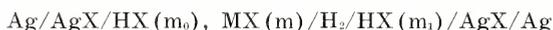


## THE DISSOCIATION CONSTANTS OF MONO- AND TRICHLOROACETIC ACIDS IN ETHYL ALCOHOL

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The purpose of this investigation was to determine the success with which the dissociation constants of organic acids in alcoholic solutions can be determined by electromotive force measurements of cells without liquid junction potentials and with easily reproducible electrodes such as the hydrogen and silver-silver chloride electrodes. The electromotive forces of cells of the type



have proved very useful in determining the activity coefficients of some strong acids and hydroxides in aqueous salt solutions. Harned and Robinson<sup>1</sup> have measured the electromotive forces of cells of the type



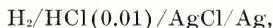
for solutions of a weak acid (HAc) in aqueous solutions of salts (MX). From these values they have determined the ionic concentrations and the activity coefficients of weak acids, such as acetic, in potassium, sodium, lithium, and barium chloride solutions. Harned and Fleysler<sup>2</sup> have measured the activity coefficient of hydrochloric acid in ethyl alcohol solutions by means of the hydrogen and silver-silver chloride electrodes. Harned and Owen<sup>3</sup> have investigated the thermodynamic properties of weak acids and bases in aqueous salt solutions and have developed an exact method for the determination of their dissociation constants from cell measurements. The question naturally arises as to whether or not measurements with the same type of cell can be extended to alcoholic solutions of weak and moderately strong organic acids.

The limitations of the method depend upon experimental accuracy, upon the difficulty of obtaining a reversible electromotive force of the hydrogen electrode when the ratio of the molality of the hydrogen ion to that of the dissolved salt is very small, and upon the successful application of the Debye-Hückel equation in determining the activity coefficient of an electrolyte in solutions of the type considered.

Let us consider in alcoholic solution the cells,



which has an electromotive force equal to  $E$ , and



with an electromotive force equal to 0.2109. This value has been taken from the results of Harned and Fleysler. HAc is used to represent any weak acid. Then the electromotive force of the cell

<sup>1</sup> Harned and Robinson, *J. Amer. Chem. Soc.*, **50**:3157 (1928).

<sup>2</sup> Harned and Fleysler, *ibid.*, **47**:82 (1925).

<sup>3</sup> Harned and Owen, *ibid.*, **52**:5079 (1930).



is given, according to the Nernst equation, as follows:

$$E - 0.2109 = \frac{RT}{F} \ln \frac{(0.563)^2(0.01)^2}{\gamma_{\text{H}}\gamma_{\text{Cl}}^m m_{\text{H}}} \quad (1)$$

or in another form as

$$16.9062 E + 0.9332 + \log m + 2 \log \gamma = -\log m_{\text{H}}, \quad (2)$$

in which 0.563 has been taken from the results of Harned and Fleysler as the activity coefficient of 0.01 molal hydrochloric acid in ethyl alcohol. The term,  $\log m$ , refers to the logarithm of the molality of the added salt. The term,  $\log \gamma$ , represents the logarithm of the activity coefficient of hydrochloric acid in a solution of a weak acid the molality of which is  $M-m_{\text{H}}$ :

$$\gamma = \sqrt{\gamma_{\text{H}}\gamma_{\text{Cl}}} \quad (2)$$

The value of  $\log \gamma$  can be determined by an application of the equation of Debye and Hückel<sup>4</sup> which has been proved valid for the low concentration of acid and salt employed. This equation is

$$-\log \gamma = \frac{A\sqrt{2\mu}}{1 + \alpha\sqrt{2\mu}} - 2B\mu, \quad (3)$$

where  $A$ ,  $B$  and  $\alpha$  are constants which are used here in the same sense as they have been defined by Hückel. Scatchard<sup>5</sup> has determined the values of these constants for lithium chloride solutions in pure ethyl alcohol as follows:

$$A = 1.973; \alpha = 2.36; B = 0.025.$$

It is assumed that the presence of the undissociated molecules of the weak acid will have no greater effect on the activity coefficient of the hydrogen ion than the molecules of the solvent. The error introduced by this assumption is recognized as one worthy of consideration in solutions containing the concentration of acid which we have employed. It is believed, however, that this error is small and in any event is unavoidable.

Since the sum of the concentrations of the dissolved salt and the hydrogen ion resulting from the dissociation of the weak acid is unknown, the ionic strength of the dissolved salt alone is used as the total ionic strength in equation (3). We are justified in doing this since it has been shown by Harned and Robinson that at concentrations of HCl up to 0.01 molal in salt solutions the activity coefficient of the hydrogen ion is independent of the concentration of the acid but dependent upon the total ionic strength. This may be readily understood, since the activity of the ion depends upon the atmosphere of ions surrounding it and not upon the proximity of any particular kind of ion. Accord-

<sup>4</sup> Hückel, *Physik. Z.*, **26**:93 (1925).

<sup>5</sup> Scatchard, *J. Amer. Chem. Soc.*, **47**:2098 (1925).

ingly, since the concentration of the hydrogen ion produced by the ionization of a weak acid is very small when compared to the concentration of the ions produced by the ionization of a salt, we may use the molality of the salt as a first approximation without introducing any great error. In the case of univalent salts the ionic strength is numerically equal to the concentration. By using the ionic strength of the dissolved salt an approximate value of  $\log \gamma$  is obtained. This value is then substituted in equation (2), and an approximate concentration of the hydrogen ion is obtained. This concentration of the hydrogen ion may now be added to the concentration of the dissolved salt to obtain a more accurate value of the total ionic strength. Thus, by the method of successive approximations, an exact value of  $m_H$  is obtained.

The thermodynamic expression for the dissociation constant of an electrolyte is:

$$K = \frac{\gamma^2 m_H^2}{\gamma_\mu M - m_H} = \frac{\gamma^2}{\gamma_\mu} k, \quad (4)$$

in which  $\frac{\gamma^2}{\gamma_\mu}$  is substituted for the more complete expression  $\frac{\gamma_H \gamma_{Ac}}{\gamma_{HAc}}$ .

HAc again represents any weak acid. This equation is valid when  $\gamma$  is equal to unity at infinite dilution of the electrolyte in any solvent. The activity coefficient has been defined as equal to unity at infinite dilution by the equation of Debye and Hückel. Thus, the value of  $k$  approaches  $K$  as the concentration of the electrolyte approaches zero. But it is not equal to  $K$  at any other concentration. The term,  $k$ , is defined by the following equation:

$$k = \frac{m_H^2}{M - m_H} \quad (5)$$

and can be easily calculated for any given concentration of the electrolyte by measuring the molality of the hydrogen ion by the method outlined above. The value of  $k$  as so determined refers to a solution containing a dissolved salt and is not the same as it would be if the acid were in a solution to which no salt had been added. Furthermore, it is impossible to extrapolate to infinite dilution the curve obtained by plotting the values of  $k$  against the molality of the dissolved salt, since the slope of the curve becomes very great as the molality becomes very small.

In order to determine the value of  $k$  in salt free solutions the following method was used. This is essentially the same method as Harned and Owen (loc. cit.) used for a similar purpose. Let us assume that the activity coefficient of the undissociated acid is unity. The basis for this assumption will be given later. Equation (4) then becomes

$$K = \gamma^2 k. \quad (6)$$

By taking the logarithm of equation (6) we obtain

$$\log K = 2 \log \gamma + \log k. \quad (7)$$

According to the Debye-Hückel equation,

$$\log \gamma = - \frac{A\sqrt{2\mu}}{1 + \alpha\sqrt{2\mu}} 2B\mu. \quad (8)$$

Substituting the value of  $\log \gamma$  in equation (7) we obtain

$$\log K = - \frac{2A\sqrt{2\mu}}{1 + \alpha\sqrt{2\mu}} + 4B\mu + \log K. \quad (9)$$

Transposing equation (9),

$$\log k - \frac{2A\sqrt{2\mu}}{1 + \alpha\sqrt{2\mu}} = \log K - 4B\mu. \quad (10)$$

Let us now define two new terms:

$$S = \frac{2A\sqrt{2\mu}}{1 + \alpha\sqrt{2\mu}}, \quad (11)$$

and

$$N = \log k - S. \quad (12)$$

Substituting these terms in equation (10) we obtain

$$N = \log K - 4B\mu. \quad (13)$$

Let us write the following equation

$$2 \log m_H = N + S + \log(M - m_H), \quad (14)$$

which is obtained from equations 5 and 12:

$$2 \log m_H = \log k + \log(M - m_H) \\ \log k = N + S.$$

The ionic strength is now plotted against  $N$ , and extrapolation is made to zero concentration of the dissolved salt. The value of  $N$  is read from the plot. An approximate value of  $m_H$  in a salt free solution is obtained by taking the molality of the hydrogen ion in the solution containing the smallest concentration of lithium chloride. This value is then substituted in the right hand member of equation 14, and a new molality of the hydrogen ion is determined. This more accurate value of  $m_H$  is in turn substituted in the right hand member of the equation, and the equation is solved again. This process may be repeated until the equation is satisfied, at which time the value of  $m_H$  obtained is the exact value which it would have in a salt-free solution.

Let us now return to the expression for the dissociation constant of an electrolyte, equation 4. It is now possible to determine  $m_H$  and  $M - m_H$  from measurements of the cells of the type already discussed, and  $\gamma$  can be evaluated by means of the Debye-Hückel equation. But  $\gamma\mu$  cannot be determined directly unless  $K$  is known or vice versa. Nevertheless,  $K$  can be readily evaluated if we supplement the data with certain assumptions which are supported by a large number of experimental facts and which lead to an indirect evaluation of  $\gamma\mu$ .

The value of  $\gamma\mu$  is found by assuming that in very dilute solutions the activity coefficient of the undissociated electrolyte is equal to unity, and that the activity, therefore, is equal to the concentration. This assumption is warranted by the success of the interionic attraction theory in explaining the activity changes of strong electrolytes in solutions of varying concentrations. If the change in the activity coefficient of an ion depends entirely upon the interionic forces, as the evidence tends to show, there is no reason to expect that the activity coefficient of a neutral molecule will vary appreciably in dilute solutions. Aside from this theoretical reasoning, there is good experimental evidence upon which to base the above assumption. Very few activity measurements have been made in solutions of non-electrolytes, but those which have been made show that the changes are very small. In aqueous glycerine solutions the activity coefficient of glycerine changes from 1 at zero concentration to 1.006 in a 0.1 molal solution.<sup>6</sup> Randall and Failey<sup>7</sup> have reviewed the work relating to the activities of neutral substances, such as gases and non-electrolytes, dissolved in salt solutions. They have shown that the quotient of the logarithm of the activity coefficient of gases and non-electrolytes and the ionic strength of the dissolved salt in aqueous salt solutions is approximately a constant. This constant varies with the salt and non-electrolyte used.

If the quotient of the logarithm of the activity coefficient of the undissociated part of the weak acid and the ionic strength of the added salt is approximately constant, it follows that

$$\log \gamma_{\mu} = C\mu,$$

As  $\mu$  becomes zero,  $\log \gamma\mu$  becomes equal to zero, or  $\gamma\mu$  equal unity.

Hence, the expression  $\frac{\gamma^2}{\gamma\mu}$  is equal to  $\gamma^2$  only at infinite dilution of the added salt. Since we are concerned only with the dissociation constant in salt-free solutions, we may write equation 4 in the following form:

$$K = \gamma^2 \frac{m_H^2}{M - m_H} \quad (15)$$

upon the basis of the simple assumption that the dissociated part of weak acids behaves in the presence of added salts in the same manner as the ions of HCl.

#### PREPARATION OF MATERIALS

**Ethyl Alcohol.** Absolute ethyl alcohol was the solvent used. This was prepared by treating 95 per cent alcohol three times with quicklime which had been freshly prepared by heating hydrated lime at a temperature of 600-700° C. in an electric furnace. One liter of alcohol was treated with 300 grams of this lime and refluxed for twelve hours. The alcohol was distilled, and the treatment was twice repeated. When needed for the preparation of solutions, the alcohol was distilled from the last portion of the lime, heated with basic lead acetate to remove

<sup>6</sup> Lewis and Randall, "Thermodynamics and the Free Energy of Chemical Substances," McGraw Hill Book Company, Inc., New York, 1923, p. 288.

<sup>7</sup> Randall and Failey, Chem. Revs., 4:271 (1927).

aldehydes, and finally distilled through a sixteen-bulb Young's fractionating column into a dry flask. The alcohol thus prepared was used at once. The usual precautions were taken to protect the alcohol from contact with moist air and corks. The water content of the alcohol was checked by means of tests with a xylene solution of aluminum ethylate.<sup>8</sup> The refractive index of each sample was also determined by means of a pulfrich refractometer. There is considerable variation in the refractive index of the alcohol produced by this method. The alcohol used possessed a refractive index  $N_D^{20}$  of 1.3592 (0.0006). Schiff's reagent was used to detect aldehydes. Such tests were negative, or very slightly positive after standing for a few minutes.

**Hydrogen.** The supply of hydrogen for the hydrogen electrode was obtained by the electrolysis of a solution of sodium hydroxide. The gas was purified by passage through tubes filled with glass-wool, calcium chloride, and platinized asbestos heated to 300° C. It was finally dried by passage through a long tube filled with calcium chloride. To prevent any change in the composition of the solution in the cell the hydrogen was passed through an efficient saturating system consisting of three or more containers which were filled with solutions of the same composition as that in the cell. A trap was fixed at the end of the hydrogen outlet of the cell for the purpose of preventing the entrance of moisture and air. This trap was filled with a solution of the same composition as that in the cell.

**Lithium Chloride.** The lithium chloride was obtained from Coleman and Bell and was of the highest purity. This was fused and cooled in a desiccator prior to use.

**Acids.** Monochloroacetic acid (Baker) and trichloroacetic acid (Eastman), of the highest purity obtainable, were dried for six days prior to use in a desiccator over P<sub>2</sub>O<sub>5</sub>.

**Silver.** The silver used in the preparation of the silver-silver chloride electrode was deposited by a current of five to seven amperes in a cell consisting of an anode of pure silver and a cathode of platinum wire immersed in a solution of silver nitrate. The silver deposited by the use of this large current was crystalline and could be dislodged easily from the platinum wire by gentle tapping. The silver was washed many times by decantation with conductivity water and was kept in conductivity water until ready for use.

**Silver Chloride.** The silver chloride was prepared by adding a solution of pure hydrochloric acid to a dilute solution of silver nitrate which was acidified with nitric acid. The silver chloride was washed many times with a dilute solution of nitric acid in conductivity water, followed by washing with conductivity water alone, and finally placed in water until required for the preparation of the electrodes. Since silver chloride is sensitive to light, the precipitation and subsequent treatment were carried out in brown bottles or in a dark-room. During use, the electrode-vessel was placed in the darkened air bath.

<sup>8</sup> Henle, Ber., 53:719 (1920).

## APPARATUS

**Potentiometer.** A Leeds and Northrup Type K Potentiometer was used with a Leeds and Northrup Type R reflecting galvanometer to measure the electromotive forces of the cells. Two Eppley Standard Cells were connected by a switch so that either cell could be used as a reference or serve as a check against the other. The calibrations of these cells were certified by the manufacturer.

**Cell.** The cell consisted of a hydrogen electrode and a silver-silver chloride electrode. These electrodes were immersed in the solution which was contained in a glass cylinder 4 centimeters in diameter and 12 centimeters in height. The hydrogen electrode, the silver-silver chloride electrode, the inlet, and the outlet for hydrogen were mounted in a rubber stopper. The cell was placed in an air bath within which the temperature was maintained at 25° C. ( $\pm 1^\circ$ ).

**Hydrogen Electrode.** The electrodes consisted of platinum foil, 5-15 millimeters. The foil was fused to platinum wire, which was sealed into a glass tube. Contact was made by filling the tube with mercury. The method of preparing the platinized electrodes (black) was that suggested by Popoff, Kunz, and Snow.<sup>9</sup> The bright platinized electrodes were prepared according to the method of Kolthoff and Kameda.<sup>10</sup>

A short length of platinum wire was first cleaned by means of a solution of potassium dichromate and concentrated sulphuric acid. The wire was then washed in distilled water and heated to dull redness. The plating bath contained a solution of chloroplatinic acid the concentration of which corresponded to 2 per cent platinum. By electrolyzing for two minutes at a current strength of twenty milliamperes, the electrodes were covered with bright platinum. After plating, the electrodes were washed for thirty minutes in conductivity water through which hydrogen was passing. Finally, they were washed with the solution to be studied, which was also saturated with hydrogen. These electrodes gave reproducible results.

**Silver-silver Chloride Electrode.** In this work the old type of electrode, which consists of silver covered with a layer of silver chloride, was replaced by finely divided silver over which a layer of silver chloride was placed. This type of electrode provides intimate contact of silver and silver chloride. The potential of this electrode does not vary as the potential has been found to do when one uses an electrode in which the silver has not crystallized freely and in which there is more or less internal strain. To prepare the electrode the required amounts of silver and silver chloride were washed separately many times by decantation with the solution to be used in the cell. The silver was then placed in the bottom of a small cup to which was sealed a bent tube. Contact was made with silver by means of a platinum wire fused in the seal and with the circuit by means of mercury placed in the tube. This tube was mounted in the rubber stopper of the cell as already described. The layer of silver chloride was then placed upon top of the silver in the cup. This electrode has been suggested by Linhart.<sup>11</sup>

<sup>9</sup> Popoff, Kunz, and Snow, *J. Phys. Chem.*, **32**:1056 (1928).

<sup>10</sup> Kolthoff and Kameda, *J. Amer. Chem. Soc.*, **53**:821 (1931).

<sup>11</sup> Linhart, *J. Amer. Chem. Soc.*, **41**:1175 (1919).

The constant temperature air bath, the potentiometer, and the galvanometer were carefully shielded to minimize the errors of variable measurements due to induction. All wiring was of solid construction.

#### EXPERIMENTAL RESULTS

**The Dissociation Constant of Monochloroacetic Acid.** The results obtained with the usual types of platinum black electrodes can be characterized as unreliable in unbuffered solutions of the type under investigation. The electromotive forces of the cells change rapidly up and down over wide ranges. Two electrodes in the same solution fail to give the same result. Even the direction of the drift of the electromotive force varies. As a general rule the electromotive force increases for a time, passes through a maximum, and finally decreases indefinitely. In some instances, when the deposit of platinum black is very light, equilibrium is reached after about five hours. The adsorption of the cation of the salt on the surface of the platinum black in a hydrogen atmosphere and the gradual release of the cation, resulting in decreasing acidity of the solution, is generally thought to be the cause of the fluctuation of potential. In the solutions used in this investigation it is possible that hydrochloric acid is liberated by the action of hydrogen upon the chloroacetic acids. This action cannot be the sole cause, however, of the variations since the drift is not always in the same direction.

The electromotive forces of cells containing monochloroacetic acid solutions were determined by the use of electrodes which were coated with very slight deposits of platinum black. In these solutions, a fair state of equilibrium was attained and fairly reproducible results were obtained. The dissociation constant of monochloroacetic acid, as reported, has been determined from measurements made with the electrodes prepared in accordance with the directions of Popoff, Kunz, and Snow. The electromotive force determinations and the values of the function employed in the calculation of the dissociation constant are given in Tables I and II.

TABLE I  
Electromotive Force Measurements  
(0.20 m Monochloroacetic Acid)

m LiCl	E. M. F.	log $\gamma$	S
0.0000	.....	-0.04933	0.09902
0.0500	0.2720	-0.35480	0.71460
0.0562	0.2737	-0.36648	0.73858
0.0839	0.2828	-0.40830	0.82498
0.0858	0.2815	-0.40901	0.82660
0.0895	0.2892	-0.41330	0.83556
0.1040	0.2928	-0.42910	0.86872
0.1297	0.2972	-0.45863	0.93022
0.1311	0.3013	-0.46981	0.94272

TABLE II

Molality of the Hydrogen Ion and Extrapolation Function  
(0.20 m Monochloroacetic Acid)

m LiCl	log $m_H$	$m_H$	N
0.0000	-3.44433	0.000359	(-6.28200)*
0.0500	-3.52106	0.000301	-7.05710
0.0562	-3.57724	0.000265	-7.19353
0.0839	-3.82143	0.000151	-7.76982
0.0858	-3.80202	0.000158	-7.73132
0.0895	-3.94794	0.000113	-8.03223
0.1040	-4.03942	0.000095	-8.24839
0.1297	-4.14340	0.000070	-8.53783
0.1311	-4.20024	0.000063	-8.65411

\*By extrapolation

Reproducible results cannot be obtained when the ratio of the molality of the lithium chloride to the molality of acid is very large or very small. To obtain reproducible results in dilute solutions of lithium chloride it is necessary to measure the electromotive force of water-alcohol mixtures in which the molalities of lithium chloride and monochloroacetic acid are constant. Extrapolation can then be made to find the value of the electromotive force when the solvent is absolute alcohol. When the logarithm of the electromotive force is plotted against the per cent of alcohol (by weight), a straight line is obtained. This permits an accurate extrapolation. In order to determine the validity of this extrapolation, the electromotive force of a solution in 100 per cent ethyl alcohol as the solvent was determined for a molality of lithium chloride which gives reproducible results. The electromotive force of the same solution was then calculated by the method of extrapolation. The results (Table III) were in good agreement.

TABLE III

Extrapolation of E. M. F. to Absolute Ethyl Alcohol  
(0.20 m Monochloroacetic Acid; 0.1297 m Lithium Chloride)

% Ethyl Alcohol	E. M. F.	log E
80	0.3603	-0.44334
85	0.3445	-0.46281
90	0.3265	-0.48612
95	0.3120	-0.50585
100 (measured)	0.3007	-0.52187
100 (extrapolated)	0.2972	-0.52700

The dissociation constant of the acid is obtained by substituting the value of  $N$  obtained by extrapolating to zero molality of lithium chloride in equation 14 and calculating the molality of the hydrogen ion in the manner described. The molality of the hydrogen ion resulting

from the dissociation of 0.20 molal monochloroacetic acid in a salt-free solution in ethyl alcohol was found to be 0.0003595. The activity of the hydrogen ion is determined by multiplying the molality of the hydrogen ion by its activity coefficient calculated at that molality by means of the Debye-Hückel equation. The ionic strength is equal to the molality of the hydrogen ion. The value of  $K$  was next obtained by means of the usual thermodynamic equation. For monochloroacetic acid in ethyl alcohol  $K$  was found to be  $5.224 \times 10^{-7}$ . This value appears to be much higher than the expected value, although the only determination with which it can be compared is that of Godlewski (*loc. cit.*) who obtained  $1.20 \times 10^{-7}$ .

The dissociation constant of monochloroacetic acid was also determined from electromotive force measurements made by using bright platinum electrodes. The results of these measurements are given in Tables IV and V.

TABLE IV  
Electromotive Force Measurements  
(0.20 m Monochloroacetic Acid)

m LiCl	E. M. F.	log $\gamma$	S
0.0000	.....	-0.06773	0.10480
0.0350	0.2729	-0.31830	0.64360
0.0496	0.2800	-0.34635	0.69770
0.0752	0.2841	-0.39621	0.80014
0.1200	0.3017	-0.44291	0.89782

TABLE V  
Molality of the Hydrogen Ion and Extrapolation Function  
(0.20 m Monochloroacetic Acid)

m LiCl	log $m_H$	$m_H$	N
0.0000	-3.41852	0.0003815	-6.24200
0.0350	-3.45437	0.0003513	-6.85363
0.0496	-3.66971	0.0002139	-7.33870
0.0752	-3.82017	0.0001513	-7.74218
0.1200	-4.22716	0.0000593	-8.65404

The dissociation constant of monochloroacetic acid as calculated from these values is  $5.220 \times 10^{-7}$ . The molality of the hydrogen ion decreases with increasing molality of lithium chloride.

**The Dissociation Constant of Trichloroacetic Acid.** The bright platinum electrodes were used in this determination. The results obtained were very satisfactorily reproducible when the ratio of the molality of lithium chloride to that of the acid was very small. These results are reported in Tables VI and VII.

TABLE VI  
Electromotive Force Measurements  
(0.10 m Trichloroacetic Acid)

m LiCl	E. M. F.	log $\gamma$	S
0.0000	.....	-0.06430	0.12922
0.0350	0.2389	-0.31830	0.64360
0.0496	0.2273	-0.34635	0.69770
0.0752	0.2206	-0.39621	0.80014
0.1000	0.2135	-0.42490	0.85980
0.1200	0.2088	-0.44291	0.89782

TABLE VII  
Molality of the Hydrogen Ion and Extrapolation Function  
(0.10 m Trichloroacetic Acid)

m LiCl	log $m_{\text{H}}$	$m_{\text{H}}$	N
0.0000	-3.21406	0.00061	(-5.49000)*
0.0350	-2.88056	0.00132	-5.40904
0.0496	-2.84978	0.00141	-5.39109
0.0752	-2.74562	0.00179	-5.28534
0.1000	-2.69287	0.00202	-5.23668
0.1200	-2.65826	0.00219	-5.20468

\*By extrapolation.

The dissociation constant of trichloroacetic acid calculated from the above data is  $3.236 \times 10^{-6}$ . Goldschmidt<sup>12</sup> obtained  $1.48 \times 10^{-6}$ . Larsson<sup>13</sup> has corrected Goldschmidt's value and obtained  $1.01 \times 10^{-6}$ . Larsson also determined the dissociation constant of trichloroacetic acid by potentiometric methods and found  $K$  to be  $2.09 \times 10^{-6}$ . The value  $4.54 \times 10^{-6}$  is quoted by Walden.<sup>14</sup>

For the solutions of trichloroacetic acids, the molality of the hydrogen ion appears to increase with increasing molality of lithium chloride. This is contrary to the effect of lithium chloride in the solutions of monochloroacetic acid. It will be noted, however, that the molalities of the hydrogen ion as determined in the trichloroacetic acid solutions are much larger than those of the monochloroacetic acid solutions. This matter is under further investigation. It also appears that further extensions of the theories and sources of information must be made before more exact determinations of dissociation constants in nonaqueous solutions can be made upon the basis of the Debye-Hückel equation.

<sup>12</sup> Goldschmidt, *Z. physik. Chem.*, **94**:46 (1916).

<sup>13</sup> Larsson, Thesis, Copenhagen (1924): "Untersuchungen über die electrolytische Dissoziation einiger Electrolyte in aethyl alkoholische Lösung." See also Kolthoff, *J. Phys. Chem.*, **35**:2732 (1931).

<sup>14</sup> Walden, "Elektrochemie nichtwässriger Lösungen," 1924, p. 361.

## CONCLUSIONS AND SUMMARY

The dissociation constants of trichloroacetic and monochloroacetic acids have been evaluated by means of the extrapolating function,  $\log k - \frac{2 \Lambda \sqrt{2\mu}}{1 + \alpha \sqrt{2\mu}}$ , from measurements of the electromotive forces of cells without liquid junctions. The method is based upon thermodynamic principles and upon assumptions which appear justified by experimental evidence. The dissociation constant of trichloroacetic acid has been found to be  $3.236 \times 10^{-6}$  and that of monochloroacetic acid  $5.224 \times 10^{-7}$  when lightly coated platinum black electrodes were used and  $5.720 \times 10^{-7}$  when platinum electrodes coated with bright platinum were employed.

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