[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY, UNIVERSITY OF MINNESOTA]

Acid–Base Equilibria in Glacial Acetic Acid. III. Acidity Scale. Potentiometric Determination of Dissociation Constants of Acids, Bases and Salts[1]

BY S. BRUCKENSTEIN[2] AND I. M. KOLTHOFF

RECEIVED JANUARY 9, 1956

Using previously determined *pK* values of hydrochloric acid and of pyridine, the *pK* values of a series of acids, bases and salts have been determined potentiometrically at 25 ± 0.1°, using a variety of cells. From the data the autoprotolysis constant of acetic acid is calculated to be 3.5×10^{-15} ($pK = 14.45$). The following summarizes the data in decreasing order of degree of dissociation. *pK* of acids: perchloric, 4.87; sulfuric, 7.24; *p*-toluenesulfonic acid, 8.44; hydrochloric, 8.55. *pK* of bases: tribenzylamine, 5.38; N,N-diethylaniline, 5.78; pyridine, 6.10; potassium acetate, 6.15; *p,p'*-N,N'-dimethylaminoazobenzene, 6.32; sodium acetate, 6.68; lithium acetate, 6.79; 2,5-dichloroaniline, 9.48; urea, 10.24. *pK* of salts: sodium perchlorate, 5.48; diethylaniline perchlorate, 5.78; tribenzylamine hydrochloride, 6.71; diethylaniline hydrochloride, 6.84; potassium chloride, 6.88; urea hydrochloride, 6.96; lithium chloride, 7.08; dodecylamine hydrochloride, 7.45.

Introduction

It is generally agreed[3,4] that acids, bases and salts are only slightly dissociated in glacial acetic acid. In this work classical potentiometric methods have been used to determine the autoprotolysis constant of acetic acid and the over-all dissociation constants of some acids, bases and salts, using as references the spectrophotometrically determined values for hydrochloric acid[5] and pyridine.[6] Both the saturated chloranil and silver–silver chloride electrodes have been used to establish the acidity scale and to provide independent checks of the previous spectrophotometric results.

Earlier potentiometric studies in acetic acid have not been interpreted from the viewpoint of incomplete dissociation. Hutchinson and Chandlee[7] used the hydrogen electrode in studying sulfuric acid in acetic acid solution at 25°. They interpreted their results assuming sulfuric acid dissociated to give three ions per molecule in acetic acid. LaMer and Eichelberger[8] pointed out that this was unlikely, and reinterpreted these data assuming sulfuric acid acted as a completely dissociated monobasic acid using the extended form of the Debye–Hückel theory proposed by Gronwall, LaMer and Sandved.

The results of Hutchinson and Chandlee for the cell without liquid junction in acetic acid

$$\mathrm{Pt\,|\,H_2\ (1\ atm.),\ H_2SO_4(C),\ Hg_2SO_4(sat.)\,|\,Hg}$$

can be interpreted on the basis of the reaction $H_2 + Hg_2SO_4 \rightleftarrows H_2SO_4 + 2Hg$, assuming sulfuric acid to be only very slightly dissociated. Since two faradays of change are involved for each mole of sulfuric acid formed, the e.m.f. of the cell is given by equation 1, where $E°$ is the unknown standard e.m.f. and $a_{H_2SO_4}$ represents the activity of sulfuric acid. It is assumed that the activity of undissociated sulfuric acid is equal to its concentration;

$$E = E° - \frac{RT}{2F}\ln a_{H_2SO_4} \qquad (1)$$

this is justified by the fact that its over-all dissociation constant as a monobasic acid is very small as shown in the present paper. A plot of E against the log of the concentration of sulfuric acid should have a slope of 0.0295, while the slope found was 0.033.

A similar treatment of the cell investigated by Hesten and Hall,[9] using a chloranil electrode in place of a hydrogen electrode, is possible.

$$\mathrm{Pt\,|\,C_6Cl_4O_2(sat.),\ C_6Cl_4(OH)_2(sat.),\ HCl(C),\ AgCl\,|\,Ag.}$$

The cell reaction is $C_6Cl_4(OH)_2 + 2AgCl \rightleftarrows C_6Cl_4O_2 + Ag + 2HCl$, and equation 2

$$E = E°' - \frac{RT}{F}\ln a_{HCl} \qquad (2)$$

the e.m.f. of the cell. The slope of a plot of *E versus* the logarithm of the concentration of hydrochloric acid should be 0.0591. Unfortunately Heston and Hall present their results graphically so that the slope could not be obtained as precisely as for the sulfuric acid cell. A value of 0.064 was found from the figure in their paper.

It is not possible to use the data of Hutchinson and Chandlee and of Heston and Hall to determine the ratio of the dissociation constants of hydrochloric and sulfuric acids since the difference of the standard half cell e.m.f.'s of the electrodes reversible to the anions are unknown. We have chosen to use cells with liquid junction, referring all e.m.f.'s to a modified calomel electrode (described under Experimental). A typical cell in acetic acid was Cell A. As Conant and Hall[10] have shown, the

$$\text{(Cell A) Ref. electrode}\ ||\ \mathrm{HX}(C_{\mathrm{HX}}),\ \mathrm{C_6Cl_4O_2(sat.),\ C_6Cl_4(OH)_2(sat.)\,|\,Pt}$$

saturated chloranil electrode functions as a hydrogen electrode, while Heston and Hall[11] reported a standard potential of +0.680 volt, referred to the hydrogen electrode. The e.m.f. of this cell, E_{HX}, is given by equation 3a where $E_{l.j.}$ is the unknown liquid junction potential and is assumed to be constant. The activity of solvated proton is related to the over-all dissociation constant ($K_{HX} = a_{H^+}a_{X^-}/(a_{HX} + a_{H^+X^-})$) by equation 3b

$$E_{HX} = E°_{HX} + \frac{RT}{F}\ln a_{H^+} + E_{l.j.} \qquad (3a)$$

$$a_{H^+} = \sqrt{K_{HX}C_{HX}} \qquad (3b)$$

---

[1] In part from a thesis by S. Bruckenstein to the Graduate School of the University of Minnesota in partial fulfillment of the requirements for the degree of Doctor of Philosophy, 1954.

[2] Du Pont Teaching Fellow, 1953–1954.

[3] T. L. Smith and J. H. Elliot, THIS JOURNAL, **75**, 3566 (1953).

[4] M. M. Jones and E. Griswold, *ibid.*, **76**, 3247 (1954).

[5] I. M. Kolthoff and S. Bruckenstein, *ibid.*, **78**, 1 (1956).

[6] S. Bruckenstein and I. M. Kolthoff, *ibid.*, **78**, 10 (1956).

[7] A. E. Hutchinson and G. C. Chandlee, *ibid.*, **53**, 2881 (1931).

[8] V. K. LaMer and W. C. Eichelberger, *ibid.*, **54**, 2763 (1932).

[9] B. O. Heston and N. F. Hall, *ibid.*, **56**, 1463 (1934).

[10] J. B. Conant and N. F. Hall, *ibid.*, **49**, 3047 (1927).

[11] B. O. Heston and N. F. Hall, *ibid.*, **55**, 4729 (1933).

where C_{HX}, the stoichiometric concentration of the acid, is assumed to be equal to the sum of the activities of the molecular and ion-pair forms of the acid and $a_{H^+} = a_{X^-}$. Combination of equations 3b and 3a yields a useful expression for E_{HX}, equation 3c which indicates that a tenfold increase in C_{HX} should be accompanied by an increase in

$$E_{HX} = E^{\circ}_{HX} + \frac{RT}{2F}\ln K_{HX} + \frac{RT}{2F}\ln C_{HX} \quad (3c)$$

e.m.f. of 0.0295 volt at 25°. Perchloric, sulfuric, hydrochloric and *p*-toluenesulfonic acids have been found to exhibit this behavior. Since K_{HCl} is known,[5] E°_{HX} can be calculated, and K_{HX} for the other acids determined.

Cell B was used to determine the over-all dissociation constants of bases ($K_B = a_{BH^+}a_{Ac^-}/(a_B + a_{BH^+Ac^-})$) and the autoprotolysis constant of acetic acid ($K_s = a_{H^+}a_{Ac^-}$). Using the same

(Cell B) Ref. electrode || $B(C_B)$, $C_6Cl_4O_2$(sat.),
$C_6Cl_4(OH)_2$(sat.) | Pt

assumptions as for cell A, the e.m.f. of this cell, E_B, is given by equation 4. This equation predicts a decrease in e.m.f. of 0.0295 volt at 25° for a ten-

$$E_B = E^{\circ}_{HX} + \frac{RT}{F}\ln K_s - \frac{RT}{2F}\ln K_B - \frac{RT}{2F}\ln C_B \quad (4)$$

fold increase in concentration of base, C_B. Lithium, sodium and potassium acetates, and pyridine, diethylaniline, tribenzylamine and 2,5-dichloroaniline yield results in accord with this prediction. Conant and Hall[10] noted similar results for diethylamine, pyridine, sodium acetate, guanidine and *o*-chloroaniline. From the spectrophotometrically determined value of K_B for pyridine,[6] K_s has been calculated as has K_B for the other bases investigated.

Cell C was used to determine the over-all dissociation constants of chlorides, K_{BHCl}. The e.m.f.

(Cell C) Ref. electrode || $BHCl(C_{BHCl})$, AgCl | Ag

of Cell C, E_{BHCl}, is given by equation 5. Hydrochloric acid, lithium chloride, potassium chloride,

$$E_{BHCl} = E^{\circ}_{BHCl} - \frac{RT}{2F}\ln K_{BHCl} - \frac{RT}{2F}\ln C_{BHCl} \quad (5)$$

diethylanilinium chloride, tribenzylamine hydrochloride and dodecylamine hydrochloride, all yield approximately a 0.0295 volt decrease in E_{BHCl} for a tenfold increase in concentration, the predicted result at 25°. E°_{BHCl} was calculated from K_{HCl}, using hydrochloric acid as the chloride and K_{BHCl} for the other compounds from the e.m.f. data.

It is possible to determine the over-all dissociation constants of salts, even when an electrode reversible to either the cation or anion is not available, by making use of the common ion effect. Consider a solution of an acid, HX, containing a salt with a common ion, BHX. The rule of electroneutrality is (neglecting acetate ion) stated

$$[H^+] + [BH^+] = [X^-] \quad (6a)$$

in equation 6a. Using the definitions of K_{HX} and K_{BHX} and assuming that $f_{H^+} = f_{BH^+} = f_{X^-}$ and that the activity coefficients of all uncharged species are one, equation 6b is obtained for the activity of hydrogen ion. The e.m.f. of Cell D,

$$a_{H^+} = \frac{K_{HX}C_{HX}}{\sqrt{K_{HX}C_{HX} + K_{BHX}C_{BHX}}} \quad (6b)$$

$E_{HX,BHX}$ is given by equation 3a, which when combined with equation 6b yields equation 6c.

(Cell D) Ref. electrode || $HX(C_{HX})$, $BHX(C_{BHX})$,
$C_6Cl_4O_2$(sat.), $C_6Cl_4(OH)_2$(sat.) | Pt

Since E°_{HX} and K_{HX} are known, K_{BHX} is determined.

$$E_{HX,BHX} = E_{HX} + \frac{RT}{F}\ln K_{HX}C_{HX} - \frac{RT}{2F}\ln(K_{HX}C_{HX} + K_{BHX}C_{BHX}) \quad (6c)$$

This cell was used for a mixture of tribenzylamine hydrochloride and hydrochloric acid. The value of K_{BHCl} found with this cell agreed well with the value found using Cell C.

A similar treatment of Cell E, yields equation 7 for the e.m.f. of a solution containing a base and a

(Cell E) Ref. electrode || $B(C_B)$, $BHX(C_{BHX})$,
$C_6Cl_4O_2$(sat.), $C_6Cl_4(OH)_2$(sat.) | Pt

salt with a common cation. K_{BHX} has been determined for sodium perchlorate and diethylanilinium perchlorate.

$$E_{B,BHX} = E^{\circ}_{HX} + \frac{RT}{F}\ln K_s - \frac{RT}{F}\ln K_BC_B + \frac{RT}{2F}\ln(K_BC_B + K_{BHX}C_{BHX}) \quad (7)$$

It is also possible to treat Cell F in a similar manner and obtain equation 8 for the e.m.f. of a silver–silver chloride half cell containing a chloride

(Cell F) Reference Electrode || $BHCl(C_{BHCl})$,
$BHX(C_{BHX})$AgCl | Ag

and another salt with the same cation as the chloride. K_{BHX} for diethylanilinium perchlorate (X = perchlorate) and tribenzylamine (X = acetate) have been calculated from the e.m.f. of such cells.

$$E_{BHCl,BHX} = E^{\circ}_{BHCl} - \frac{RT}{F}\ln K_{BHCl}C_{BHCl} + \frac{RT}{2F}\ln(K_{BHCl}C_{BHCl} + K_{BHX}C_{BHX}) \quad (8)$$

Values of K_{BHX} derived from e.m.f. data using Cell F are ultimately based on the value of K_{HCl}, since all dissociation constants of chlorides are based on K_{HCl}. Values of K_{BHX} using Cell E are ultimately based on K_B for pyridine since all the dissociation constants of bases are referred to pyridine. The dissociation constant of diethylanilinium perchlorate was determined, using both Cell E and Cell F, and close agreement found for K_{BHClO_4}, thus providing excellent support for the reliability of the dissociation constants of pyridine and hydrochloric acid, as derived from spectrophotometric data.[5,6] Similarly, the dissociation constant of tribenzylamine was determined, using Cell B (K_B based on pyridine) and Cell F (K_B based on HCl) and excellent agreement found again. These results all indicate our approximations concerning activities and liquid junction potentials introduce very small errors only.

Experimental

Materials. Acetic acid and all other materials not listed below have been described previously.[5,6] The water content was less than 0.01% as determined by the Karl Fischer method unless otherwise stated.

Chloranil.—An Eastman Kodak product was used.

Diethylaniline.—An Eastman Kodak product was distilled and titrated in acetic acid with perchloric acid, using crystal violet as the indicator. The purity was found to be 100.3%.

Diethylanilinium Chloride.—Diethylaniline was dissolved in benzene and dry hydrogen chloride passed through the solution until precipitation was complete. The precipitate was washed thoroughly with benzene and dried *in vacuo* at 50° for 24 hours.

Diethylanilinium Perchlorate.—Aqueous 72% perchloric acid was cautiously mixed with an equal volume of ethanol and added to a chilled solution of diethylaniline (5% excess) in ethanol. The product was washed thoroughly with ether, recrystallized twice from ethanol, and once from acetic acid, and dried *in vacuo* at 50° to constant weight.

2,5-Dichloroaniline.—An Eastman Kodak product was used.

Dodecylamine Hydrochloride.—The method of Kolthoff and Bovey[12] was used to prepare this compound.

Lithium Acetate.—Thirty grams of Coleman and Bell lithium acetate dihydrate was cautiously added to 75 ml. of boiling acetic anhydride and 25 ml. of acetic acid added after the reaction ceased. On cooling, 50 ml. of benzene was added. The precipitate was filtered and washed thoroughly with benzene, and dried at 50° *in vacuo* for one week.

Potassium Acetate.—J. T. Baker reagent grade was used.

Sodium Acetate.—Mallinckrodt Analytical Reagent was recrystallized twice from acetic acid and dried at 200° for 24 hours.

Sodium Perchlorate.—Anhydrous sodium perchlorate (G. Frederick Smith Co.) was recrystallized once from acetic acid and dried at 180° for 24 hours.

Tribenzylamine.—An Eastman Kodak product was used.

Tribenzylammonium Chloride.—Tribenzylamine was dissolved in benzene and dry hydrogen chloride passed through until the precipitation was complete. The filtered precipitate was washed with benzene and dried *in vacuo* at 50° for 24 hours.

***p*-Toluenesulfonic Acid (HTs).**—Two samples were used. One was prepared from an Eastman Kodak product by the acetone–benzene method described previously[5] and another by recrystallization from chloroform. Both samples are identical results.

Tetrachlorohydroquinone.—An Eastman Kodak product was used.

Techniques. E.m.f. Measurements.—E.m.f. measurements were made, using a commercial potentiometer (both Leeds and Northrup and Rubicon instruments have been found satisfactory) in conjunction with a vacuum tube electrometer as null-point detector in place of the conventional galvanometer. Beckman Model H and H-2 line operated *p*H meters have been used after modifying their circuits so that it was possible to substitute a 166 ohm, 30 microampere meter for the meter supplied with the commercial instrument. The procedure followed in an e.m.f. measurement was to short the input of the *p*H meter, note the deflection of the meter supplied with the instrument and then, with the microammeter substituted, place the *p*H meter in the potentiometric circuit and adjust the e.m.f. until the instrument meter and then the microammeter deflect to the short circuit position. A precision of ±0.1 millivolt was obtained, provided the a.-c. line voltage did not fluctuate during the time of the measurement. When rapid and large fluctuations in line voltage did occur, it was necessary to operate the *p*H meter in conjunction with a 0.01% regulated voltage supply to obtain this precision.

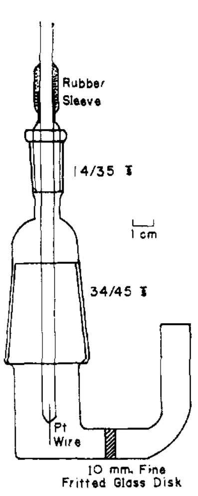

Fig. 1.—Indicator electrode half-cell.

Indicator Electrode Half-cell.—The type of cell used is shown in Fig. 1. A platinum wire electrode (or silver–silver chloride electrode) is introduced through the top joint; a rubber sleeve makes the connection between the electrode and the joint air-tight. Twenty ml. of solution is sufficient for a measurement. Acetic acid was dispensed from an automatic buret[5] directly into the cell, the buret tip entering the cell through the 14/35 joint.

In order to make hydrogen ion activity measurements, 0.3 g. each of chloranil and tetrachlorohydroquinone was added to the cell, the cell warmed to 50° and stirred with a magnetic stirrer for five minutes. After cooling to 25.0 ± 0.1° in a thermostat, the solute was added. This cooling is especially important for bases, since there was definite visual evidence of decomposition of either chloranil or tetrachlorohydroquinone if the addition was made at elevated temperatures. Decomposition with drift in potentials did occur on long standing at 25°, *e.g.*, solution of 0.05 *M* sodium acetate turned from a clear yellow to a dirty violet color over a period of two weeks. Normally no change in e.m.f. was observed during the time of the experiment.

The silver–silver chloride electrodes were prepared by plating a rotating platinum wire electrode (20 gage, 100 mm. long) with silver from 0.05 *M* aqueous solution of potassium silver cyanide for three hours, using a current of three milliamperes. After thorough washing the electrode was made anodic in 0.1 *M* hydrochloric acid and a current of three milliamperes passed for 40 minutes.

Reference Half-cell.—Conant and Hall[10] reported that intercomparison of reference half-cells, using acetic acid as a solvent, gave results which varied as much as 5 millivolts. We have found that a modified calomel electrode can be prepared in anhydrous glacial acetic acid with a reproducibility of about ±0.25 millivolt. Our early cell designs used Tygon tubing in direct contact with acetic acid, but the tubing eventually hardened, and potentials would drift as the cell aged. An all-glass cell design was adopted using a 1 mm. drawn down capillary to form the liquid junction. A stopcock was placed between the cell proper and the capillary tip to prevent drainage of the cell on long storage. The cell is filled with mercury, mercury–calomel paste and a solution saturated with calomel, sodium chloride and sodium perchlorate. The solubility of sodium chloride in acetic acid is 0.0125 *M*. The sodium perchlorate was added to decrease the electrical resistance of the cell. A slight positive pressure is maintained in the cell (by occasionally restoppering the cell rapidly) so that a flowing junction is formed when the stopcock is opened and any precipitate formation does not clog the capillary orifice. The sintered glass disk separating the side arm and the main body of the indicator electrode half-cell prevents any significant diffusion during the time of a measurement. In order to prevent contamination in the indicator half-cell the salt bridge electrolyte used was the same as in the indicator half-cell.

Shielding.—It was found necessary to shield the cells during a measurement. This was accomplished by placing the cells in a grounded stainless steel box which was partially submerged in a water thermostat at 25.0 ± 0.1°.

Over-all Precision of an E.m.f. Measurement.—With the refined potentiometric technique described it is possible to detect an unbalance of 0.1 millivolt. However, when two platinum wire electrodes were submerged in the same chloranil half cell, an e.m.f. within 0.5 millivolt was usually found, though occasional variations of 1 millivolt have been noted. Similar results were found with silver–silver chloride electrodes so that all the data have been rounded off to the nearest 0.0005 volt. The error of a single measurement corresponds to ±0.017 in the *pK* value.

Experimental Results and Discussion

Table I contains the e.m.f. of cells of type A for the four acids, perchloric, sulfuric, hydrochloric and *p*-toluenesulfonic. It was necessary to correct the perchloric acid data for the reaction $HClO_4 + H_2O \rightleftarrows HClO_4{\cdot}H_2O$, using the equilibrium constant found earlier[5] in order to calculate the concentration of unreacted perchloric acid. When E_{HX} was plotted against log C_{HX} the slopes obtained were: $HClO_4$, 0.0335; H_2SO_4, 0.0295; HTs, 0.0285; and HCl, 0.0295. The deviation for perchloric acid solutions is probably caused by the repression of the dissociation of perchloric acid by the perchlorate ion arising from hydronium per-

---

[12] I. M. Kolthoff and F. Bovey, This Journal, **70**, 792 (1948).

TABLE I

DISSOCIATION CONSTANTS OF SOME ACIDS OBTAINED WITH CELL A

Acid	Acid, $M \times 10^2$	E.m.f.	pK
Perchloric[a]	0.0628 (0.0360)	0.6580	5.06
	.324 (.177)	.6835	4.87
	.510 (.296)	.6890	4.92
	.970 (.589)	.6995	4.87
	2.03 (1.28)	.7130	4.75
	3.87 (2.54)	.7205	4.78
	19.3 (17.6)	.7430	4.88
Sulfuric	.858	.6340	7.24
	9.00	.6640	7.25
HTs	5.00	.6210	8.46
	8.30	.6280	8.43
	15.1	.6340	8.49
	29.2	.6430	8.47
HCl[b]	.636	.6210	(8.55)
	6.40	.6505	(8.55)

[a] The figures in parentheses represent the molarity of the sum of $HClO_4$ and $H^+ClO_4^-$ allowing for the reaction $H_2O + HClO_4 \rightleftarrows H_2O \cdot HClO_4$, using the equilibrium constant found earlier.[5] The total water present was calculated, allowing for the water added from the stock perchloric acid solution in acetic acid (0.22%) to the solvent containing 0.044% water initially. [b] E°_{HX} is found to be 0.9095 volt, using $pK_{\mathrm{HCl}} = 8.55$.

TABLE II

THE DISSOCIATION CONSTANTS OF SOME BASES OBTAINED WITH CELL B

Base	Base, $M \times 10^2$	E.m.f.	pK
Tribenzylamine	0.985	0.2725	5.32
	9.85	.2465	5.44
Diethylaniline	.255	.3000	5.65
	.510	.2930	5.71
	1.02	.2885	5.87
	2.04	.2775	5.79
	4.08	.2690	5.81
	8.15	.2600	5.80
	16.3	.2520	5.83
Pyridine[a]	2.444	.2835	(6.10)
	6.070	.2720	(6.10)
Potassium acetate	14.13	.2645	6.20
	1.549	.2900	6.10
DMAAB	1.06	.3015	6.32
Lithium acetate	1.242	.3140	6.79
	11.16	.2850	6.79
Sodium acetate	1.77	.3010	6.56
	4.96	.2895	6.59
	9.14	.2815	6.58
	9.74	.2800	6.55
	19.2	.2715	6.56
	39.4	.2625	6.62
2,5-Dichloroaniline	1.92	.3870	9.46
	3.75	.3800	9.50
	7.80	.3700	9.50
Urea	21.7	.3785	10.24

[a] Assuming $pK_{\mathrm{Py}} = 6.10$, $pK_s = 14.45$.

chlorate. The value of E°_{HX} (equation 3c) is +0.9095 volt, using $pK_{\mathrm{HCl}} = 8.55$.[5] The average values for the acids are: perchloric, 4.87 ± 0.07; sulfuric, 7.24 ± 0.01; and *p*-toluenesulfonic acid, 8.46 ± 0.02. The value for *p*-toluenesulfonic acid does not agree very well with an earlier value, 8.14.[5] Using the conductivity data of Kolthoff and Willman,[13] Smith and Elliot[3] reported values of 6.07, 8.13 and 9.19 for perchloric, sulfuric and hydrochloric acids, respectively. These authors carried out a Fuoss–Kraus treatment of the perchloric acid data, but they assumed that the limiting equivalent conductance of the other two acids was the same as for perchloric acid and obtained the other constants reported by comparing the ratios of the observed conductance in 3×10^{-4} molar solutions. This assumption may be the cause of an appreciable error. It is evident from our results that the Fuoss–Kraus extrapolation method in a solvent like acetic acid yields results which are subject to relatively large errors.

Table II lists the results obtained for nine bases in Cell B. The slope of plots of E_{B} against log C_{B} were: tribenzylamine, −0.026; pyridine, −0.028; potassium acetate, 0.027; sodium acetate, −0.030; diethylaniline, −0.030; lithium acetate, 0.030; and 2,5-dichloroaniline, −0.030. Using the value 6.10 for the negative logarithm of the dissociation constant of pyridine,[6] the autoprotolysis constant of acetic acid is calculated from equation 4 to be 14.45. The value of 15.0 estimated by Kolthoff and Willman from conductivity data appears to be of the right order of magnitude. The pK_{B} for the other compounds studied were in order of decreasing basicity: tribenzylamine, 5.36 ± 0.06; diethylaniline, 5.78 ± 0.07, potassium acetate, 6.10 ± 0.5; *p,p'*,N,N'-dimethylaminoazobenzene, 6.32; sodium acetate, 6.58 ± 0.02; lithium acetate, 6.79; 2,5-dichloroaniline, 9.48 ± 0.01; and urea, 10.24. The value for dimethylaminoazobenzene is in excellent agreement with our previous spectrophotometric value,[6] 6.35.

The order of basicity of the alkali metal acetates is in agreement with results of the indicator studies by Kolthoff and Willman,[14] but is different from that found by Jones and Griswold at 30°.[4] From conductivity measurements and Fuoss–Kraus plots these authors obtained for pK_{B}: lithium acetate, 6.22; sodium acetate, 6.68; and potassium acetate, 6.44. The sodium and potassium acetate values are in fair agreement with our values, while the lithium acetate value seems to be out of the order expected from potentiometric and colorimetric results. The authors state that the slope of the Fuoss–Kraus plot is high and admit that the extrapolation to determine the limiting equivalent conductance is subject to considerable uncertainty.

Table III contains the results obtained with different chlorides in Cell C. $E^{\circ}_{\mathrm{BHCl}} = 0.3928$ using $pK_{\mathrm{HCl}} = 8.55$, and in order of decreasing dissociation, pK_{BHCl} was found to have the indicated value for the other compounds; tribenzylamine hydrochloride, 6.71 ± 0.01; diethylaniline hydrochloride, 6.84 ± 0.01; potassium chloride, 6.88 ± 0.02; lithium chloride, 7.08 ± 0.02; and dodecylamine hydrochloride, 7.45 ± 0.05. The slopes of a plot of E_{BHCl} against −log C_{BHCl} were

---

(13) I. M. Kolthoff and A. Willman, THIS JOURNAL, **56**, 1007 (1934).

(14) I. M. Kolthoff and A. Willman, *ibid.*, **56**, 1014 (1934).

Table III

Dissociation Constants of Some Chlorides Obtained from Cell C

Chloride	$M \times 10^2$	E.m.f.	pK
Tribenzylamine hydrochloride	1.602	−0.1410	6.70
	7.717	− .1610	6.72
Diethylaniline hydrochloride	1.083	− .1320	6.85
	6.163	− .1550	6.83
	10.83	− .1620	6.84
Potassium chloride	.1825	− .1090	6.85
	1.825	− .1370	6.90
Lithium chloride	.728	− .1205	7.06
	7.28	− .1490	7.10
Dodecylamine hydrochloride	.738	− .1105	7.41
	7.38	− .1380	7.48
Hydrochloric acid[a]	1.28	− .0835	(8.55)
	12.8	− .1140	(8.55)

[a] Assuming $pK_{HCl} = 8.55$, $E^0_{BHX} = -0.3928$ volt.

0.0305, 0.0305, 0.0290, 0.0282 and 0.0275 for the compounds in the order listed above. From conductance data Smith and Elliot[3] estimated that $pK_{LiCl} = 7.13$, but the agreement must be considered fortuitous.

Table IV contains the results obtained with Cells D, E and F. The value of the negative logarithm of the dissociation constants for the compounds studied were: urea hydrochloride, 6.94 using Cell D, 6.98 using Cell E; sodium perchlorate, 5.48 ± 0.06; diethylaniline perchlorate, 5.82 ± 0.07 using Cell E and 5.75 ± 0.05 using Cell F; and tribenzylamine, 5.40. A plot of $E_{B'BHX}$ against log C_B for sodium acetate in the presence of a large excess of sodium perchlorate and for diethylaniline in the presence of a large excess of diethylaniline perchlorate yielded slopes of −0.061 and −0.060, respectively. The predicted slope is −0.0591 in a solution in which the concentration of the cation of the base is held constant, as it is in these experiments. Higuchi, Danguilan and Cooper[15] noted such a relationship for the sodium acetate–sodium perchlorate system and qualitatively interpreted the results as indicating sodium perchlorate is more dissociated than sodium acetate. Their data were presented graphically so that it is difficult to compare their figures with ours; however, rough calculations indicate agreement.

Table IV

The Dissociation Constants of Some Compounds Obtained with Cells D, E and F

Cell	Molarity of soln.		E.m.f.	pK^a
D[b]	Hydrochloric acid	Urea hydrochloride		
	0.221	0.0942	0.5995	6.94
E[c]	Urea	Urea hydrochloride		
	0.095	0.115	0.4870	6.98
E	Sodium acetate	Sodium perchlorate		
	0.0168	0.246	0.3730	5.39
	.0344	.246	.3545	5.40
	.0707	.246	.3360	5.40
	.1495	.246	.3160	5.43
	.295	.246	.2975	5.47
	.529	.246	.2825	5.51
	.394	.0179	.2682	5.51
	.394	.0358	.2710	5.59
	.394	.0632	.2760	5.54
	.394	.142	.2830	5.57
	.394	.276	.2915	5.50
E	Diethylaniline	Diethylaniline perchlorate		
	.000637	0.0918	0.3870	5.74
	.00127	.0918	.3680	5.78
	.00255	.0918	.3570	5.76
	.00510	.0918	.3340	5.63
	.0102	.0918	.3160	5.75
	.0204	.0918	.2985	6.06
	.0408	.0918	.2825	5.81
	.0815	.0918	.2675	5.87
	.0204	.0148	.2845	5.92
	.0204	.0347	.2905	5.82
	.0204	.0726	.2955	5.90
	.0204	.1026	.3010	5.81
	.0204	.1611	.3055	5.81
F	Tribenzylamine hydrochloride	Tribenzylamine		
	0.01602	0.193	−0.0705	5.40
	Diethylaniline hydrochloride	Diethylaniline perchlorate		
	0.05913	0.0650	−0.1210	5.80
	0.01083	0.1098	−0.0690	5.70

[a] The pK refers to the second compound listed under the heading "molarity of solution." [b,c] These solutions were prepared by mixing standard solutions of urea and hydrochloric acid.

The synopsis summarizes all the experimental results. As has been mentioned earlier, Cells A, C, D and F use hydrochloric acid as the reference compound, while Cells B and E use pyridine as the reference compound. The pK of tribenzylamine was determined using both Cells B and F, that of diethylaniline perchlorate using Cells E and F, and that of urea hydrochloride using Cells B and E. Excellent agreement was found in all cases showing that our independently determined values for the dissociation constant of hydrochloric acid and pyridine are consistent with the potentiometric measurements.

Another check between the present potentiometric work and our earlier spectrophotometric work is possible. The equilibrium constant for the reaction between urea, U, and hydrochloric acid, $K_i^{UHCl} = [UHCl]/[U][HCl]$ was determined by an indicator method[5] and shown to be equal to $K_{HCl}K_U/K_SK_{UHCl}$. The value of log K_i^{UHCl} calculated from the potentiometric data is 2.62, while the spectrophotometric value is 2.69. It is highly unlikely that such agreement is the result of chance.

These experimental data show that classical potentiometric methods are capable of yielding

---

[15] T. Higuchi, M. L. Danguilan and A. D. Cooper, *J. Phys. Chem.*, **58**, 1167 (1954).

dissociation constants in acetic acid solution in a straightforward manner, and that these results are in better agreement with spectrophotometric results than are equilibrium constants derived from conductivity data.

Acknowledgment.—Acknowledgment is made to the Graduate School of the University of Minnesota for financial support of part of this research during the summer of 1955.

MINNEAPOLIS, MINNESOTA

[CONTRIBUTION FROM THE DEPARTMENTS OF CHEMISTRY AND PHYSICS OF THE PENNSYLVANIA STATE UNIVERSITY]

Polarographic Diffusion Coefficients of Oxygen Defined by Activity Gradients in Viscous Media

BY JOSEPH JORDAN, EUGENE ACKERMAN AND ROBERT L. BERGER

RECEIVED JANUARY 16, 1956

Fick diffusion coefficients of oxygen in aqueous sucrose solutions and in glycerol–water mixtures have been evaluated polarographically on the basis of the Lingane–Loveridge equation, in a range of viscosities (η) between 0.9 and 125 centipoise. These diffusion coefficients strikingly failed to satisfy the Stokes–Einstein relation. In terms of activity gradients, a new polarographic diffusion coefficient has been defined which varies linearly with η^{-1} between 2 and 125 centipoise. A phenomenological interpretation is presented on the basis of the Eyring discrete transition theory of diffusion and viscous flow. A corresponding polarographic diffusion current equation is derived.

The correlation between diffusion and viscosity coefficients in liquids warrants considerable fundamental interest as a possible clue to the detailed mechanism of the two processes and to the structure of liquids in general. Several studies have been reported in the literature devoted to the variation with viscosity of diffusion currents, i_d, at the dropping mercury electrode of ions and of oxygen in various solvents,[1,2] results being interpreted on the basis of the "original" Ilkovič Equation[1] which implies that

$$D_{\text{Fick}} \propto i_d^2 \qquad (1)$$

where D_{Fick} denotes a conventional diffusion defined in terms of concentration gradients.[3] The determination at the dropping mercury electrode of the diffusion coefficient of oxygen is described in this paper on the basis of the "modified" (expanded) Ilkovič equation[4–9] in media covering a more than hundred-fold range of viscosities. In accordance with a suggestion by Hohn[10] a new polarographic diffusion coefficient D_a has been defined in terms of activity gradients in order to correlate diffusive and viscous properties in the several media. D_a satisfies at 25° a Stokes–Einstein type relationship

$$D_a\eta = \text{const.} \qquad (2)$$

in a range of viscosities between 2 and 125 centipoise, while D_{Fick} does not. A phenomenological interpretation is offered in terms of the "hole" theory of diffusion and viscous flow in liquids and a corresponding generalized form of the Ilkovič equation is presented and discussed.

Experimental

Chemicals.—C.P. chemicals and triply distilled conductivity water were used throughout.

Polarographic Procedure.—Solutions of desired viscosity were made up by mixing appropriate weight fractions of water and sucrose, or of water and glycerol. To serve as suitable supporting electrolytes, these solutions were made 0.1 *M* in potassium chloride and a phosphate buffer of *p*H 7 (0.01 *M* in total phosphate) was added. Buffering was considered desirable, because results by Foffani and Vecchi[2] seem to indicate that the polarographic diffusion coefficient of oxygen may vary with *p*H. As maximum suppressor, 0.01% gelatin was used, due precautions being taken to ascertain that it did not depress the relevant diffusion currents.[1,11] Gelatin was selected as maximum suppressor in preference to methyl red, because appreciable concentrations of the latter were found to be required in the viscous solutions (0.008%, as compared to 0.0001% customarily used in pure aqueous solutions) necessitating awkwardly large residual current corrections. A trace of a defoaming agent (Silicone Antifoam A, supplied by the Dow Corning Co., Midland, Michigan) was also added and had no measurable effect on the c.v. curves. Aliquots of the solutions at 25.00 ± 0.02° were equilibrated under the prevailing barometric pressure with air and with pure oxygen, respectively. This was accomplished by bubbling at a rate of 10 l./min. with the aid of an extra coarse Corning fritted glass gas dispersion cylinder for a period of 5 to 40 minutes. The time in each solution required for equilibration was ascertained polarographically and was found to increase with viscosity. The molarity of oxygen in the various solutions was calculated from its experimentally determined solubility in the given medium (*vide infra*) and the prevailing barometric pressure, the volume per cent. of oxygen in dry air being taken equal to 20.75.[12]

Current–voltage (c.v.) curves at the dropping mercury electrode (DME) were recorded at 25.00 ± 0.02° with a Leeds and Northrup Model E Electrochemograph, using an external Hume–Harris type saturated calomel reference electrode (SCE).[13] The DME was operated under a head of mercury of 60 cm. and had the following characteristics in 0.1 *M* aqueous potassium chloride solution: $m = 1.9657$

---

[1] I. M. Kolthoff and J. J. Lingane, "Polarography," Vol. I, Second Ed., Interscience Publishers, Inc., New York, pp. 43, 97, 100, 164; Vol. II, p. 552; 1952.

[2] A. Foffani and E. Vecchi, "Proc. I. Internat. Polarographic Congress," Vol. I, Prague, Czechoslovakia, 1951, p. 64.

[3] E. A. Guggenheim, *Trans. Faraday Soc.*, **50**, 1048 (1954).

[4] J. J. Lingane and B. A. Loveridge, THIS JOURNAL, **72**, 438 (1950).

[5] H. Strehlow and M. von Stackelberg, *Z. Elektrochem.*, **54**, 51 (1950).

[6] T. Kambara and I. Tachi, *Bull. Chem. Soc. Japan*, **25**, 284 (1952).

[7] J. Koutecky, *Czechoslov. J. Phys.*, **2**, 50 (1953).

[8] O. H. Müller, N.B.S. Circular 524 (1953), p. 289.

[9] M. von Stackelberg and V. Toome, *Z. Elektrochem.*, **58**, 226 (1954).

[10] H. Hohn, *Chemische Analysen mit dem Polarographen*, Julius Springer, Berlin, 1937, p. 36.

[11] L. Meites, "Polarographic Techniques," Interscience Publishers, Inc., New York, N. Y., 1955, p. 140.

[12] "International Critical Tables," Vol. I, McGraw-Hill Book Co., Inc., New York, N. Y., 1926, p. 393.

[13] D. N. Hume and W. E. Harris, *Ind. Eng. Chem., Anal. Ed.*, **15**, 465 (1943).