Part II

PHYSICAL PROPERTIES

EVALUATION OF COMPOUNDS AND MATERIALS

Acid-Base Dissociation Constants in 1.0M Sodium Chloride

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DURING a study (2) of the Type II spectrophotometric titration plot first proposed by Higuchi, Rehm, and Barnstein (4) for use in glacial acetic acid as a solvent, it became apparent that relative concentration dissociation constants of acids and bases could be obtained by using the technique of Higuchi and coworkers in aqueous salt solutions. In a mixture of a base, B, its conjugate acid, HB, an indicator base, I, and its conjugate acid, HI, the concentration constant for the reaction

$$I + HB \rightleftarrows HI + B \qquad (1)$$

can be evaluated from spectrophotometrically determined values of $[I]$ and $[HI]$ and titration data. Type II plots are applicable to aqueous salt solutions of B, HB, I, and HI, regardless of the charge types of these species, provided the ionic strength is held constant during titration. The ionic strength was held constant by titrating dilute ($< 0.07M$) solutions of weak acids and bases in $1.0M$ sodium chloride with $1.0M$ strong bases and acids.

Under these conditions Equation 2 is valid (*2*, *4*). In the titration of a weak

$$\left\{ \frac{[HI]}{[I]} \right\}^{\pm 1} = - \left[\frac{(\mathrm{K}_{HB})_c}{(\mathrm{K}_{HI})_c} \right]^{\pm 1} + \left[\frac{(\mathrm{K}_{HB})_c}{(\mathrm{K}_{HI})_c} \right]^{\pm 1} \frac{S}{X} \qquad (2)$$

acid with strong base, the positive exponents in Equation 2 are used, where S is the volume of standard strong base equivalent to the weak acid being titrated, and $[HI]/[I]$ is the spectrophotometrically determined indicator ratio when X ml. of standard base have been added, $X < S$. $(\mathrm{K}_{HB})_c$ and $(\mathrm{K}_{HI})_c$ represent concentration acid dissociation constants of HB and HI, respectively. (The negative

Table I. Relative Concentration Constants for Reaction 1 as Determined by Type II in 1.0M Sodium Chloride at 25° ± 2° C.

HB[a, b]	Indicator[c]	Intercept[d] $(\mathrm{K}_{HB})_c/(\mathrm{K}_{HI})_c$	Intercept, Std. Dev.	Number of Titrations
Acetic acid	BCG	0.976	0.059	2
Acetic acid (acetate)	BCG	0.951	0.022	3
Acetic acid	PNP	237.1	0.7	2
$H_2PO_4^-$	PNP	3.51	0.20	3
$H_2PO_4^-$	TB	206	10	6
p-Hydroxybenzoic acid, K_1	PNP	364	3	2
p-Hydroxybenzoic acid, K_2	TB	1.56	0.20	3
Phenylalanine	TB	0.540	0.038	2
HCO_3^- (CO_3^{-2})	TB	0.194	0.006	3

[a] Parenthesis following acid listed indicates that conjugate base listed was actually titrated with strong acid. In these cases, the reciprocal of the intercept obtained was used to calculate the value given in third column.

[b] Concentration of acid or base titrated was usually in range 0.05 to $0.07M$. In the case of H_2PO_4, three titrations were of $0.010M$ solutions.

[c] BCG = bromocresol, green; PNP = *p*-nitrophenol, TB = thymol blue.

[d] Weighted mean value of all experiments, weighted according to square of standard deviation of an individual measurement.

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Table II. Concentration Dissociation Constants in 1.0M Sodium Chloride at 25° ± 2° C.

Acid	$(K_{HB})_c^a$	$100\ \sigma_{HB}/(K_{HB})_c^b$	$(K_{HB})_c/K_{HB}^c$	Reference
Acetic	(3.06×10^{-5})		(1.7)	(*5*)
p-Hyrdoxybenzoic, K_1	4.70×10^{-5}	1.0	1.42	(*11*)
p-Nitrophenol	1.29×10^{-7}	0.3	1.29	(*3*)
Phenylalanine	1.18×10^{-9}	10.4	1.59	(*3*)
Bromocresol green	3.21×10^{-5}	2.2	1.83	(*7*)
$H_2PO_4^-$	4.53×10^{-7}	5.7	7.36	(*1*)
Thymol blue, K_2	2.21×10^{-9}	7.6	1.75	(*7*)
p-Hydroxybenzoic, K_2	3.41×10^{-9}	14.8	8.54	(*11*)
HCO_3^-	4.25×10^{-10}	8.3	9.16	(*10*)

[a] Calculated from Table I using K_c of acetic acid in 1.0*M* sodium chloride equal to 3.06×10^{-5}. [b] Coefficient of variation of K_c = (100 × standard dev. of K_c/K_c. $K_c/K = f_{HB}/f_H \quad f_B$. The source of *K* thermodynamic acid dissociation constant) is from the listed reference. In the case of acetic acid (*5*) gives the experimentally determined value of $(K_{HB})_c/K_{HB}$.

exponents in Equation 2 are used in the titration of a weak base with strong acid.) Thus a plot of $[HI]/[I]$ *vs.* $1/X$ yields the relative concentration dissociation constant of *HB* to that of *HI*—i.e., the concentration constant for Reaction 1.

If the same acid is titrated with two different indicators, the relative dissociation constants of these indicators can be calculated. Similarly, if two different acids are titrated using the same indicator, the relative dissociation constants of these acids can be determined. Combining these two techniques permits establishment of a quantitative order of dissociation constants referred to a reference acid (acetic acid in this work). If the absolute value of the concentration constant of the reference acid is known in 1.0*M* sodium chloride, all other concentration constants can be evaluated.

The apparatus, chemicals, and techniques used have been described (*2, 9*).

RESULTS

Several acids and bases were titrated in 1.0*M* sodium chloride using different indicators and the intercept of Equation 2 and its standard deviation were obtained by the method of least squares (Table I). The first column lists the acid titrated, except in the two cases where the conjugate base of the acid listed follows in parentheses. In these two experiments, the conjugate base was titrated with strong acid. The second column lists the indicators used in the titration, while the third column gives the weighted mean of $(K_{HB})_c/(K_{HI})_c$ calculated from individual least square values and the standard deviation of the individual values. The fourth column gives the standard deviation of $(K_{HB})_c/(K_{HI})_c$ calculated on the basis of weighted deviations of individual values from the mean. The fifth column gives the number of titrations performed.

DISCUSSION

The concentration dissociation constants of the various acids examined in 1.0*M* sodium chloride are given in the second column of Table II. The concentration dissociation constant of acetic acid in 1.0*M* sodium chloride was taken as 3.06×10^{-5} on the basis of results obtained by Kilpatrick (*5*) and literature values quoted by him. The third column lists the coefficient of variation of the concentration dissociation constant, assuming a negligible error in the concentration dissociation constant for acetic acid. The fourth column gives the ratio of concentration to the thermodynamic acid dissociation constant.

All acids investigated with the exception of thymol blue and bromocresol green fall into two groups, depending upon the charge type of the parent acid, as shown by the ratio of K_c/K. However, for thymol blue and bromocresol green, even though the dissociation constant listed corresponds to the dissociation $HI^- \rightleftarrows H^+ + I^{-2}$, the salt effect more closely resembles that of an uncharged acid. This result is in agreement with previously summarized results obtained with these and other sulfonephthalein indicators (*6, 8*).

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