Physical Chemistry

The Regularities of Electrolytic Dissociation of Aconitic Acid

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ABSTRACT. The parameters of dissociation of biologically active aconitic acid in its dilute (0.0001-0.01M) solutions were determined with the aid of original exact and approximate equations.

Key words: *degree of dissociation, dissociation step, dissociation constant, hydrogen ion concentration, cis- and trans-aconitic acid.*

Aconitic acid (1-propene-1,2,3-tricarboxylic acid) exists in two forms: cis- and trans- forms. Cis-Aconitic acid participates in the cycle of tricarboxylic acids (Krebs cycle, citric acid cycle) as the intermediate compound between citric and isocitric acids; with the aid of this complex fermentative process in vital organisms the oxidation of the main intermediate products of the cleavage of carbohydrates, fats and proteins is near completion. In this work with the aid of original equations suggested by us [1-5] the various dissociation parameters for the dilute solutions of biologically active aconitic acid have been determined. The obtained results may be used in the interpretation of mechanisms of separate steps of Krebs cycle.

Because of the very small value of the third dissociation constant, tribasic aconitic acid may be considered as dibasic acid from the standpoint of formation of the hydrogen ion concentration. The mass action equations for both dissociation steps in this case may be expressed by original equations suggested by us:

$$K_1 = \frac{c(\alpha_1^2 - \alpha_2^2)}{1-\alpha_1}F_1 = \frac{\alpha_1^2[1-(\alpha_2^{'})^2]c}{1-\alpha_1}F_1\ , \qquad (1)$$

$$K_2 = \frac{c\alpha_2(\alpha_1 + \alpha_2)}{\alpha_1 - \alpha_2}F_2 = \frac{\alpha_1\alpha_2^{'}[1+\alpha_2^{'}]c}{1-\alpha_2^{'}}F_2, \qquad (2)$$

where α_1 and α_2 are the degrees of dissociation of the first and second dissociation steps, $\alpha_2^{'}$ is the "partial" degree of dissociation of the second step ($\alpha_2^{'} = \alpha_2/\alpha_1$), c is the total (analytical) concentration of acid, F_1 and F_2 are the quotients of activity coefficients:

$$F_1 = \frac{f_{H^+}f_{HA^-}}{f_{H_2A}} \qquad (3)$$

$$F_2 = \frac{f_{H^+}f_{A^{2-}}}{f_{HA^-}} \qquad (4)$$

According to equations (1) and (2) the degrees of dissociation α_1 and α_2 can be evaluated successively by iterative solution of two quadratic equations:

$$\alpha_1 = \frac{1}{2}\left[-\frac{K_1}{cF_1} + \sqrt{\left(\frac{K_1}{cF_1}\right)^2 + 4\left(\alpha_2^2 + \frac{K_1}{cF_1}\right)}\right] \qquad (5)$$

$$\alpha_2 = \frac{1}{2}\left[-\left(\frac{K_2}{cF_2} + \alpha_1\right) + \sqrt{\left(\frac{K_2}{cF_2} + \alpha_1\right)^2 + \frac{4K_2\alpha_1}{cF_2}}\right] \qquad (6)$$

The values of the activity coefficients were calculated with the aid of the Debye-Huckel expression:

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

where α_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. Ionic strength $I = c(\alpha_1 + 2\alpha_2)$.

With the aid of equations (5) and (6) the values of the degrees of dissociation for dilute (0.0001 – 0.01M) solutions of trans- and cis-aconitic acid have been calculated. The K_1 and K_2 values for two forms of this acid were taken from [6]. The values of α_i for mono- and dianions of aconitic acid and hydrogen ion, A and B were taken from [7]. The α_1, α_2, α_2' and pH values for the dilute solutions of cis- and trans-aconitic acids at 25°C are presented in Tables 1 and 2. The concentrations of dissociated and undissociated forms may be determined with the aid of the following equations:

$$[H_2A^-] = c(\alpha_1 - \alpha_2) \qquad (8)$$

$$[HA^{2-}] = c\alpha_2 \qquad (9)$$

$$[H^+] = c(\alpha_1 + \alpha_2) \qquad (10)$$

$$[H_3A] = c(1 - \alpha_1) \qquad (11)$$

Taking into account the comparative complexity of calculations with the aid of equations (5) and (6), we obtained

Table 1

The parameters of dissociation of cis-aconitic acid in dilute solutions at 25°C

Concentration of acid, M	α_1	α_2	α_2'	pH
0.0001	0.9919	0.2289	0.2308	3.919
0.0002	0.9837	0.1399	0.1422	3.656
0.0004	0.9683	0.0807	0.0833	3.387
0.0006	0.9541	0.0574	0.0601	3.229
0.0008	0.9409	0.0448	0.0476	3.117
0.001	0.9284	0.0368	0.0397	3.030
0.002	0.8755	0.0199	0.0228	2.766
0.004	0.7984	0.0107	0.0134	2.515
0.006	0.7429	0.0075	0.0101	2.375
0.008	0.6999	0.0058	0.0082	2.279
0.01	0.6651	0.0047	0.0071	2.207

Table 2

The parameters of dissociation of trans-aconitic acid in dilute solutions at 25°C

Concentration of acid, M	α_1	α_2	α_2'	pH
0.0001	0.9477	0.2251	0.2375	3.937
0.0002	0.9027	0.1367	0.1514	3.690
0.0004	0.8336	0.0783	0.0940	3.447
0.0006	0.7814	0.0555	0.0710	3.310
0.0008	0.7398	0.0431	0.0583	3.215
0.001	0.7054	0.0354	0.0502	3.143
0.002	0.5915	0.0189	0.0320	2.930
0.004	0.4773	0.0100	0.0210	2.730
0.006	0.4147	0.0069	0.0167	2.619
0.008	0.3732	0.0053	0.0142	2.543
0.01	0.3430	0.0043	0.0126	2.485

the following simple empirical equations for fast approximate calculation of the α_1 and α_2 values for dilute solutions of trans- and cis-aconitic acids (c = 0.0001 – 0.004M for cis-form and c = 0.0001 – 0.002M for trans-form):

Trans-aconitic acid:

$$\alpha_1 = 2.696 - 0.957 pK_1 - 0.5058 \cdot 10^{-8.257\sqrt{K_1}} \lg c \quad (12)$$

$$\alpha_2 = 337 K_2^{1.426+0.1785\lg c} \quad (13)$$

Cis-aconitic acid:

$$\alpha_2 = 337 K_2^{1.426+0.17893\lg c} \quad (14)$$

$$pH = -1.489 + 0.8 pK_1 - (1.185 - 0.14 pK_1)\lg c \quad (15)$$

The difference between the results obtained with the aid of the approximate equations (12) – (15) and the corresponding exact equations (5), (6) and (10) does not exceed 10%.

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