The values of $\alpha$ are listed in Table V in terms of the solubility of gas at 1 mm. pressure.[39]

Table V. Olefin Solubilities

| Olefin | Henry's law constant, $M$/mm. $\times 10^6$ |
|---|---|
| Propylene | 6.4 |
| 1-Butene | 6.2 |
| cis-2-Butene | 9.1 |
| trans-2-Butene | 7.3 |
| Isobutene | 6.9 |

(39) The values for cis- and trans-2-butene do not agree very closely

with those previously reported.[40] However, if the values for the two olefins are interchanged the agreement would be much better.

(40) M. M. Kreevoy, L. L. Schaleger, and J. C. Ware, *Trans. Faraday Soc.*, 58, 2433 (1962).

# Calibration of the Glass Electrode in Acetonitrile. Shape of Potentiometric Titration Curves. Dissociation Constant of Picric Acid[1]

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*Contribution from the School of Chemistry, University of Minnesota, Minneapolis, Minnesota 55455. Received June 28, 1965*

*An equation has been derived for the calculation of $pa_H$ in the neutralization with tetraalkylammonium hydroxide in acetonitrile of a weak acid with known dissociation constant $K_{HA}$ and homoconjugation constant $K_{HA_2}-$. The assumption was made that the tetraalkylammonium salts of the acid are completely dissociated. At 50% neutralization $pa_H = pK_{HA}$. When the product of initial acid concentration and $K_{HA_2}-$ is greater than about 10, the buffer capacity has a pronounced minimum at 50% neutralization. Equations are derived to calculate $K_{HA}$ and $K_{HA_2}-$ from $pa_H$, measured with the glass electrode in mixtures of an acid and its tetraalkylammonium salt. $pK_{HA}$ and $pK_{2(HA)}$ of methanesulfonic acid (I) and 2,5-dichlorobenzenesulfonic acid (II) have been determined by various methods and the following values were found: 10.0 and 3.8 for I and 6.2 and 2.65 for II, respectively. The glass electrode in AN has been calibrated in mixtures of I and of II with their tetraethylammonium salts and in mixtures of o-nitroaniline and perchloric acid. $pK_{HA}$ of picric acid was determined potentiometrically and a value of 11.0 $\pm$ 0.1 was found. This was confirmed by spectrophotometric measurements in buffer mixtures of I and conductometric measurements in mixtures of o-nitroaniline and picric acid. The homoconjugation of picrate with picric acid is very slight, $K_{HA_2}-$ being of the order of 2.*

## Introduction

The glass electrode has been used quite generally as an indicator electrode for hydrogen ions in potentiometric titrations of acids and bases in a host of organic solvents. In order to obtain from the e.m.f. the hydrogen ion activity, it is necessary to calibrate the glass electrode in solutions of known hydrogen ion activity. The present paper deals with the calibration of the glass electrode for $pa_H$ measurements in acetonitrile (AN) as a solvent. Several authors[2,3] have found the kind of glass electrode generally used for $pa_H$ measurements in aqueous medium suitable for similar measurements in AN.

Perchloric acid behaves as a strong acid in AN, but in agreement with Coetzee[4] we found that the potential of the glass electrode in solutions of this acid was poorly reproducible. Coetzee and Padmanabhan[3] calibrated the glass electrode in buffer solutions of picric acid and tetrabutylammonium picrate in which stable and reproducible potentials were measured. The $pa_H$ of the solutions was calculated from the dissociation constant of picric acid in AN, which was reported by Kolthoff, *et al.,*[5] to be $10^{-8.9}$. Later work in this laboratory revealed that this constant is considerably smaller than $10^{-8.9}$. In the earlier work[5] it was not realized that traces of impurities in the solvent have a large effect on the apparent degree of dissociation of such a weak acid.

In the present work we have made an effort to use mixtures of sulfuric acid and tetraethylammonium bisulfate for the calibration of the glass electrode. In earlier work[5] $K_{HA}$ and $K_{2(HA)}$ of sulfuric acid had been determined and, as shown below, it is possible to calculate $a_{H^+}$ in the above mixtures. Unfortunately,

(1) This work was supported by the Directorate of Chemical Sciences, Air Force Office of Scientific Research, under Grant AF-AFOSR-28-63.

(2) J. Badoz-Lambling, J. Desbarres, and J. Tacussel, *Bull. soc. chim. France*, 53 (1962).

(3) (a) J. F. Coetzee and G. Padmanabhan, *J. Phys. Chem.*, 66, 1708 (1962); (b) H. K. Hall, *ibid.*, 60, 63 (1956).

(4) Private communication with Dr. J. F. Coetzee.

(5) I. M. Kolthoff, S. Bruckenstein, and M. K. Chantooni, Jr., *J. Am. Chem. Soc.*, 83, 3927 (1961).

the potential of the glass electrode in such mixtures was found poorly reproducible. After trying several systems, it was found that the glass electrode in mixtures of 2,5-dichlorobenzenesulfonic acid and methanesulfonic acids with their tetraethylammonium salts are well reproducible.

In acetonitrile over-all dissociation of the acids as represented by eq. 1 is sufficiently extensive so as to allow the direct calculation of $K_{2(\text{HA})}$ from spectrophotometric and conductometric measurements.

$$K_{2(\text{HA})} = \frac{[\text{H}^+][\text{HA}_2^-]f^2}{[\text{HA}]^2} \quad (1)$$

$$f = f_\text{H} = f_{\text{HA}_2^-}$$

The hydrogen ion concentration in mixtures of 2,5-dichlorobenzenesulfonic acid and its tetraethylammonium salt was determined spectrophotometrically using o-nitroaniline as indicator. From the results $K_\text{HA}$ could be calculated.

The constant

$$K_{\text{HA}_2^-} = \frac{[\text{HA}_2^-]}{[\text{HA}][\text{A}^-]} \quad (2)$$

for methanesulfonic acid was found from the solubility of the sodium salt in the presence of varying concentrations of free acid.[6] The simple dissociation constant, $K_\text{HA}$, then was found from the relation $K_\text{HA} = K_{2(\text{HA})}/K_{\text{HA}_2^-}$.

An independent determination of $K_{\text{HA}_2^-}$ of the above acids was obtained from analysis of the potentiometric data using the glass electrode in mixtures of the acid and the corresponding tetraethylammonium salt.

Reproducible glass electrode potentials were also obtained in mixtures of o-nitronailine and perchloric acid. In a previous study[5] the formation constant of o-nitroanilinium ion, $K^f_{\text{HI}^+}$, had been determined and found to be $7 \times 10^4$. The hydrogen ion activity in mixtures of the base with perchloric acid was calculated from the simple relation

$$a_{\text{H}^+} = \frac{[\text{HI}^+]f_{\text{HI}^+}}{[\text{I}]K^f_{\text{HI}^+}} \quad (3)$$

using the simple Debye–Hückel expression $-\log f = 1.5\sqrt{\mu}$ at 25°.

After determining the calibration curve of the glass electrode, the $pa_\text{H}$ of a set of buffers composed of mixtures of picric acid and tetrabutylammonium picrate was measured. As picric acid is shown in this paper not to form a stable homoconjugate with the picrate ion, the $pa_\text{H}$ of the mixtures and $K_\text{HPi}$ could be calculated in the classical way. In order to check the reliability of the glass electrode results $K_\text{HPi}$ was also determined spectrophotometrically in mixtures of methanesulfonic acid and its tetraethylammonium salt of suitable pH. As a further check the conductance of mixtures of o-nitroaniline and picric acid yielded a value of $pK_\text{HPi}$.

*Calculation of $a_{\text{H}^+}$ in Mixtures of 2,5-Dichlorobenzenesulfonic and Methanesulfonic Acids and Their Tetraethylammonium Salts.* The relation between the hydrogen ion activity, $a_{\text{H}^+}$, the analytical acid concen-

(6) I. M. Kolthoff and M. K. Chantooni, Jr., *J. Phys. Chem.*, **66**, 1675 (1962).

tration, $C_\text{a}$, the salt concentration, $C_\text{s}$, and the constants $K_\text{HA}$ and $K_{\text{HA}_2^-}$ is derived below.

In a mixture of an undissociated acid, HA, and its tetraalkylammonium salt, which is regarded to be completely dissociated, the electroneutrality condition is

$$C_\text{s} = [\text{A}^-] + [\text{HA}_2^-] \quad (4)$$

Since the acid, HA, is very weak, $[\text{H}^+]$ is negligible. The total acid species is given by eq. 5. The relation

$$C_\text{a} = [\text{HA}] + [\text{HA}_2^-] \quad (5)$$

between the hydrogen ion activity and $C_\text{s}$ (eq. 6) is derived by combining eq. 1, 2, 4, and 5.

$$f^2 C_\text{s} a_{\text{H}^+}{}^2 - f a_{\text{H}^+} K_\text{HA}\{(C_\text{a} + C_\text{s}) + K_{\text{HA}_2^-}(C_\text{s} - C_\text{a})^2\} + K_\text{HA}{}^2 C_\text{a} = 0 \quad (6)$$

At the midpoint of the titration curve, *i.e.*, when $C_\text{a} = C_\text{s}$, eq. 6 reduces to $f a_{\text{H}^+} = K_\text{HA}$, as in the case of simple acid dissociation. The $pa_\text{H}$ at the midpoint, which is dependent only upon $K_\text{HA}$, is independent of $K_{\text{HA}_2^-}$ and $C_\text{a}$.

It is of interest to note that the value of $K_{\text{HA}_2^-}$ can be found from the ratio, $r$, of the experimentally determined values of $a_{\text{H}^+}$ on the neutralization curve to the value $a_{\text{H}^+ 1/2}$ at the half-neutralization point

$$r = \frac{a_\text{H} f}{a_{\text{H}^+ 1/2} f_{1/2}}$$

when the ionic strength is kept constant, $a_{\text{H}^+} = r K_\text{HA}/f$.

Introducing this value of $a_{\text{H}^+}$ into eq. 6, we obtain upon simplification

$$K_{\text{HA}_2^-} = \frac{C_\text{s} r^2 - r(C_\text{a} + C_\text{s}) + C_\text{a}}{r(C_\text{s} - C_\text{a})^2} \quad (7)$$

In order to get most reliable values of $K_{\text{HA}_2^-}$, it is desirable to select points where the ratio $r$ is greater than about 5 or less than about 0.2.

In solutions containing a large excess of acid over salt, the hydrogen ion activity, $a_{\text{H}^+}$, is given by eq. 1, whereas in solutions containing a large excess of salt over acid the hydrogen ion activity, $a_{\text{H}^+}{}'$, is given by

$$a_{\text{H}^+}{}' = \frac{K_\text{HA}}{K_{\text{HA}_2^-}} \frac{[\text{HA}_2^-{}']}{[\text{A}^-{}']^2 f} \quad (8)$$

The primed superscripts refer to solutions containing excess salt. Equation 8 is obtained by combining the expression of the equilibrium constant $K_\text{HA}$ and eq. 2. Dividing eq. 1 by eq. 8 and solving for $K_{\text{HA}_2^-}$, eq. 9 results.

$$K_{\text{HA}_2^-}{}^2 = \frac{a_{\text{H}^+}}{a_{\text{H}^+}{}'} \frac{[\text{HA}_2^-{}'][\text{HA}_2^-]}{[\text{HA}]^2[\text{A}^-{}']^2} =$$

$$\frac{a_{\text{H}^+}}{a_{\text{H}^+}{}'} \frac{C_\text{a}' C_\text{s}}{(C_\text{a} - C_\text{s})^2(C_\text{s}' - C_\text{a}')^2} \quad (9)$$

As a first approximation it is assumed that $[\text{A}^-]$ in eq. 4 and $[\text{HA}]$ in eq. 5 are negligible. If desirable the calculation is repeated introducing the approximate value of $[\text{A}^-]$ in eq. 4 and of $[\text{HA}]$ in eq. 5.

## Experimental Section

*Chemicals. Acetonitrile* was purified and dispensed as described elsewhere.[5]

*Perchloric acid*, 2.16 and 0.489 *M* in anhydrous

acetic acid, was prepared and standardized as described by Coetzee.[7]

*o-Nitroaniline* was the same product as used previously.[5]

*Picric Acid.* Baker's Analyzed product was purified by dissolving 30 g. in 500 ml. of hot Merck reagent grade benzene. After cooling, the solution was transferred to a 1-l. separatory funnel and shaken with 3–10-ml. portions of 12 *M* hydrochloric acid (Du Pont reagent grade) to convert ammonium picrate, a common contaminant, to picric acid. The benzene layer was shaken with 10-ml. portions of water until the aqueous layer gave a negative test for chloride, and then evaporated at 50–60° *in vacuo* until the picric acid crystallized out. The product was recrystallized from benzene and dried *in vacuo* at 70°, m.p. 121°, lit.[8] m.p. 121°.

*Methanesulfonic acid*, Aldrich Chemical Co. (purity not specified), was vacuum distilled at 137° at 0.25 mm. pressure. A fractionating column 1 m. long was packed with glass helices. Only the middle third fraction was used. The purity as determined by titration with sodium hydroxide in aqueous medium was 99.6%.

*2,5-Dichlorobenzenesulfonic acid*, Eastman Kodak White Label, was recrystallized from toluene and dried at 80° *in vacuo* for 4 hr., m.p. 104–105°, lit.[8] m.p. 92–93°. The purity as determined by titration with sodium hydroxide was 98.9%. A 0.1 *M* solution of the acid in water gave a very slight turbidity with barium chloride.

*Tetraethylammonium Methanesulfonate and Tetraethylammonium 2,5-Dichlorobenzenesulfonate.* Aqueous solutions of the acids were neutralized with a 1 *M* aqueous solution of tetraethylammonium hydroxide, which was prepared as previously described.[5] Phenolphthalein served as the external indicator. The solutions were then evaporated to dryness. The methanesulfonate was washed twice with Merck reagent grade anhydrous ether but not recrystallized. The 2,5-dichlorobenzenesulfonate was recrystallized from a 10:1 benzene–acetone mixture. Both salts were dried at 65° *in vacuo* for 6 hr. A 0.1 *M* aqueous solution of both salts gave very slight turbidity with barium chloride.

*Sodium Methanesulfonate.* A cold ethanolic methanesulfonic acid solution was neutralized with aqueous sodium hydroxide. Phenolphthalein served as external indicator. After evaporating the solvent, the salt was recrystallized from ethanol and dried *in vacuo* at 70°.

*Tetrabutylammonium picrate* was supplied by Gracias.[9]

*Potassium Picrate.* Baker's reagent grade picric acid was neutralized in aqueous solution with Merck reagent grade potassium carbonate. The salt was recrystallized from ethanol and dried *in vacuo* at 70°.

*Conductivity Measurements.* The conductivity cell, Industrial Instruments RC-M 15, conductivity bridge, and thermostat have been described previously.[5] All measurements were made at 25 ± 0.1°.

*Solubility Measurements.* The solubility of sodium methanesulfonate in the presence of methanesulfonic acid was determined by conductometric titration with perchloric acid as described elsewhere,[10] while the solubility of potassium picrate in the presence of picric acid was determined by spectrophotometric titration in acetonitrile of the saturated solution at 430 mμ with 0.5 *M* perchloric acid in acetic acid.

*Spectrophotometric Measurements.* A 1.8-cm. cylindrical glass-stoppered Pyrex spectrophotometer cell was used[5] for all spectrophotometric measurements with a Beckman DU spectrophotometer with auxiliary power supply.

*Potentiometric Measurements. Glass Electrode Half-Cell.* A single Beckman 1190-80 general purpose glass electrode was used for all e.m.f. measurements. In aqueous 0.05 *M* potassium acid tartrate and Beckman pH 7.0 buffers, a response of 59 mv./pH unit was found.

When not in use the electrode was kept in water. Just prior to use the glass bulb was rinsed several times with absolute ethanol and dried in a current of dry nitrogen. Next the electrode was soaked in purified acetonitrile for 20 min. and then inserted into the buffer solution in the glass electrode compartments through a hole in a polyethylene cap which fitted tightly over the rim of the electrode compartment. After completion of a series of measurements, the cap and electrode were removed from the cell; the electrode was rinsed with ethanol and dried as above. In general, a stable potential (±2 mv./30 min.) was obtained in 5–10 min.

*Reference Electrode.* A flowing junction silver–0.01 *M* silver nitrate (in AN) reference half-cell, as designed by Kolthoff and Reddy[11] was used. A platinum wire fused into the bottom of the cell was plated with silver from a 0.05 *M* argentocyanide solution in the conventional way. The reference half-cell and its side arm were filled with a 0.010 *M* silver nitrate solution in AN.

*Glass Electrode Cell.* A three-compartment cell similar to the one used by Padmanabhan[3] was employed. The side arm of the external reference electrode half-cell dipped into the 0.1 *M* tetraethylammonium perchlorate solution contained in the small side compartment (10 mm. o.d. tubing) of the three-compartment cell. This compartment was connected to the middle compartment (12-mm. o.d. tubing) by a fine porosity, sintered glass disk. The middle compartment also contained 0.1 *M* tetraethylammonium perchlorate solution which was introduced through a small (4 mm. o.d.) tube attached to the top of this compartment. This tube was plugged after filling the middle compartment. A stopcock located at the bottom of the middle compartment provided drainage after each set of measurements.

In turn the middle compartment was connected to the large (20 mm. o.d.) glass electrode side compartment by another fine porosity, sintered glass disk. The two sintered glass disks at either end of the middle compartment were 3.5 cm. apart.

For e.m.f. measurements 5 ml. of a solution of a known concentration of the tetraethylammonium salt

(7) J. F. Coetzee and I. M. Kolthoff, *J. Am. Chem. Soc.*, 79, 6110 (1957).
(8) "Handbook of Chemistry and Physics," Chemical Rubber Publishing Co., Cleveland, Ohio, 1962.
(9) C. Gracias, Ph.D. Thesis, University of Minnesota, 1961.
(10) I. M. Kolthoff and M. Chantooni, Jr., *J. Am. Chem. Soc.*, 85, 426 (1963).
(11) I. M. Kolthoff and T. B. Reddy, *Inorg. Chem.*, 1, 189 (1962).

of the acid under study was placed into the glass electrode compartment, and increments of pure acid or freshly prepared stock solution in AN of an appropriate concentration were added. For e.m.f. measurements in o-nitroaniline buffers, increments of 0.489 $M$ perchloric acid were added to a solution of known concentration of o-nitroaniline. All e.m.f. measurements were made with a Beckman Model G pH meter using the millivolt scale.

### Results

*Ion Mobilities. Methanesulfonic Acid.* The mobility of the homoconjugate $HA_2^-$ ion was estimated by measuring the conductivity of tetraethylammonium methanesulfonate in a concentration range between $6 \times 10^{-4}$ and $3 \times 10^{-3}$ $M$ in the presence of 0.06 or 0.03 $M$ acid. As shown in the next section no correction needs to be applied for dissociation of the acid or for the presence of $A^-$ ions. At salt concentrations of $1 \times 10^{-3}$ and $3 \times 10^{-3}$ $M$, the mobility of the $HA_2^-$ ion was 65 and 55, respectively. Considering that the size of the methanesulfonate conjugate is close to that of the bisulfate–sulfuric acid homoconjugate we have taken $\lambda_{0_{HA_2^-}}$ equal to 65 which is the $\lambda_0$ value of the bisulfate conjugate.[6]

*2,5-Dichlorobenzenesulfonic Acid.* Using the conductance data of $8.4 \times 10^{-4}$ to $3.3 \times 10^{-3}$ $M$ tetraethylammonium 2,5-dichlorobenzenesulfonate presented in Table I, a graph of $\Lambda$ vs. $\sqrt{C}$ was made. The

**Table I.** Conductance of Salts in Acetonitrile at 25.0°

| o-Nitroanilinium perchlorate[a] in 1.27 × 10⁻² M base | | Tetraethylammonium 2,5-dichloroben- zenesulfonate | | Sodium methanesulfonate | |
|---|---|---|---|---|---|
| $M \times 10^4$ | $\Lambda$ | $M \times 10^3$ | $\Lambda$ | $M \times 10^5$ | $\Lambda$ |
| 1.95 | 161 | 0.84 | 144.8 | 1.34 | 161 |
| 2.93 | 166 | 2.10 | 140.5 | 2.42 | 157 |
| 4.89 | 157 | 5.25 | 130.4 | 4.04 | 153 |
| 9.78 | 154.4 | 14.5 | 124 | 12.1 | 134 |
| 19.5 | 147.8 | 33.4 | 106.5 | $\Lambda_0$ 166 | |
| 29.3 | 138 | $\Lambda_0$ 155 | | | |
| 48.4 | 127 | | | | |
| 96.1 | 110 | | | | |
| $\Lambda_0$ 174.4 | | | | | |

[a] Prepared in solution by adding 0.489 $M$ perchloric acid in acetic acid to $1.27 \times 10^{-2}$ $M$ o-nitroaniline.

Onsager slope was 344, while the calculated slope is 340, indicative of practically complete dissociation of the salt in the above concentration range. Above $5 \times 10^{-3}$ $M$ the salt is incompletely dissociated, the dissociation constant being about $3 \times 10^{-2}$. A value of $\lambda_{0_{A^-}}$ = 69 is obtained, using Walden's[12] value of 86 for $\lambda_{0_{Et_4N^+}}$.

An effort was made to determine the mobility of the homoconjugate ion of the acid by measuring the conductance at various concentrations of the tetraethylammonium salt in presence of a large excess of the acid. Corrections were applied for the dissociated fraction of the acid. However, these corrections are so large that large fluctuations in the mobility of the homoconjugate were found. Since the acid has mo-

(12) P. Walden and E. Birr, *Z. physik. Chem.*, **144**, 269 (1929).

lecular dimensions of the order of magnitude of 3,5-dinitrobenzoic acid,[10] we have estimated $\lambda_0$ of the homoconjugate to be equal to 50.

*o-Nitroanilinium Ion, IH⁺.* From the conductance data in Table I of solutions $1.23 \times 10^{-2}$ $M$ in o-nitroaniline and from $1.95 \times 10^{-4}$ to $9.61 \times 10^{-3}$ $M$ in perchloric acid, $\lambda_{0_{IH^+}}$ = 70.4 using Walden's value of $\lambda_{0_{ClO_4^-}}$ = 104.[12] The calculated Onsager slope was 358 while the observed slope was 654, indicating extensive salt dissociation. In the above solutions and also in similar mixtures used in the calibration of the glass electrode IH·I⁺ formation can be neglected.[13]

Viscosity correction of conductance data, except in Table VIII, were negligible.

*Over-all Dissociation Constant $K_{2(HA)}$ of Methanesulfonic Acid and 2,5-Dichlorobenzenesulfonic Acid. Conductance Method. Methanesulfonic Acid.* The equivalent conductances of $5.93 \times 10^{-3}$ to $1.92 \times 10^{-1}$ $M$ methanesulfonic acid solutions are given in Table II. The equivalent conductance of methane-

**Table II.** Conductance of Acids in Acetonitrile at 25.0°

| Methanesulfonic acid | | 2,5-Dichlorobenzene- sulfonic acid | |
|---|---|---|---|
| $M \times 10^2$ | $\Lambda$ | $M \times 10^3$ | $\Lambda$ |
| 0.59 | 0.14 | 0.248 | 5.13 |
| 1.19 | 0.13 | 0.490 | 4.32 |
| 2.40 | 0.12 | 0.965 | 3.60 |
| 4.80 | 0.12 | 1.42 | 2.57 |
| 9.60 | 0.12 | 2.27 | 3.01 |
| 19.2 | 0.14 | 3.44 | 2.82 |
| | | 4.17 | 2.79 |
| | | 7.15 | 2.70 |
| | | 12.2 | 2.67 |
| | | 27.9 | 3.01 |
| | | 41.9 | 3.25 |
| | | 58.6 | 3.46 |

sulfonic acid is essentially constant over the concentration range studied, hence $[HA_2^-] \gg [A^-]$ and $K_{2(HA)} = \alpha^2 f^2$ (*cf.* eq. 1), where $\alpha = \Lambda/\Lambda_0$ = degree of dissociation. Taking $\lambda_{0_{H^+}}$ = 80[7] and $\lambda_{0_{HA_2^-}}$ for the methanesulfonate homoconjugate, a value of $pK_{2(HA)}$ equal to $6.1 \pm 0.1$ is obtained.

*2,5-Dichlorobenzenesulfonic Acid.* The equivalent conductances of $2.48 \times 10^{-4}$ to $5.86 \times 10^{-2}$ $M$ dichlorobenzenesulfonic acid solutions are presented in Table II. In these solutions the concentration of $A^-$ cannot be neglected as compared to that of $HA_2^-$. A plot of $\Lambda\sqrt{C_a[C_a + 1/K_{HA_2^-}]}$ vs. $C_a$[14] yields a straight line with an intercept of $5.2 \times 10^{-3}$ and a slope of 2.30. From these values and from $\lambda_{0_{A^-}}$ = 69 and $\lambda_{0_{HA_2^-}}$ = 50, values of $K_{HA_2^-}$ equal to $5 \pm 1 \times 10^2$ and of $pK_{HA}$ equal to 6.23 are found. Thus $pK_{2(HA)}$ = 3.54.

*Spectrophotometric Method.* The hydrogen ion activity in mixtures of the acids with their tetraethylammonium salts was determined spectrophotometrically using o-nitroaniline as indicator and measuring the absorption of the yellow form at 410 m$\mu$. A value of

(13) J. F. Coetzee, G. Padmanabhan, and G. Cunningham, *Talanta*, **11**, 93 (1964).
(14) C. M. French and I. G. Roe, *Trans. Faraday Soc.*, **49**, 314 (1953).

Table III. Indicator Ratio of o-Nitroaniline in Methanesulfonic Acid–Tetraethylammonium Methanesulfonate Solutions

| $C_s$, $M \times 10^5$ | $A_{410}$ | [I], $M \times 10^5$ | [HI+], $M \times 10^5$ | [HI+]/[I] | [H+], $M \times 10^5$ | [HA2-], $M \times 10^5$ | $f^2$ | $K_{2(HA)} \times 10^7$ |
|---|---|---|---|---|---|---|---|---|
| | | | $C_a = 0.0322\ M$, [HA] = 0.032 $M$ | | | | | |
| 0 | 0.282 | 2.82 | 3.46 | 1.23 | 1.7 | ... | ... | ... |
| 2.38 | 0.343 | 3.43 | 2.85 | 0.84 | 1.2 | 6.4 | 0.99 | 7 |
| 4.75 | 0.384 | 3.84 | 2.44 | 0.63 | 0.90 | 8.1 | 0.99 | 7 |
| 9.48 | 0.454 | 4.54 | 1.74 | 0.38 | 0.54 | 11.8 | 0.98 | 6 |
| 14.2 | 0.489 | 4.89 | 1.39 | 0.28 | 0.40 | 16.0 | 0.96 | 6 |
| 21.3 | 0.524 | 5.24 | 1.04 | 0.20 | 0.28 | 23 | 0.92 | 6 |
| 35.6 | 0.558 | 5.58 | 0.70 | 0.125 | 0.18 | 37 | 0.90 | 6 |
| 59.3 | 0.576 | 5.76 | 0.52 | 0.090 | 0.13 | 60 | 0.85 | 7 |
| | | | $C_a = 0.0682\ M$, [HA] = 0.068 $M$ | | | | | |
| 0 | 0.083 | 0.83 | 4.24 | 5.11 | 7.2 | ... | ... | |
| 9.54 | 0.183 | 1.83 | 3.24 | 1.77 | 2.5 | 15 | 0.98 | 8 |
| 17.9 | 0.231 | 2.31 | 2.76 | 1.20 | 1.7 | 22 | 0.95 | 8 |
| 23.8 | 0.259 | 2.59 | 2.48 | 0.96 | 1.3 | 28 | 0.93 | 8 |
| 35.7 | 0.299 | 2.99 | 2.08 | 0.70 | 1.0 | 38 | 0.90 | 8 |
| 59.5 | 0.332 | 3.32 | 1.75 | 0.53 | 0.74 | 62 | 0.85 | 9 |
| 83.6 | 0.366 | 3.66 | 1.41 | 0.39 | 0.54 | 85 | 0.82 | 8 |
| 143 | 0.417 | 4.17 | 0.90 | 0.22 | 0.30 | 143 | 0.76 | 7 |
| | | | | | | | | Av. 7 × 10⁻⁷ |

$K^f_{HI^+}$ equal to 7 × 10⁴ ⁵ was used in eq. 3 to calculate the hydrogen ion activity.

*Methanesulfonic Acid.* Since the acid was in large excess in all the mixtures [A⁻] could be neglected and

$$[HA_2^-] = C_s + [H^+] + [HI^+]$$

$$[HA] = C_a - [HA_2^-] \sim C_a$$

where $C_a$ and $C_s$ represent the analytical acid and salt concentrations, respectively. Equation 1 was used to calculate $K_{2(HA)}$. From the data in Table III an average value of $pK_{2(HA)}$ of 6.1₂ was found, as compared to the value of 6.1 derived from the conductometric data.

*2,5-Dichlorobenzenesulfonic Acid.* Experimental data and calculated values of [H⁺] and $K_{HA}$ are presented in Table IV. In the mixtures, [A⁻] is not negligible as

Table IV. Indicator Ratio of o-Nitroaniline in Mixtures of 2,5-Dichlorobenzenesulfonic Acid and Its Tetraethylammonium Salt

| [HA], $M \times 10^3$ | $C_s$, $M \times 10^4$ | $A_{410}$ | [I], $M \times 10^5$ | [HI+]/[I] | [H+], $M \times 10^5$ | $K_{HA} \times 10^7$ |
|---|---|---|---|---|---|---|
| | | o-Nitroaniline, 3.3 × 10⁻⁵ $M$ | | | | |
| 1.30 | 0.135 | 0.132 | 1.3 | 1.49 | 2.1 | 6 |
| 1.30 | 0.404 | 0.159 | 1.6 | 1.06 | 1.5 | 5 |
| 1.30 | 0.674 | 0.178 | 1.8 | 0.80 | 1.1 | 5 |
| 1.30 | 1.08 | 0.202 | 2.0 | 0.62 | 0.86 | 6 |
| 1.28 | 1.90 | 0.231 | 2.3 | 0.40 | 0.66 | 7 |
| 1.26 | 2.72 | 0.249 | 2.5 | 0.30 | 0.42 | .. |
| 1.24 | 5.40 | 0.265 | 2.8 | 0.19 | 0.26 | .. |
| | | o-Nitroaniline, 4.0 × 10⁻⁵ $M$ | | | | |
| 2.53 | 0.261 | 0.131 | 1.3 | 2.08 | 2.9 | 5 |
| 2.53 | 0.522 | 0.145 | 1.5 | 1.67 | 2.3 | 5 |
| 2.52 | 1.04 | 0.173 | 1.7 | 1.35 | 1.9 | 6 |
| 2.52 | 1.81 | 0.201 | 2.0 | 1.00 | 1.4 | 6 |
| 2.50 | 3.10 | 0.235 | 2.4 | 0.67 | 0.94 | 7 |
| | | | | | | Av. 6 × 10⁻⁷ |

compared to [HA₂⁻]. From the electroneutrality rule we have

$$[Et_4N^+] + [HI^+] + [H^+] = [A^-] + [HA_2^-] \quad (10)$$

Substituting eq. 2 and 3 into eq. 10, eq. 11 results.

$$[Et_4N^+] + [H^+]\{1 + K^f_{HI}\cdot[I]\} = \frac{K_{HA}[HA]}{[H^+]}\{1 + K_{HA_2}\cdot[HA]\} \quad (11)$$

The tetraethylammonium salt has been found to be practically completely dissociated to at least 5 × 10⁻³ $M$. Under these conditions, [Et₄N⁺] = $C_s$, the analytical salt concentration in eq. 11. Because of repression of dissociation of the acid by the salt, the analytical and equilibrium concentration of the acid can be considered equal; hence $C_a$ = [HA].

Finally, $K_{HA}$ is calculated from eq. 11, knowing $C_s$, [H⁺], and [HA]$K^f_{HI}$, and using the value of $K_{HA_2}^-$ of 5 × 10² derived from conductometric data we find $pK_{HA}$ = 6.2₄ as compared to 6.2₃ derived from conductometric data. When $K_{HA_2}^-$ is taken equal to 4.0 × 10² instead of 5 × 10², a value of $pK_{HA}$ equal to 6.2₂ is found.

*Determination of $K_{HA_2}^-$ of Methanesulfonic Acid from Solubility Data.* The solubility of sodium methanesulfonate both in the absence and presence of methanesulfonic acid and the conductivities of the saturated solutions are reported in Table V. The solubility was determined by conductometric titration of 1 to 5 ml. of the saturated solution with 0.489 $M$ perchloric acid.[10] The solubility of sodium methanesulfonate in absence of methanesulfonic acid was found equal to 1.2 × 10⁻⁴ $M$. From the specific conductance, $L$, of the saturated solution, 1.85 × 10⁻⁵ ohm⁻¹ cm.⁻¹ (Table V), and the value of 166 for $\Lambda_{0_{NaA}}$, as given in Table I, $K_{sp}$ is calculated to be 0.9 × 10⁻⁸, $K^d_{NaA}$ = 3.6 × 10⁻⁴, and [NaA] = 2.5 × 10⁻⁵ $M$.

In the presence of methanesulfonic acid $K_{HA_2}^-$ is calculated from the solubility, $s$, using the relation $s$ = [Na⁺] + [NaA] + [NaHA₂] = [Na⁺] + 2.5 × 10⁻⁵ + [NaHA₂], and [A⁻] = $K_{sp}$/[Na⁺] and $f_{Na^+}$ = $f_A$ = 1.

At solubilities greater than 0.001 $M$ it appeared

**Table V.** Solubility and Conductance of Saturated Solutions of Sodium Methanesulfonate in the Presence of Methanesulfonic Acid

| $M_{CH_3SO_3H}$ | Solubility, $M \times 10^4$ | Specific conductance, $L \times 10^5$ | $\Lambda_{NaHA_2}$ calcd. (Onsager) | $[Na^+]$, $M \times 10^4$ | $[HA]$, $M \times 10^3$ | $f^2$ | $K_{HA_2^-} \times 10^{-3}$ |
|---|---|---|---|---|---|---|---|
| 0 | 1.2 | 1.85 | | 1.0 | 0 | 0.93 | 7 |
| $3.15 \times 10^{-3}$ | 4.5 | 5.69 | 128 | 4.4 | 2.7 | 0.88 | 6 |
| $1.24 \times 10^{-2}$ | 10.5 | 12.3 | 125 | 10 | 11.5 | 0.81 | 7 |
| $2.48 \times 10^{-2}$ | 16.1 | 18.2 | 123 | 15 | 24 | 0.76 | 8 |
| $4.96 \times 10^{-2}$ | 30.1 | 28.2 | 120 | 23 | 47 | 0.71 | 9 |
| | | | | | | | Av. $7 \times 10^3$ |

necessary to correct for undissociated $NaHA_2$ which was done by calculating $\alpha = \Lambda_{exptl}/\Lambda_{calcd}$, in which $\Lambda_{calcd}$ was derived with the aid of the Onsager equation, taking $\lambda_{0_{Na^+}} = 70$ and $\lambda_{0_{HA_2^-}} = 65$. Values of $\Lambda_{calcd}$ are introduced into Table V. An average value of $7 \pm 1 \times 10^3$ for $K_{HA_2^-}$ was obtained.

The salt $NaHA_2$ is a fairly strong electrolyte, its dissociation constant being estimated to be $1.5 \pm 0.5 \times 10^{-2}$.

*Picric Acid.* The value of $K_{HA_2^-}$ of picric acid was estimated from the increase in solubility of potassium picrate in the presence of picric acid. All solubility determinations were made by titrating spectrophotometrically the picrate plus the homoconjugate anion at 430 m$\mu$ with perchloric acid.

From the value of $6.7 \times 10^{-3}$ reported by Walden[12] for the dissociation constant of potassium picrate and the solubility in the absence of picric acid found equal to $1.19 \times 10^{-2}$ $M$ (Table VI), the solubility product is found to be $2.8 \times 10^{-5}$.

**Table VI.** Solubility of Potassium Picrate in the Presence of Picric Acid

| $[HPi]$, $M$ | Solubility,[a] $M \times 10^2$ | $f^2$ | $K_{HA_2^-}$ |
|---|---|---|---|
| 0 | 1.19 | 0.52 | .. |
| 0.201 | 1.30 | 0.52 | 2 |
| 0.292 | 1.35 | 0.51 | 2 |
| 0.493 | 1.46 | 0.51 | 3 |
| | | | Av. 2 |

[a] $K_{sp} = 2.8 \times 10^{-5}$, $K^d_{KPi} = 6.7 \times 10^{-3}$.

The solubility data of potassium picrate in the presence of picric acid given in Table VI together with the values of $K_{sp}$ and $K^d_{KPi}$ yield a value of the order of two for $K_{HA_2^-}$.

*Estimation of $pK_{HA}$ of Picric Acid. $pK_{HPi} - pK_{HA}$. Spectrophotometric.* The spectrophotometrically determined ratio $[HPi]/[Pi^-]$ in mixtures of $4.24 \times 10^{-4}$ to $2.86 \times 10^{-3}$ $M$ methanesulfonic acid and $3.00 \times 10^{-3}$ $M$ tetraethylammonium methanesulfonate using picrate as indicator was determined. The indicator was added in the form of a mixture of picric acid $(HPi)$ and tetrabutylammonium picrate $(Pi^-)$, the analytical concentration of HPi in the mixtures being $1.99 \times 10^{-5}$ $M$ and that of $Pi^-$, $1.07 \times 10^{-5}$ $M$. Using the values $pK_{2(HA)} = 6.1$ and $K_{HA_2^-} = 7 \times 10^3$ of methanesulfonic acid, the hydrogen ion activity in the above solutions was calculated from eq. 6 and listed in Table VII. The dissociation constant $K_{HPi}$ was

calculated from the values of $a_{H^+}$ and $[HPi]/[Pi^-]$. An average value of $pK_{HPi}$ equal to 11.1 was obtained.

**Table VII.** Reaction between Methanesulfonic Acid and Tetra-*n*-butylammonium Picrate[a]

| $M_{CH_3SO_3H} \times 10^4$ | $A_{440}$ | $[HPi]$, $M \times 10^5$ | $[Pi^-]$, $M \times 10^5$ | $[HPi]/[Pi^-]$ | $pa_H$[b] | $pK_{HPi}$ |
|---|---|---|---|---|---|---|
| 4.24 | 0.443 | 0.28 | 2.78 | 0.10 | 11.97 | 11.1 |
| 6.35 | 0.406 | 0.51 | 2.55 | 0.20 | 11.73 | 11.1 |
| 8.47 | 0.372 | 0.72 | 2.34 | 0.308 | 11.49 | 11.1 |
| 10.6 | 0.332 | 0.98 | 2.08 | 0.47 | 11.35 | 11.1 |
| 13.2 | 0.279 | 1.27 | 1.79 | 0.71 | 11.16 | 11.2 |
| 15.9 | 0.229 | 1.63 | 1.44 | 1.14 | 10.98 | 11.1 |
| 17.0 | 0.206 | 1.77 | 1.29 | 1.37 | 10.90 | 11.1 |
| 19.6 | 0.163 | 2.04 | 1.02 | 2.00 | 10.71 | 11.1 |
| 22.8 | 0.098 | 2.44 | 0.63 | 3.89 | 10.44$_5$ | 11.1 |
| 28.6 | 0.055 | 2.71 | 0.35 | 7.71 | 10.21 | 11.2 |
| | | | | | | Av. 11.1 |

[a] Indicator: $1.99 \times 10^{-5}$ $M$ HPi, $1.07 \times 10^{-5}$ $M$ Bu$_4$NPi; $C_s = 3.00 \times 10^{-3}$ $M$ tetraethylammonium methanesulfonate. [b] Calculated using $pK_{2(HA)} = 6.1$, $K_{HA_2^-} = 7 \times 10^3$.

*Conductometric.* In Table VIII are presented conductance data of mixtures containing 0.0915 to 0.537 $M$ and 0.102 to 0.905 $M$ *o*-nitroaniline with 0.0371 and 0.0717 $M$ picric acid, respectively. From the mobility of 78[12] for the picrate ion and 70.4 for the *o*-nitroanilinium ion, the value of $[HI^+]$, taken equal to that of $[Pi^-]$, is calculated. This is permissible because $[H^+]$ is negligible.

**Table VIII.** Conductance of Mixtures of Picric Acid and *o*-Nitroaniline in AN

| $[o\text{-}NA]$, $M$ | Specific conductance $\times 10^5$ | Viscosity | $[HI^+] = [Pi^-]$, $M \times 10^4$ | $K^t_{HI^+K_{HPI}} \times 10^6$ |
|---|---|---|---|---|
| | | 0.0371 $M$ HPi | | |
| 0.0915 | 0.665 | 0.348 | 0.45 | 0.6 |
| 0.195 | 0.993 | 0.354 | 0.67 | 0.6 |
| 0.328 | 1.40 | 0.360 | 0.94 | 0.7 |
| 0.537 | 1.89 | 0.368 | 1.28 | 0.8 |
| | | 0.0717 $M$ HPi | | |
| 0.102 | 1.30 | 0.352 | 0.88 | 1.0 |
| 0.218 | 1.74 | 0.356 | 1.18 | 0.9 |
| 0.409 | 2.39 | 0.336 | 1.61 | 0.9 |
| 0.593 | 2.89 | 0.376 | 1.96 | 0.9 |
| 0.905 | 3.58 | 0.390 | 2.42 | 0.9 |
| | | | | Av. $8 \times 10^{-7}$ |

The equilibrium constant $K$ is

$$K = \frac{a_{HI^+} a_{Pi^-}}{[I][HPi]} = K^t_{HI^+} K_{HPi}$$

Correcting for viscosity and activity coefficients, calculated values of $K^f_{HI^+}K_{HPi}$ are given in Table VIII. Using the known value[5] of $K^f_{HI^+} = 7.1 \times 10^4$, the calculated average value of $pK_{HPi}$ is 10.9₀.

*Calibration of the Glass Electrode. Mixtures of Methanesulfonic Acid and 2,5-Dichlorobenzenesulfonic Acid with Their Tetraethylammonium Salts.* E.m.f. data obtained with the glass electrode in these mixtures are reported in Tables IX and X. Values of $K_{HA_2}$-

**Table IX.** Glass Electrode Potentials in Methanesulfonic Acid-Tetraethylammonium Methanesulfonate Mixtures[a]

| $C_s$, $M \times 10^3$ | $C_a$, $M \times 10^2$ | $E$, mv. | $K_{HA_2}$- $\times 10^{-3}$ | $f$ | $pa_H{}^b$ (calcd.) |
|---|---|---|---|---|---|
| 2.38 | 2.71 | +435 | 3 | 0.76 | 6.74 |
| 2.38 | 4.66 | 467 | 4 | 0.76 | 6.16 |
| 2.38 | 6.50 | 488 | 4 | 0.76 | 5.86 |
| 3.00 | 0.106 | 160 | 7 | 0.83 | 11.36 |
| 3.00 | 0.159 | 182 | 7 | 0.83 | 10.97 |
| 3.00 | 0.196 | 200 | 6 | 0.83 | 10.71 |
| 5.95 | 3.90 | 432 | 4 | 0.76 | 6.76 |
| 5.95 | 5.40 | 456 | 6 | 0.76 | 6.43 |
| 5.95 | 8.40 | 490 | 7 | 0.76 | 6.01 |
| 14.5 | 0.60 | 134 | 6 | 0.66 | 11.76 |
| 14.5 | 0.90 | 167 | 5 | 0.66 | 11.23 |
| 14.5 | 1.20 | 207 | 9 | 0.66 | 10.57 |
| 14.5 | 1.80 | 296 | 6 | 0.66 | 8.75 |
| 14.5 | 2.45 | 338 | 5 | 0.66 | 8.13 |
| 14.5 | 4.10 | 390 | 6 | 0.66 | 7.30 |
| 14.5 | 6.50 | 431 | 8 | 0.66 | 6.74 |

[a] Reference electrode: 0.010 $M$ AgNO₃| Ag in AN. [b] Constants used in calculation of $pa_H$ in eq. 6; $pK_{HA} = 10.0$, $pK_{HA_2}- = 3.78$. Half-neutralization potential, +245 mv.

**Table X.** Glass Electrode Potentials in 2,5-Dichlorobenzenesulfonic Acid-Tetraethylammonium 2,5-Dichlorobenzenesulfonate Mixtures

| $C_s$, $M \times 10^3$ | $C_a$, $M \times 10^3$ | $E$, mv. | $K_{HA_2}{}^{-a}$ $\times 10^2$ | $pa_H{}^b$ (calcd.) |
|---|---|---|---|---|
| 2.71 | 0.11 | +345 | 4 | 7.85 |
| 2.71 | 0.22 | 365 | 4 | 7.52 |
| 2.68 | 0.45 | 384 | 4 | 7.17 |
| 2.66 | 1.01 | 412 | 4 | 6.58 |
| 2.64 | 1.58 | 425 | ... | 6.51 |
| 2.60 | 2.16 | 439 | ... | 6.26 |
| 2.58 | 2.68 | 449 | ... | 6.19 |
| 2.54 | 3.67 | 465 | ... | 5.61 |
| 2.47 | 5.11 | 481 | 4 | 5.58 |
| 2.30 | 8.55 | 512 | 4 | 5.11 |
| 2.12 | 12.2 | 533 | 4 | 4.74 |
| 1.81 | 18.7 | 557 | 3 | 4.27 |
| | | | Av. 4 | |

[a] Half-neutralization potential, +448 mv. [b] Constants used in calculation of $pa_H$ using eq. 6: $pK_{HA} = 6.2_3$, $K_{HA_2}- = 4 \times 10^2$.

were calculated using eq. 7 and 9, respectively. In these calculations a 59.1-mv. change in potential per $pa_H$ unit was taken. Values of the half-neutralization potentials and $K_{HA_2}$- are: methanesulfonic acid, +245 mv. and 6 × 10³; 2,5-dichlorobenzenesulfonic acid, +448 mv. and 4 × 10², respectively. These values of $K_{HA_2}$- compare favorably with the value of 7 × 10³ derived from solubility measurements of sodium methanesulfonate in the presence of free acid, and of 5 × 10² derived from the conductometric data in solutions of 2,5-dichlorobenzenesulfonic acid. The

calculated $pa_H$ values of the mixtures are given in the last column of Tables IX and X.

*Mixtures of o-Nitroaniline with Perchloric Acid.* The results are presented in Table XI.

**Table XI.** Glass Electrode Potentials in Mixtures of o-Nitroaniline, I, and Perchloric Acid[a]

| [I], $M \times 10^3$ | [HI⁺], $M \times 10^3$ | Log [HI⁺]/ [I] | $E$, mv. | $f$ | $pa_H{}^b$ (calcd.) |
|---|---|---|---|---|---|
| Total o-Nitroaniline Concentration = [I] + [HI⁺] = 3.40 × 10⁻³ $M$ | | | | | |
| 3.31 | 0.091 | −1.56 | +432 | 0.85 | 6.48 |
| 3.22 | 0.181 | −1.25 | 458 | 0.84 | 6.17 |
| 3.04 | 0.362 | −0.92 | 478 | 0.84 | 5.85 |
| 2.49 | 0.906 | −0.44 | 510 | 0.81 | 5.38 |
| 1.86 | 1.54 | −0.08 | 530 | 0.80 | 5.03 |
| 1.14 | 2.26 | +0.29₆ | 553 | 0.79 | 4.66 |
| 0.50 | 2.90 | +0.76 | 572 | 0.78 | 4.20 |
| Total o-Nitroaniline Concentration 1.20 × 10⁻² $M$ | | | | | |
| 11.8 | 0.191 | −1.79 | +428 | 0.85 | 6.71 |
| 11.6 | 0.382 | −1.48 | 446 | 0.83 | 6.41 |
| 11.2 | 0.764 | −1.17 | 467 | 0.82 | 6.10 |
| 10.6 | 1.43 | −0.87 | 484 | 0.80 | 5.82 |
| 9.8 | 2.20 | −0.65 | 498 | 0.79 | 5.60 |
| 9.1 | 2.86 | −0.50 | 507 | 0.77 | 5.46 |
| 7.7 | 4.30 | −0.25 | 523 | 0.75 | 5.22 |
| 5.3 | 6.69 | +0.10 | 545 | 0.72 | 4.89 |

[a] All solutions 2 × 10⁻³ $M$ in Et₄NClO₄. [b] $pK^f_{HI^+} = -4.85$; half-neutralization point +536.

Figure 1 gives the calibration of our glass electrode, which is a plot of $pa_H$ values *vs.* the e.m.f. in millivolts. The best straight line, with a slope of 59.1 mv., has been drawn using the data presented in Tables IX-XI. The equation for the calculation of $pa_H$ from glass electrode measurements is $pa_H = (821 - E)/59.1$, where $E$ is given in millivolts. This equation refers to our glass electrode.

Quite generally, we would recommend mixtures of picric acid with its tetrabutylammonium salt for calibration purposes of the glass electrode in AN. These mixtures are well buffered, homoconjugation can be neglected, and the $pa_H$ is calculated using the simple classical equation.

*The Dissociation Constant of Picric Acid from Glass Electrode Measurements.* Data are given in Table XII

**Table XII.** Glass Electrode Potentials in Picric Acid-Tetra-n-butylammonium Picrate Buffers

| [HPi], $M \times 10^4$ | [Bu₄NPi], $M \times 10^3$ | $E$, mv. | $pa_H{}^a$ (calcd.) | Log $f$ | $pK_{HPi}$ |
|---|---|---|---|---|---|
| 0.949 | 1.93 | +098 | 12.2 | −0.06₆ | 11.0 |
| 2.37 | 1.91 | 122 | 11.8 | −0.06₆ | 11.0 |
| 4.64 | 1.90 | 139 | 11.5₄ | −0.06₆ | 11.0 |
| 9.20 | 1.86 | 157 | 11.2₄ | 0.06₅ | 11.0 |
| 21.7 | 1.76 | 183 | 10.8 | 0.06₃ | 11.0 |
| 39.5 | 1.61 | 202 | 10.4₄ | 0.06₀ | 10.9 |
| 67.6 | 1.38 | 218 | 10.2 | 0.05₆ | 11.0 |
| 4.72 | 7.72 | 108 | 12.1 | −0.13 | 10.9 |
| 9.25 | 7.45 | 125 | 11.8 | −0.13 | 11.0 |
| 21.8 | 7.05 | 152 | 11.3 | 0.13 | 10.9 |
| 79.0 | 5.15 | 189 | 10.7 | −0.11 | 11.0 |
| 302 | 5.15 | 227 | 10.1 | −0.11 | 10.9 |
| 860 | 5.15 | 256 | 9.6 | −0.11 | 10.9 |
| | | | | Av. | 11.0 |

[a] $pa_H$ calculated from the equation $pa_H = (821 - E)/59.1$.

with the calculated values of $pK_{HPi}$. The average is 11.0.

## Discussion

Many authors have reported half-neutralization potentials (h.n.p.) in potentiometric titration of uncharged weak acids with tetraalkylammonium hydroxide in nonaqueous solvents.[15-18] In several instances the difference in h.n.p. of various acids in the particular solvent has been compared with the difference of $pK_{HA}$ of these acids in water.

In solvents of not too low dielectric constant and at small ionic strength, the tetraalkylammonium salts may be considered completely dissociated, while activity coefficients are taken equal to unity. Furthermore, the acid and salts are considered monomeric. Under these conditions at the h.n.p., $fa_{H^+} = K_{HA}$ as follows from eq. 6. This same relation is obtained simply by equating eq. 4 and 5. At the midpoint $C_a = C_s$ and $[HA] = [A^-]$.

$$K_{HA} = a_{H^+}f[A^-]/[HA] = fa_{H^+}$$

Equation 6 remains the same when $K_{HA_2^-}$ in eq. 6 is multiplied by a factor $g$ while $C_a$ and $C_s$ are divided by the same factor. According to this modified expression the shape of the neutralization curve simply depends upon the product $bK_{HA_2^-}$, $b$ being equal to $(C_a + C_s)$ and being kept constant during the titration. Figure 2 illustrates this dependence at various values of $bK_{HA_2^-}$, the activity coefficient considered to be constant.

In order to eliminate the effects of alcohol or dioxane present in solutions of tetraalkylammonium hydroxide and of water formed in the titration, the curves in Figure 2 give $pa_H$ values of mixtures of an acid and its tetraalkylammonium salt.

The titration curves in Figure 2 are symmetrical about the midpoint. This is seen by setting $[H^+]$ equal to $K_{HA}$ multiplied by a factor $h$ in eq. 6. Upon interchanging $C_a$ and $C_s$, the resulting expression is the same as when $[H^+]$ is set equal to $K_{HA}/h$.

When $K_{HA_2^-}$ is zero, the titration curve is identical with that of a weak acid with a strong base in water. When $K_{HA_2^-}$ is greater than zero, the shape of the curves becomes dependent on the concentration of acid. For example, with $K_{HA_2^-}$ equal to $10^4$ curve 1 in Figure 2 represents the titration curve of 0.1 $M$ acid, curve 2 of 0.01 $M$ acid, curve 3 of 0.001 $M$ acid, and curve 4 of 0.0001 $M$ acid.

It is also of interest to consider the buffer capacity of mixtures of acids and their salts.

In general, the buffer capacity, $\beta$, at a given point on the titration curve is defined as

$$\beta = -(2.303)[H^+]\frac{dC_s}{d[H^+]} \qquad (12)$$

For simplicity, it is assumed that $[HA_2^-] >> [A^-]$ at the beginning of the titration curve, i.e., the acid dissociates according to $2HA \rightleftharpoons H^+ + HA_2^-$ (cf. eq. 1). Neglecting $[A^-]$ the electroneutrality condition is

$$C_s + [H^+] = [HA_2^-] \qquad (13)$$

(15) G. Harlow and G. Wyld, *Anal. Chem.*, **30**, 69 (1958).
(16) J. Fritz and S. Yamamura, *ibid.*, **29**, 1079 (1957).
(17) R. Miron and D. Hercules, *ibid.*, **33**, 1770 (1961).
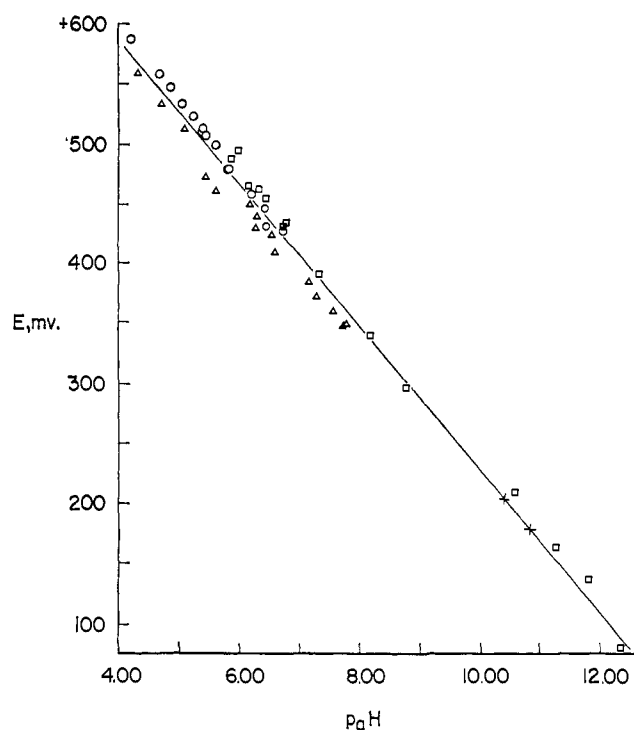(18) L. Chatten and L. Harris, *ibid.*, **34**, 1495 (1962).

Figure 1. Glass electrode calibration curve in acetonitrile: O, o-nitroaniline; △, 2,5-dichlorobenzenesulfonic acid; □, methanesulfonic acid (slope = 59.1).

Combining eq. 1 and 13, eq. 14 is obtained.

$$[H^+]^2 + C_s[H^+] - a^2K_{HA}K_{HA_2^-} = 0 \qquad (14)$$

$$f_{H^+} = f_{HA_2^-} = 1$$

Differentiating (14) implicitly, solving for $dC_s/d[H^+]$, and substituting the resulting expression into (12), eq. 15 results.

$$\beta = 2.303\{C_s + 2[H^+]\} \qquad (15)$$

The formulation of a general relation describing the buffer capacity in a mixture of the acid HA and its tetraalkylammonium salt is presented below. This relation (eq. 16) is applicable to most of the titration curve except at the very beginning when $[H^+] > C_s$ and close to 100% neutralization. Setting $b = C_a + C_s$ and $f = 1$ in eq. 6, eq. 6a results. Differentiating

$$C_s[H^+]^2 - [H^+]K_{HA}\{b + K_{HA_2^-}(2C_s - b)^2\} + K^2_{HA}(b - C_s) = 0 \qquad (6a)$$

eq. 6a with respect to $[H^+]$, solving for $dC_s/d[H^+]$, and substituting the resulting expression into eq. 12, eq. 16 results.

$$\beta = -2.303 \times$$
$$\left[\frac{K_{HA}K_{HA_2^-} - \{b - 2C_s\}^2 + K_{HA}b - 2C_s[H^+]}{[H^+] + 4K_{HA}K_{HA_2^-}\{b - 2C_s\} - K_{HA}^2/[H^+]}\right] \qquad (16)$$

Plots of buffer capacity vs. calculated pH (eq. 6) at various values of $K_{HA_2^-}$ taking $b = 0.100$ are constructed with the aid of eq. 16 and presented in Figure 3. From this figure it is evident that the buffer capacity has a minimum at the half-neutralization point when $bK_{HA_2^-}$ is greater than about 10, whereas it has a maximum at this point when $K_{HA_2^-}$ is zero, as is the case in water or in the titration of an acid with $K_{HA_2^-} = 0$ in AN.

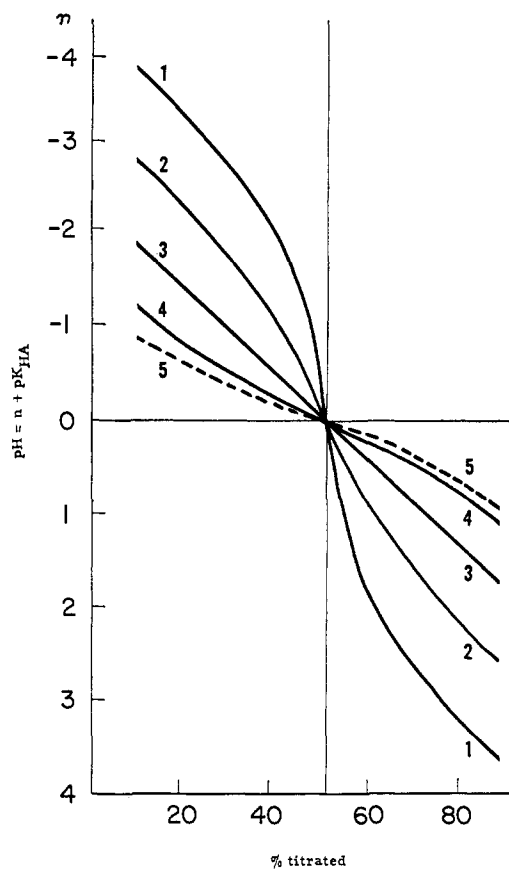Figure 2. Calculated potentiometric titration curve of HA with Et₄NOH for various values of $bK_{HA_2^-}$: curve 1, $bK_{HA_2^-} = 10^3$; curve 2, $10^2$; curve 3, $10^1$; curve 4, 1; curve 5, simple acid dissociation, i.e., $K_{HA_2^-} = 0$.



Figure 3. Calculated buffer capacity plots as a function of pH and $bK_{HA_2^-}$ in mixtures of HA and Et₄NA: A, simple dissociation; B, $bK_{HA_2^-} = 10^3$; C, $10^2$; D, 10; E, 1 ($b = 1 \times 10^{-1}$).

At the midpoint of the titration curve $C_a = C_s = b/2$ and pH = p$K_{HA}$. Equation 16 then takes on the indeterminate value 0/0. The numerator and denominator of eq. 16 are separately differentiated implicitly with respect to [H⁺], and the quotient formed is equated to $dC_s/d[H^+]$. Setting $C_a = C_s = b/2$ and simplifying, eq. 17 results

$$\beta_{1/2} = -\frac{2.303}{4}\left\{\frac{1 - \sqrt{1 + 2bK_{HA_2^-}}}{K_{HA_2^-}}\right\} \quad (17)$$

the subscript ¹/₂ referring to the midpoint. When $bK_{HA_2^-} \gg 1$

$$\beta_{1/2} = \frac{2.303}{2}\sqrt{\frac{b}{2K_{HA_2^-}}} \quad (17a)$$

When the product $bK_{HA_2^-}$ is of the order of 10 or greater, $K_{HA_2^-}$ can advantageously be found from the potentiometric titration curve (eq. 7 or 9). Large differences in potential are encountered between the midpoint and suitable points on the titration curve where excess acid or salt is present. Hence an uncertainty in the location of the midpoint of the order of ±5 mv., in part as a consequence of poor buffering in the region of the midpoint, does not produce large errors in $K_{HA_2^-}$. When $K_{HA_2^-}$ is greater than about $10^5$, the solubility method is unreliable because of the great uncertainty with which the low equilibrium acid con-
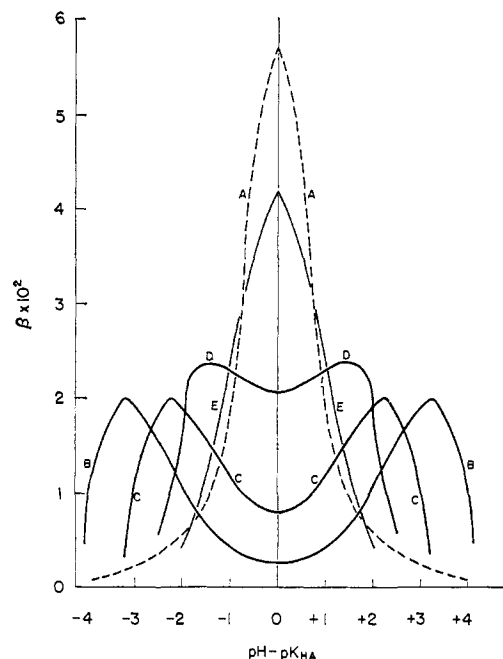
centration can be found in the saturated solutions of the salt in the presence of acid.

On the other hand, when $bK_{HA_2^-}$ is of the order of 100 or less, the solubility method is preferred over the potentiometric method in the estimation of $K_{HA_2^-}$. Quite generally, the solubility method is preferred when $K_{HA_2^-}$ is equal to or smaller than $10^3$. The solubility and potentiometric methods have been used (Experimental Section) in the determination of $K_{HA_2^-}$ of methanesulfonic acid, and the resulting values were in close agreement.

Several authors have estimated the dissociation constant $K_{HPi}$ in AN from measurements in unbuffered solutions of picric acid. The following values have been reported: conductometrically, 6.36,[19] 5.6,[20] 8.9[5]; spectrophotometrically, 4.3,[21] 4.0,[22] 8.9.[5]

The values vary tremendously. Picric acid is such a weak acid that no reliable value of the constant can be expected from measurements in unbuffered solutions. Previously we[5] reported a p$K$ value of 8.9. Recently we repeated the measurements in highly purified and freshly distilled AN and obtained a value of 10. In the present work it appears that p$K_{HPi}$ is equal to 11.0 ± 0.1.

In a recent paper[23] we referred to the work of Coetzee and Padmanabhan,[3] who reported that $K^d_{BH^+}$ of pyridine is smaller by a factor of $10^5$ in AN than in water. They based their measurements on our value of p$K_{HPi}$ of 8.9. With the new value of p$K_{HPi}$ of 11.0, we calculate the p$K_{HA}$ of 3,5-dinitrobenzoic acid[23] equal to 17.2 instead of 15.1, as previously reported, taking p$K_{HPi}$ equal to 8.9.

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