sensitive to variations in the field; on the other hand, acetic acid has a much larger Wien effect for a given change in field, as one may observe from Table I. The net effect of polarization is to increase the resistance of the cell, but this increase of resistance is confined to a very thin layer near the electrode at which the process takes place. Across this thin layer a correspondingly larger voltage gradient is built up, and thus across the bulk of the solution between the electrodes of the conductance cell the voltage gradient will be correspondingly smaller. The increase in conductance of the acetic acid solution would thus be smaller than that expected for a given value of applied field since the field is not effectively applied to the entire solution volume between the electrodes. Fuoss and Elliott[8] observed a phenomenon of this type in solutions of tributylammonium picrate in tricresyl phosphate, at fields so low that Wien effects were absent.

Added verification of the contention that polarization is the cause of the effects described above may be derived from the observation that the greatest deviations from theory are found at the higher temperatures. At higher temperatures the velocity of the hydrogen ions is much greater for a particular value of field and thus the concentration would be expected to be greater. Although polarization is ordinarily lessened by higher temperatures, in the high field case a new influence—the high field itself—is present which prevents the departure of H^+ ions from the vicinity of the electrode at which polarization takes place. The predominant effect is that which results from the increased rate at which H^+ ions arrive at the negative electrode.

Onsager[3] has pointed out that hydrodynamic interactions were neglected in the derivation of his theory for weak electrolytes. A correction for the ratio, $K(X)/K(O)$, is available in the form

$$\frac{K(X)}{K(O)} = F(2\beta q) + O(\beta^{n+1}\rho q^n) \qquad (5)$$

with the terms as defined by Onsager.[3] This correction is of such a nature that hydrodynamic interactions would give rise to an increase in the quotient $\Delta\lambda/\lambda_0$, if hydrodynamic interactions were important at the fields in question. It is of interest to note that Schiele's data[2] show a small positive deviation from the Onsager theory; this is most probably a temperature effect, however. Onsager's correction is also interpreted to mean that the deviation from theory would be positive with increasing temperature. The fact that our observations are in the reverse direction suggests that hydrodynamic interactions are not responsible for the deviation from theory which we have reported or are of lesser importance, and that another explanation such as polarization is required.

One may postulate further that if Schiele used conductance cells in which the high field resulted from the interposition of tiny holes between the electrodes, rather than (as in the present experiment) from the close juxtaposition of the electrodes, the polarization phenomena near the electrodes would not affect the field to which the acetic acid was subjected. It would thus be possible to explain the disparity between Schiele's positive deviation and our negative deviations from theory.

Onsager assumed that Schiele's measurements were performed at 25° in making the calculation for comparison with Schiele's results, but recognized that in European laboratories it was customary to maintain thermostats at 15° or 18° rather than at higher temperatures. It will be seen that had Schiele done his work at 15° the slope of his experimental curve would have been greater than had he done his work at 25°; this is indeed the deviation from Onsager's theory which is observed in the case of Schiele's data.

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[8] R. M. Fuoss and M. A. Elliott, THIS JOURNAL, **67**, 1339 (1945).