

Determination of the Mixed Dissociation Constants of Dibasic Acids by a Successive Linear Regression

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A linear analysis is presented which enables the mixed dissociation constants of dibasic acids to be determined by using pH-titration data. The proposed method is based on the linear equations in which the successive dissociation constants and the activity coefficient of the hydrogen or hydroxide ion are unknown constants. Linear equations are solved by a combination of a least squares method and an iteration technique, *i.e.*, a successive linear regression analysis. The validity of the method was proved by the determination of mixed constants for tartaric and succinic acids.

The advantage of the method is that it does not require knowledge of the activity coefficients of the hydrogen and hydroxide ions for the determination of mixed constants.

1. Introduction

The mixed dissociation constants of acids, the activities of the hydrogen and hydroxide ions being used in conjunction with concentrations of other species, are widely utilized in the fields of the equilibrium calculations¹⁾ and quantitative analysis of weak acids²⁾⁻⁴⁾.

In earlier methods⁵⁾⁻⁷⁾ for determining mixed constants, activity coefficients of the hydrogen and hydroxide ions, which may not even be estimated experimentally without non-thermodynamic assumption, should be known beforehand.

In the preceding papers⁸⁾⁹⁾, we proposed two methods for the determination of the mixed dissociation constants of monobasic weak acids. In a first method⁸⁾, the approximate mixed constants ranging from 10^{-4} to 10^{-10} are determined by linearization of the pH-titration data, *i.e.*, from the slope of a linear plots of v vs. $v \cdot 10^{-\text{pH}}$ where v is the volume of titrant added. The main advantage of the proposed method is that neither concentrations of the acid and titrant nor the volume of acid is required for the determination of mixed constants; hence the time-consuming standardization of the acid and titrant is unnecessary. In a second method⁹⁾, the mixed constants of monobasic acids are determined by solving the linear equations in which the dissociation constants and concentrations of acids, and activity coefficients of the hydrogen and hydroxide ions are unknown constants.

The determination of the mixed dissociation constants of a dibasic acid, on the other

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hand, have not been yet studied without the utilization of activity coefficients of the hydrogen and hydroxide ions.

This paper describes an approach to the determination of successive dissociation constants of dibasic acids in which the ratio of two successive constants is less than 10^3 . In the proposed method, calculations are based on a least squares method in combination with an iterative procedure in which activity coefficients of the hydrogen and hydroxide ions need not be known.

2. Linear Equations for the Determination of Mixed Dissociation Constants

For convenience, all signs of charge are omitted throughout the paper. Consider the case where a dibasic acid H_2W with initial volume V and concentration c_w is titrated with a strong base of initial concentration c_b and the deprotonation reaction is followed pH-metrically by using glass and reference electrodes calibrated with pH-standards. All titrations are performed at constant ionic strength, and then the ionic activity coefficients and liquid junction potentials are assumed to remain constant during the course of a pH-metric titration.

The mixed successive constants, K^M , in the successive dissociation stage of H_2W are given by Eqs. (1) and (2):

$$K_1^M = \frac{a_H \cdot [HW]}{[H_2W]} \quad (1)$$

$$K_2^M = \frac{a_H \cdot [W]}{[HW]}, \quad K_1^M > K_2^M \quad (2)$$

where a_H denotes the activity of hydrogen ions and $[]$ the concentration of species.

The following equation is valid for each titration point⁽⁴⁾.

$$([H] - [OH]) + \frac{c_B \cdot v}{V + v} = \frac{K_1^M \cdot a_H^{-1} + 2 \cdot K_1^M \cdot K_2^M \cdot a_H^{-2}}{1 + K_1^M \cdot a_H^{-1} + K_1^M \cdot K_2^M \cdot a_H^{-2}} \cdot \frac{c_w \cdot V}{V + v} \quad (3)$$

where v is the volume of titrant added.

Rearrangement of Eq.(3) yields

$$y = -\frac{1}{K_1^M} \cdot x_1 + K_2^M \cdot x_2 - \frac{1}{c_B} \cdot ([H] - [OH]) \cdot (V + v) \cdot \left(1 + \frac{a_H}{K_1^M} + \frac{K_2^M}{a_H}\right) \quad (4)$$

where

$$y = v - v_e \quad (5)$$

$$x_1 = v \cdot a_H \quad (6)$$

$$x_2 = \frac{2 \cdot v_e - v}{a_H} \quad (7)$$

and $v_e (= c_w \cdot V / c_B)$ is the volume of titrant required to neutralize the acid in the first dissociation stage, *i.e.*, the equivalence volume of the acid.

In acidic regions ($[H] \gg [OH]$), Eq. (4) gives

$$y = -\frac{1}{K_1^M} \cdot x_1 + K_2^M \cdot x_2 - \frac{1}{c_B \cdot \gamma_H} \cdot x_0 \quad (8)$$

where

$$x_0 = (V + v) \cdot a_H \cdot \left(1 + \frac{a_H}{K_1^M} + \frac{K_2^M}{a_H} \right) \quad (9)$$

and γ_H is the activity coefficient of hydrogen ions.

In alkaline regions ($[H] \ll [OH]$), Eq. (4) gives

$$y = -\frac{1}{K_1^M} \cdot x_1 + K_2^M \cdot x_2 + \frac{K_W \cdot a_{H_2O}}{c_B \cdot \gamma_{OH}} \cdot x'_0 \quad (10)$$

where

$$x'_0 = \frac{V + v}{a_H} \cdot \left(1 + \frac{a_H}{K_1^M} + \frac{K_2^M}{a_H} \right) \quad (11)$$

, γ_{OH} = activity coefficient of the hydroxide ion, K_W = thermodynamic dissociation constant of water, and a_{H_2O} = activity of water.

Eq. (8) or (10) is a linear equation with four variables and solved by a least squares method. Eq. (8) or (10), however, requires the knowledge of K_i^M ($i=1,2$) in x_0 or x'_0 . This dilemma can be solved by an iteration technique, *e.g.*, by starting an approximate value for K_i^M ($i=1,2$) and calculating a value for x_0 or x'_0 by using Eq. (9) or (11) and then using this value for x_0 or x'_0 in Eq. (8) or (10) for evaluating K_i^M ($i=1,2$). The x_0 -term containing the approximate values of dissociation constants becomes small in comparison with other terms

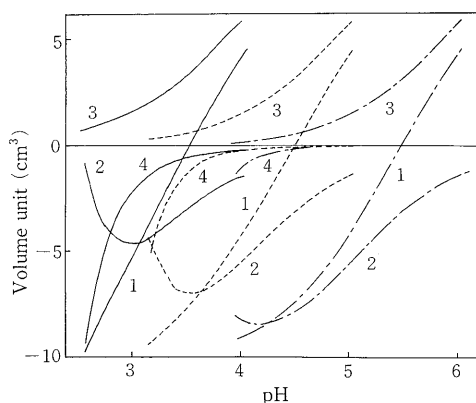


Fig. 1 Contributions of the different terms in Eq. (8) to the y -value at different pH-values. It is valid for a titration of 100 cm^3 of $0.01 \text{ mol} \cdot \text{dm}^{-3}$ solution of an acid having different $\text{p}K_i^M$ -values, with $0.1 \text{ mol} \cdot \text{dm}^{-3}$ KOH $\gamma_H = 1$.

— $\text{p}K_1^M = 3$ and $\text{p}K_2^M = 4$, - - - $\text{p}K_1^M = 4$
and $\text{p}K_2^M = 5$, - · - $\text{p}K_1^M = 5$ and $\text{p}K_2^M = 6$;
1, y ; 2, $-x_1/K_1^M$; 3, $K_2^M \cdot x_2$; 4, $-x_0/c_B$.

as the titration proceeds, and so fast convergence may be expected in most cases (see Fig. 1 in which the values of the terms y , x_1/K_1^M , $K_2^M \cdot x_2$ and x_0/c_B in Eq. (8) are shown for different pH-values). Several iterations are usually sufficient to obtain two consecutive values for K_i^M ($i=1,2$), which do not differ by more than, for example, 0.1%. The approximate values for $\text{p}K_1^M$ and $\text{p}K_2^M$ may be taken as equal to the pH values corresponding to the 1/2- and 3/2-neutralisation points respectively.

In neutral regions ($[H] \approx [OH]$), mixed constants are directly determined by solving the linear equations with three variables of y , x_1 , and x_2 because the last term in the right-hand side of Eq. (4) may be negligible in comparison with other terms. According to the numerical calculations, Eq. (8) is available in the range $pH < 8$ and Eq. (10) in the range $pH > 6$.

3. Results and Discussion

Numerical Considerations on the Accuracy of the Proposed Method

The accuracy of the proposed method in acidic regions was examined for different values of K_1^M by using theoretical titration data. The calculations were made for a titration of 100 cm^3 of 0.01 $mol \cdot dm^{-3}$ acid with 0.1 $mol \cdot dm^{-3}$ potassium hydroxide. It was assumed that $pK_2^M = pK_1^M + 1$, $\gamma_H = 1$, and the pH-values and volumes of titrant are measured to three decimal places. In these examples, first and second dissociations overlap each other. Titration data from the beginning of the titration to $pH = pK_2^M$ at 0.2-pH intervals were

Table 1 Errors in mixed constants and activity coefficient of the hydrogen ion resulting from systematic errors in the pH values and volumes of titrant for a titration of 100 cm^3 of 0.01 $mol \cdot dm^{-3}$ acid with 0.1 $mol \cdot dm^{-3}$ KOH^{a)}

$\Delta pH^{b)}$	Errors in			$\Delta v/\%^{d)}$	Errors in		
	pK_1^M	pK_2^M	$\gamma_H^{c)}$		pK_1^M	pK_2^M	$\gamma_H^{c)}$
(1) $pK_1^M=3$ and $pK_2^M=4$; $pH^{e)}$ =2.6-4.0.							
0.00	0.000	0.000	<0.1	0.0	0.000	0.000	<0.1
0.01	0.010	0.010	-2.3	0.1	0.000	-0.003	-0.1
0.02	0.020	0.020	-4.5	0.2	0.001	-0.005	-0.1
(2) $pK_1^M=4$ and $pK_2^M=5$; $pH^{e)}$ =3.2-5.0.							
0.00	0.000	0.000	<0.1	0.0	0.000	0.000	<0.1
0.01	0.010	0.010	-2.2	0.1	0.000	-0.003	<0.1
0.02	0.020	0.020	-4.5	0.2	-0.001	-0.005	-0.1
(3) $pK_1^M=5$ and $pK_2^M=6$; $pH^{e)}$ =4.0-6.0.							
0.00	0.000	0.000	0.5	0.0	0.000	0.000	0.5
0.01	0.010	0.010	-1.8	0.1	0.000	-0.002	0.5
0.02	0.020	0.020	-4.2	0.2	0.000	-0.005	0.4
(4) $pK_1^M=6$ and $pK_2^M=7$; $pH^{e)}$ =5.0-7.0.							
0.00	0.000	0.000	-2.5	0.0	0.000	0.000	-2.5
0.01	0.010	0.010	-5.2	0.1	0.000	-0.002	-2.3
0.02	0.020	0.020	-7.3	0.2	-0.001	-0.005	-1.7

a) It was assumed that $pK_2^M = pK_1^M + 1$ and the activity coefficient of the hydrogen ion is unity.

b) Systematic errors in the pH values.

c) Percent relative errors.

d) Systematic errors in the volumes of titrant.

e) The pH range used for the calculation.

utilized for the calculation. A desk programmable calculator is sufficient for evaluations to be made.

The errors in mixed constants and activity coefficient of the hydrogen ion resulting from the systematic errors in the pH values and volumes of titrant are shown in Table 1. In Table 1, the iteration is repeated until two successive values for K_i^M ($i=1,2$) agree to within 0.1%. Table 1 shows that errors in the pH value directly affect the mixed constants, *i.e.*, errors in pK_1^M - and pK_2^M -values are identical with ΔpH . In contrast, the volume errors do not significantly affect the pK_1^M value but slightly affect the pK_2^M value at the rate of -0.002_5 pK^M unit/0.1% Δv , as is evident from Table 1.

An error in activity coefficient of the hydrogen ion increases with an increase in the pK_1^M value even when $\Delta pH=0$ or $\Delta v=0\%$. This is due to the fact that the third term in the right-hand side of Eq. (8) becomes small relatively in comparison with other terms as the pH value increases. It should be noted, however, that the ionic activity coefficients obtained by Eq. (8) or (10) are the apparent values including the changes in liquid junction potentials.

Consequently, in order to determine the mixed constants with an accuracy of less than ± 0.01 pK^M unit the pH values should be measured with an accuracy of less than ± 0.01 pH unit and the volume of titrant with an accuracy of less than $\pm 0.4\%$.

Examples

To examine the applicability of the proposed method, pK_i^M values calculated from titration data reported by Ivaska⁴⁾ were compared with the values given in the literature.

Mixed constants of tartaric and succinic acids determined by using Eq. (8) are summarized in Table 2. The pH values utilized have been measured to 0.001 pH unit. In

Table 2 Determination of dissociation constants of dibasic acids at 25°C
Ionic strength; 0.1 mol·dm⁻³ (KCl)

Acids	Tartaric acid	Succinic acid
(1) Experimental conditions		
Concn. of titrant (mol · dm ⁻³)	0.1008 (KOH)	0.1008 (KOH)
Initial volume (cm ³)	50.82	51.21
Concn. of acid (mol · dm ⁻³)	$9.89_0 \cdot 10^{-3}$	$8.52_5 \cdot 10^{-3}$
pH range used for the calculation	3.29-4.11	4.30-5.23
(2) Results		
pK_1^M { This method	2.88 ₈	4.08 ₀
{ Literature ⁴⁾	2.87 ₈	4.07 ₇
pK_2^M { This method	4.01 ₁	5.33 ₇
{ Literature ⁴⁾	4.01 ₁	5.33 ₅

Table 2, the literature values were determined graphically as follows; (1) The activity coefficient of the hydrogen ion is assumed to be 0.794 at an ionic strength of 0.1 mol·dm⁻³. This value was calculated from the measured pH value in hydrochloric acid of known

concentration according to the equation $\gamma_{\text{H}} = 10^{-\text{pH}} / [\text{H}]$ and may include the error based on the change in liquid junction potentials. (2) The K_2^{M} value is formulated as a function of K_1^{M} , v , and $[\text{H}]$. (3) By assuming different values for $\text{p}K_1^{\text{M}}$ and calculating the corresponding $\text{p}K_2^{\text{M}}$, a line valid for one titration point can be plotted in co-ordinates $\text{p}K_1^{\text{M}}$ and $\text{p}K_2^{\text{M}}$. Different titration points give different lines and their point of intersection gives the desired values of $\text{p}K_1^{\text{M}}$ and $\text{p}K_2^{\text{M}}$.

The values of mixed constants obtained by the present method, $\text{p}K_1^{\text{M}} = 2.89$ and $\text{p}K_2^{\text{M}} = 4.01$ for tartaric acid and 4.08 and 5.34 for succinic acid, agree with the values given in the literature⁴⁾, 2.88 and 4.01, and 4.08 and 5.34 respectively within 0.01 $\text{p}K^{\text{M}}$ unit. These results suggest that the γ_{H} value used in Ivaska's work is reasonable. In fact, the γ_{H} value calculated from the coefficient of x_0 in Eq. (8) by using the titration data for tartaric acid which is a stronger acid than succinic acid was 0.804 and approximately agreed with the value, 0.794, used by Ivaska.

The main advantage of the proposed method in comparison with the previous method⁴⁾ is that activity coefficients of the hydrogen and hydroxide ions need not be known for the determination of the mixed dissociation constants. Thus, an error arising from a specified value for activity coefficients of the hydrogen and hydroxide ions, which can not be determined without non-thermodynamic assumptions, is avoided in the present method. The drawback of the method is that a least squares analysis cannot produce accurate results from inadequate data and needs many data in order to obtain reliable results.

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