[Contribution from the Laboratory of Physical Chemistry of the Polytechnic Institute of Copenhagen]

THE DISSOCIATION OF MONOCHLORO-ACETIC ACID IN AQUEOUS SOLUTION

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The determination of H_3O^+ concentrations by the catalytic hydrolysis of dimethyl acetal and of ethylene acetal as proposed by Brönsted and Grove[2] is particularly useful in the determination of H_3O^+ concentrations in solutions of pure weak acids where there is only a small ionic concentration and consequently practically no salt effect upon the hydrolytic reaction. From such measurements, of course, the dissociation constant of the acid is readily calculated. The velocity of hydrolysis of the acetal—a linear function of the H_3O^+ concentration—is readily determined by a simple dilatometric method.

In the present work this method has been applied to the determination of the H_3O^+ concentrations of solutions of monochloro-acetic acid from 0.003 to 0.30 molar.

Theoretical

In an aqueous solution of any weak acid, HA, the following equilibrium is found to obtain

$$\mathrm{HA} + \mathrm{H_2O} \rightleftharpoons \mathrm{A^-} + \mathrm{H_3O^+}$$

The classical mass action expression for this equilibrium is given by

$$K_c = \frac{c_{\mathrm{A^-}} \cdot c_{\mathrm{H_3O^+}}}{c_{\mathrm{HA}} \cdot c_{\mathrm{H_2O}}} \tag{1}$$

where the c's are the concentrations of the respective ions and compounds. This quantity K_c, however, is not a true constant but varies with the ionic strength. If the ionic concentrations be replaced by their respective activities, the resulting expression

$$K_a = \frac{a_{\mathrm{A^-}} \cdot a_{\mathrm{H_3O^+}}}{a_{\mathrm{HA}} \cdot a_{\mathrm{H_2O}}} \tag{2}$$

shows a quantity K_a which is a true constant, independent of the ionic strength. From the fundamental equation for the activity

$$a = cf \tag{3}$$

where f is the activity coefficient, we arrive at the following equation which relates K_c to K_a

$$K_a = \frac{a_{\mathrm{A^-}} \cdot a_{\mathrm{H_3O^+}}}{a_{\mathrm{HA}} \cdot a_{\mathrm{H_2O}}} = \frac{c_{\mathrm{A^-}} \cdot c_{\mathrm{H_2O^+}}}{c_{\mathrm{HA}} \cdot c_{\mathrm{H_2O}}} \cdot \frac{f_{\mathrm{A^-}} \cdot f_{\mathrm{H_3O^+}}}{f_{\mathrm{HA}} \cdot f_{\mathrm{H_2O}}} = K_c \cdot \frac{f_{\mathrm{A^-}} \cdot f_{\mathrm{H_3O^+}}}{f_{\mathrm{HA}} \cdot f_{\mathrm{H_2O}}} \tag{4}$$

Applying the Debye–Hückel expression for the change in activity coefficient with the ionic strength

$$-\log f = \alpha z \sqrt[2]{\mu} + \beta\mu \tag{5}$$

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[1] Fellow of the American–Scandinavian Foundation, 1928–1929.

[2] Brönsted and Grove, This Journal, 52, 1394 (1930).

where z is the valence, μ the ionic strength and α and β are constants, to Equation 4, we arrive at an expression for the variation of the classical "constant" with the ionic strength

$$\log K_c = \log K_a - z_A \sqrt{\mu} - \beta\mu \qquad (6)$$

For an electrolyte which on dissociation produces a univalent negative ion along with the hydroxonium ion, Equation 6 assumes the form

$$\log K_c = \log K_a + \sqrt{\mu} - \beta\mu \qquad (7)$$

Experimental

The solutions of monochloro-acetic acid were prepared by weighing out rapidly the necessary quantities of pure monochloro-acetic acid which had been recrystallized from benzene and dried *in vacuo* over sulfuric acid, and dissolving in distilled water. Solutions could be prepared in this manner to within 1% of the desired concentration, the solutions later being adjusted to the exact strength desired. The stock solutions were standardized against a solution of sodium hydroxide of accurately known titer. The solutions used were made up by dilution of these stock solutions immediately before the experiments were made.

The velocities of hydrolysis at acid concentrations of 0.003 to 0.015 molar were determined by the use of dimethyl acetal and the H_3O^+ concentrations were calculated from the expression given by Brönsted and Grove for the relation of the velocity of hydrolysis to the H_3O^+ concentration

$$0.434\ k_{H_3O^+} = 3.92 \text{ or } c_{H_3O^+} = 0.434\ k/3.92$$

At acid concentrations from 0.05 to 0.30 molar, the velocities of hydrolysis were determined by the use of ethylene acetal and the H_3O^+ concentrations

TABLE I

RESULTS OF EXPERIMENTS

c_{ClCH_2COOH}	$c_{H_3O^+}$	$\sqrt{\mu}$	$K_c \times 10^3$	Log K_c
0.003	0.00151	0.0388	1.53	7.185–10
	.00151		1.53	7.185–10
.005	.00212	.0460	1.56	7.193–10
	.00211		1.54	7.188–10
.010	.00327	.0567	1.58	7.193–10
	.00325		1.56	7.199–10
.015	.00416	.0646	1.59	7.201–10
	.00417		1.60	7.204–10
.050	.00823	.0908	1.62	7.210–10
	.00823		1.62	7.210–10
.100	.0120	.110	1.64	7.215–10
	.0121		1.66	7.220–10
.200	.0175	.132	1.68	7.225–10
	.0174		1.67	7.223–10
.300	.0217	.147	1.69	7.228–10
	.0216		1.68	7.225–10

were calculated from the expression for the catalytic hydrolysis of this acetal

$$c_{\mathrm{H_3O^+}} = 0.434\ k/0.180 + 0.19\ c_{\mathrm{H_3O^+}}$$

The results of these experiments are given in Table I.

The only other results with which these may be compared are those given in Table II, determined by Ostwald[3] using a conductivity method employing platinized electrodes which, he states, caused some alteration of the acid; and those given in Table III, determined by van't Hoff and Reicher,[4] who avoided alteration of the acid by the use of bright platinum electrodes but whose results are, nevertheless, less consistent than those of Ostwald. Since these measurements were interpreted in the classical way by

TABLE II

DATA OF OSTWALD

$c_{\mathrm{HICH_2COOH}}$	K_c	$c_{\mathrm{ClCH_2COOH}}$	K_c
0.0625	0.00155	0.0039	0.00146
.0312	.00155	.0020	.00147
.0156	.00152	.0010	.00147
.0078	.00150		

TABLE III

DATA OF VAN'T HOFF AND REICHER

$c_{\mathrm{ClCH_2COOH}}$	K_c
0.05	0.00165
.0049	.00151
.00245	.00162
.0003	.00162

$$\alpha = \mu/\mu_{\infty}$$

where α is the degree of dissociation and μ and μ_{∞} are the equivalent conductances of the solution being measured and of the same electrolyte at infinite dilution, respectively, an exact agreement cannot be expected.

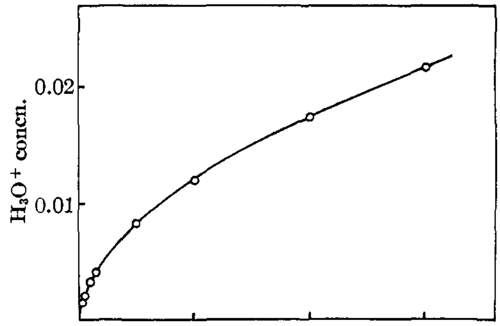

Fig. 1.—The change of H_3O^+ concentration with the concentration of monochloro-acetic acid.

The results given in the first two columns of Table I are plotted in Fig. 1, showing the variation of the H_3O^+ concentration with the acid concentration. In Fig. 2 the log K_c has been plotted against $\sqrt{\mu}$, showing a

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[3] Ostwald, *Z. physik. Chem.*, **3**, 170 (1889).

[4] Van't Hoff and Reicher, *ibid.*, **2**, 777 (1888).

curve of the form required by Equations 6 and 7. From this curve and the third and fifth columns of Table I, we find the following expression for

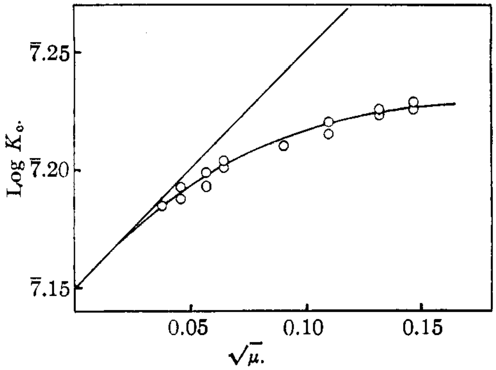

Fig. 2.—The relation of $\log K_c$ to $\sqrt{\mu}$.

the dissociation of pure monochloro-acetic acid in the concentration range 0.003 to 0.300 molar

$$\log K_c = (7.150 - 10) + \sqrt{\mu} - 3.2\mu$$

Summary

1. The H_3O^+ concentrations of solutions of monochloro-acetic acid from 0.003 to 0.300 molar have been determined.

2. From these measurements, the dissociation constant of monochloro-acetic acid has been determined. It has been shown to vary with the ionic strength in the manner required by theory.

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A MERCURY–BASIC MERCURIC SULFATE VOLTAIC CELL[1]

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The lead storage cell can be considered as a modification of the cell

$$\mathrm{M} \mid \mathrm{M^IX\ (sat.)} \mid \mathrm{M^IX\ (sat.),\ M^{II}X_2\ (sat.)} \mid \mathrm{(Pt)} \qquad (1)$$

where M^I and M^{II} stand for a metallic element in two states of oxidation and M^IX_2 has a small solubility. In the storage cell M^IX is lead sulfate, but $M^{II}X_2$ is replaced by the higher oxide. Sulfuric acid must then be present in the electrolyte, and the electromotive force depends upon the concentration of the acid.

It has been found in this investigation that a cell analogous to the lead storage cell, namely

$$\mathrm{Hg} \mid \mathrm{Hg_2SO_4},\ xM\ \mathrm{H_2SO_4} \mid xM\ \mathrm{H_2SO_4},\ \mathrm{Hg_2SO_4},\ \mathrm{3HgO{\cdot}SO_3} \mid \mathrm{(Au)} \qquad (2)$$

is reproducible and constant over short periods of time.

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[1] Taken from a thesis presented by Oscar N. Lackey in partial fulfilment of the requirements for the degree of Doctor of Philosophy at Duke University in June, 1929.