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The determination of acidity of the dilute solutions of weak multibasic organic acids

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ABSTRACT

The new theoretical method for the accurate determination of acidity of dilute solutions of weak multibasic organic acids (which are widely used in medicine, pharmacology, various branches of industry and participate in important biological processes in living organisms) is suggested. The concepts of the contributions of the separate dissociation steps to the [H^+] value, x_m, are used for an analysis of complex equilibria of the processes of dissociation of these acids. The cases of weak dibasic and tribasic organic acids with the "overlapping" dissociation equilibria and a general case of weak multibasic acids, H_nA, are considered. From the conditions of equality of the concentrations of various ionized and non-ionized forms in the dilute solutions of weak multibasic organic acids the areas of dominance of these forms in connection with the corresponding x_m values are formulated.

Keywords: Dibasic Acids; Tribasic Acids; Hydrogen Ions Concentration; Equations

1. INTRODUCTION

Weak multibasic organic acids are widely used in medicine, pharmacology, chemical, food and cosmetic industries. Some of these acids participate in a series of important biological processes occurring in living organisms (for example, in the Krebs cycle). The majority of drugs are weak acids and/or bases. Their biopharmaceutical properties are directly connected with the dissociation constants and degrees of these compounds, consequently, with acidity of their solutions. The latter is the very factor which affects in physiological systems the rate at which the compound is able to diffuse across membranes and various obstacles, determines the acid-base homeostasis and enzyme kinetics in the cell and in the body. It is possible to say that an acidity of the weak multibasic organic acids determines, as a rule, all their useful (or harmful) properties.

Many weak multibasic organic acids have comparatively close values of the dissociation constants for the various steps; this fact causes their simultaneous participation in the determining the hydrogen ion concentration in solutions of these acids (*i.e.*, "overlapping" dissociation equilibria). In this paper a new theoretical method for determination of acidity of the dilute (0.0001-0.1 mol·dm^{-3}) solutions of such acids is suggested.

2. RESULTS AND DISCUSSION

2.1. Dibasic Acids

Dibasic acids form the most numerous group of weak multibasic organic acids with the "overlapping" equilibria effect. In dilute aqueous solutions the primary and secondary steps of dissociation are

$$H_2A \leftrightarrow H^+ + HA^- \quad (1)$$

$$HA^- \leftrightarrow H^+ + A^{2-} \quad (2)$$

In our previous communications [1,2] we have used the concepts of the contributions to the total hydrogen ion concentration, [H^+], being assigned to the primary and secondary dissociation steps, x_1 and x_2, such that $x_1 + x_2 = [H^+]$. The corresponding mass-action equations for both steps dissociation constants are

$$K_1 = \frac{[H^+](x_1 - x_2)}{c - x_1} F_1 = \frac{x_1^2 - x_2^2}{c - x_1} F_1 \quad (3)$$

$$K_2 = \frac{[H^+]x_2}{x_1 - x_2} F_2 = \frac{x_2(x_1 + x_2)}{x_1 - x_2} F_2 \quad (4)$$

where K_1 and K_2 are the thermodynamic dissociation constants, c is the total (analytical) concentration of acid, F_1 and F_2 are the quotients of the activity coefficients:

$$F_1 = \frac{f_{H^+} f_{HA^-}}{f_{H_2A}} \quad (5)$$

$$F_2 = \frac{f_{H^+} f_{A^{2-}}}{f_{HA^-}} \quad (6)$$

The values of the activity coefficients may be approximated by the Debye-Huckel equation:

$$\log_{10} f_i = -\frac{z_i^2 A\sqrt{I}}{1+a_i B\sqrt{I}} \quad (7)$$

where a_i is the cation-anion distance of closest approach, A and B are constants depending on the properties of water at given temperature, z_i is the charge of ion. The ionic strength is given by $I = x_1 + 2x_2$. The activity coefficient of undissociated acid is assumed to be unity.

According to the (3) and (4) the x_1 and x_2 values (and then their sum – the $[H^+]$ value) can be calculated successively by an iterative solution of two quadratic equations:

$$x_1 = \frac{1}{2}\left[-\frac{K_1}{F_1} + \sqrt{\left(\frac{K_1}{F_1}\right)^2 + 4\left(x_2^2 + \frac{K_1 c}{F_1}\right)}\right] \quad (8)$$

$$x_2 = \frac{1}{2}\left[-\left(\frac{K_2}{F_2} + x_1\right) + \sqrt{\left(\frac{K_2}{F_2} + x_1\right)^2 + \frac{4K_2 x_1}{F_2}}\right] \quad (9)$$

We suggest also the empirical equation for the fast approximate determination of the pH values of dilute (0.0001-0.01 mol·dm^{-3}) solutions of weak dibasic (and tribasic with the low K_3 values) organic acids:

$$pH = -1.489 + 0.8pK_1 - (1.185 - 0.14pK_1)\lg c \quad (10)$$

The maximum value of the relative error for this equation for a series of weak dibasic and tribasic organic acids with the pK_1 values in the interval: 2.5-5 does not exceed 5% (the relative error is the ratio of the difference between the approximate pH value and corresponding accurate value, divided by the approximate pH value, and converted to percent).

2.2. Tribasic Acids

In case of weak tribasic organic acids with the “overlapping” dissociation equilibria, the mass-action equations may be expressed as follows:

$$K_1 = \frac{[H^+](x_1 - x_2)}{c - x_1} F_1 = \frac{(x_1 + x_2 + x_3)(x_1 - x_2)}{c - x_1} F_1 \quad (11)$$

$$K_2 = \frac{[H^+](x_2 - x_3)}{x_1 - x_2} F_2 = \frac{(x_1 + x_2 + x_3)(x_2 - x_3)}{x_1 - x_2} F_2 \quad (12)$$

$$K_3 = \frac{[H^+]x_3}{x_2 - x_3} F_3 = \frac{(x_1 + x_2 + x_3)x_3}{x_2 - x_3} F_3 \quad (13)$$

where

$$F_1 = \frac{f_{H^+} f_{H_2A^-}}{f_{H_3A}} \quad (14)$$

$$F_2 = \frac{f_{H^+} f_{HA^{2-}}}{f_{H_2A^-}} \quad (15)$$

$$F_3 = \frac{f_{H^+} f_{A^{3-}}}{f_{HA^{2-}}} \quad (16)$$

and $I = x_1 + 2x_2 + 3x_3$

The x_1, x_2 and x_3 values (and then their sum – the $[H^+]$ value) can be calculated successively by an iterative solution of three quadratic equations:

$$x_1 = \frac{1}{2}\left[-\left(\frac{K_1}{F_1} + x_3\right) + \sqrt{\left(\frac{K_1}{F_1} + x_3\right)^2 + 4\left(x_2^2 + x_2 x_3 + \frac{K_1 c}{F_1}\right)}\right] \quad (17)$$

$$x_2 = \frac{1}{2}\left[-\left(\frac{K_2}{F_2} + x_1\right) + \sqrt{\left(\frac{K_2}{F_2} + x_1\right)^2 + 4\left(x_3^2 + x_1 x_3 + \frac{K_2 x_1}{F_2}\right)}\right] \quad (18)$$

$$x_3 = \frac{1}{2}\left[-\left(\frac{K_3}{F_3} + x_1 + x_2\right) + \sqrt{\left(\frac{K_3}{F_3} + x_1 + x_2\right)^2 + \frac{4K_3 x_2}{F_3}}\right] \quad (19)$$

2.3. Acids with the Higher Basicity

It is necessary at first to consider the general case of the weak multibasic organic acid H_nA with the “overlapping” dissociation equilibria. For this case we may write the equations connecting the values of x_1, x_2, x_3, … x_{n-1}, x_n with the concentrations of various anions:

$$x_1 = [H_{n-1}A^-] + [H_{n-2}A^{2-}] + [H_{n-3}A^{3-}] + \ldots + [HA^{(n-1)-}] + [A^{n-}] \quad (20)$$

$$x_2 = [H_{n-2}A^{2-}] + [H_{n-3}A^{3-}] + \ldots + [HA^{(n-1)-}] + [A^{n-}] \quad (21)$$

$$x_3 = [H_{n-3}A^{3-}] + \ldots + [HA^{(n-1)-}] + [A^{n-}] \quad (22)$$

$$x_{n-1} = [HA^{(n-1)-}] + [A^{n-}] \quad (23)$$

$$x_n = [A^{n-}] \quad (24)$$

In a general form for the m dissociation step we may write:

$$x_m = [H_{n-m}A^{m-}] + x_{m+1} \quad (25)$$

The total hydrogen ion concentration may be expressed as follows:

$$[H^+] = \sum_{m=1}^{n} m[H_{n-m}A^{m-}] = \sum_{m=1}^{n} x_m \quad (26)$$

The mass-action equation for the m dissociation step may be expressed by the following equations:

$$K_m = \frac{[H^+](x_m - x_{m+1})}{x_{m-1} - x_m} F_m = \frac{(x_m - x_{m+1})\sum_{m=1}^{n} x_m}{x_{m-1} - x_m} F_m \quad (27)$$

where

$$F_m = \frac{f_{H^+} f_{H_{n-m}A^{m-}}}{f_{H_{n-(m-1)}A^{(m-1)-}}} \tag{28}$$

The equation for an ionic strength may be written as follows:

$$I = \sum_{m=1}^{n} m x_m \tag{29}$$

In case of weak organic acids with the high (more than tribasic) basicity the conversion of (27) to the forms of (8-9, 17-19) leads to the very complicated expressions. That is why we suggest to solve the complicated problem of determining of acidity of the high-basic acids solutions by more simple method. Let us consider this method for the most difficult case of hexabasic mellitic (benzenehexacarboxylic) acid. First, assume that this acid can be treated as a tribasic acid (taking into account that the main contribution to the $[H^+]$ value is made by first three dissociation steps). Then the x_1, x_2 and x_3 values are determined successively by an iterative solution of (17-19), where the values of F_1, F_2 and F_3 were assumed to be unity. The obtained x_1, x_2 and x_3 values are then used for the determination of the initial estimate of $[H^+]$. Then, with the aid of $[H^+]$ value and the iterative solution of the following equations (which are obtained from (27) for the corresponding dissociation steps):

$$x_4 = \frac{K_4 x_3 + [H^+]F_4 x_5}{K_4 + [H^+]F_4} \tag{30}$$

$$x_5 = \frac{K_5 x_4 + [H^+]F_5 x_6}{K_5 + [H^+]F_5} \tag{31}$$

$$x_6 = \frac{K_6 x_5}{K_6 + [H^+]F_6} \tag{32}$$

the initial values of x_4, x_5 and x_6 are determined (assuming that F_4, F_5 and F_6 values to be unity). These values are used for a correction to the $[H^+]$ value:

$$[H^+] = \sum_{m=1}^{6} x_m$$

and then obtaining the final (for this stage) x_4, x_5 and x_6 values. Then with the aid of the following equations (where F_4, F_5 and F_6 values are assumed to be unity):

$$x_1 = \frac{K_1 c + [H^+]F_1 x_2}{K_1 + [H^+]F_1} \tag{33}$$

$$x_2 = \frac{K_2 x_1 + [H^+]F_2 x_3}{K_2 + [H^+]F_2} \tag{34}$$

$$x_3 = \frac{K_3 x_2 + [H^+]F_3 x_4}{K_3 + [H^+]F_3} \tag{35}$$

improved x_1, x_2 and x_3 values are obtained. At the following stage, with the aid of the obtained six x_m values, the ionic strength I is calculated with the aid of (29). The values of the activity coefficients of H^+ and all anions are approximated by the Debye-Huckel (7). With the aid of the activity coefficient values and (28) the F_1, F_2, F_3, F_4, F_5 and F_6 values are calculated. Using these values in (30) to (35), corrected values of all six x_m values are obtained. With the aid of the latters, the final $[H^+]$ value is determined.

2.4. The Use of the X_m Concept for a Determination of the Concentrations of the Ionized and Non-Ionized Forms and their Distribution in the Dilute Solutions of Weak Multibasic Acids

The determination of the x_m values gives us also the opportunity to calculate the important dissociation parameters: the concentrations of all ionized and non-ionized forms of weak multibasic organic acids in their dilute solutions. For this goal in general case of H_nA acid can be used (25) and (26). Taking into account also the following equation:

$$[H_nA] = c - x_1 \tag{36}$$

We can formulate the conditions of an equality of the concentrations of ionized and non-ionized forms:

$$[H^+] = [H_nA]{:}c = 2x_1 + \sum_{m=2}^{n} x_m \tag{37}$$

$$[H_{n-1}A^-] = [H_nA]{:}c = 2x_1 - x_2 \tag{38}$$

$$[H_{n-2}A^{2-}] = [H_nA]{:}c = x_1 + x_2 - x_3 \tag{39}$$

$$[H_{n-m}A^{m-}] = [H_nA]{:}c = x_1 + x_m - x_{m+1} \tag{40}$$

$$[A^{n-}] = [H_nA]{:}c = x_1 + x_n \tag{41}$$

Taking into account these conditions, we may formulate the areas of dominance of various ionized and non-ionized forms of acid:

$$[H^+] > [H_nA]{:}c < 2x_1 + \sum_{m=2}^{n} x_m \tag{42}$$

(and vice versa)

$$[H_{n-1}A^-] > [H_nA]{:}c < 2x_1 - x_2 \tag{43}$$

(and vice versa)

$$[H_{n-2}A^{2-}] > [H_nA]{:}c < x_1 + x_2 - x_3 \tag{44}$$

(and vice versa)

$$[H_{n-m}A^{m-}] > [H_nA]{:}c < x_1 + x_m - x_{m+1} \tag{45}$$

(and vice versa)

$$[A^{n-}] > [H_nA]{:}c < x_1 + x_n \tag{46}$$

(and vice versa)

3. CONCLUSIONS

Many weak multibasic organic acids have the comparatively close values of the dissociation constants of the different steps. This fact causes the participation of all steps in formation the hydrogen ions total concentration in the solutions of such acids. We suggest the new theoretical method for a determination of acidity of these solutions using the concepts of the contributions of the separate dissociation steps to the $[H^+]$ value, x_m. The equations for the accurate calculation of the $[H^+]$ values in cases of dibasic and tribasic acids and also in general case of weak multibasic acid, H_nA, are suggested. The comparatively simple method for a determination of acidity of the dilute solutions of high-basic (more than tribasic) acids is also described. With the aid of the formulated by us conditions of an equality of the concentrations of various ionized and non-ionized forms in the dilute solutions of weak multibasic organic acids the areas of dominance of these forms in connection with the corresponding x_m values are formulated.

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