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Physical Chemistry

The Electrolytic Dissociation of Tartronic Acid

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ABSTRACT. The parameters of electrolytic dissociation of tartronic acid in its dilute (0.0001-0.1M) solutions were determined with the aid of original exact and approximate equations suggested by the authors. *© 2010 Bull. Georg. Natl. Acad. Sci.*

Key words: *tartronic acid, dissociation constant, degree of dissociation, dissociation step, hydrogen ion concentration.*

Tartronic acid (2-hydroxymalonic acid) is one of the important representatives of the group of hydroxycarboxylic acids. This acid is best known as a reactant in the catalytic oxidation with air to form mesoxalic acid. It is also used as oxygen scavenger. In this work the regularities of the electrolytic dissociation of tartronic acid were determined with the aid of original equations suggested by us for the calculation of the degrees of dissociation and other dissociation parameters of weak dibasic organic acids with "overlapping" equilibria [1-6].

The equations for the law of dilution for both dissociation steps of dibasic tartronic acid may be presented as follows:

$$\mathrm{K}_1 = \frac{c(\alpha_1^2 - \alpha_2^2)}{1-\alpha_1} F_1 = \frac{\alpha_1^2 [1-(\alpha_2^{'})^2] c}{1-\alpha_1} F_1 \qquad (1)$$

$$\mathrm{K}_2 = \frac{c\alpha_2(\alpha_1 + \alpha_2)}{\alpha_1 - \alpha_2} F_2 = \frac{\alpha_1 \alpha_2^{'} (1+\alpha_2^{'}) c}{1-\alpha_2^{'}} F_2 \qquad (2)$$

where K_1 and K_2 are the thermodynamic dissociation constants of the first and second dissociation steps, α_1 and α_2 are the "usual" degrees of dissociation of these steps, $\alpha_2^{'}$ is the "partial" degree of dissociation of the second step (the term of the "partial" degree of dissociation for intermediate dissociation steps was first suggested by us [1,2]), c is the total (analytical) concentration of acid, F_1 and F_2 are the quotients of the activity coefficients:

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

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

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:

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

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

Table 1.

The parameters of dissociation of tartronic acid in dilute solutions at 25ºC

Concentration of acid, M	α_1	α_2	α'_2	pH
0.0001	0.9765	0.2004	0.2052	3.935
0.0002	0.9544	0.1200	0.1257	3.675
0.0004	0.9160	0.06805	0.07429	3.415
0.0006	0.8884	0.04800	0.05403	3.262
0.0008	0.8552	0.03725	0.04356	3.159
0.001	0.8303	0.03053	0.03677	3.079
0.002	0.7372	0.01633	0.02215	2.840
0.004	0.6275	0.008681	0.01383	2.617
0.006	0.5605	0.005994	0.01069	2.494
0.008	0.5136	0.004615	0.008986	2.410
0.01	0.4779	0.003765	0.007878	2.347
0.02	0.3751	0.002005	0.005345	2.157
0.04	0.2877	0.001072	0.003726	1.978
0.06	0.2444	0.0007456	0.003051	1.876
0.08	0.2171	0.0005767	0.002656	1.806
0.1	0.1977	0.0004729	0.002392	1.752

The value of the "partial" degree of dissociation α_2' according to equation (2) may be calculated with the aid of the following equation:

$$\alpha_2' = \frac{1}{2}\left[-\left(\frac{K_2}{\alpha_1 c F_2}+1\right)+\sqrt{\left(\frac{K_2}{\alpha_1 c F_2}+1\right)^2+\frac{4K_2}{\alpha_1 c F_2}}\right] \quad (7)$$

or with the aid of α_1 and α_2 values:

$$\alpha_2' = \alpha_2 / \alpha_1. \quad (8)$$

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

$$\lg f_i = -\frac{z_i^2 A\sqrt{I}}{1+a_i B\sqrt{I}} \quad (9)$$

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 $I = c(\alpha_1 + 2\alpha_2) = c\alpha_1(1+2\alpha_2')$. The activity coefficient of undissociated acid is assumed to be unity.

Equations (5), (6) and (8) were used for the calculation of the values of "usual" and "partial" degrees of dissociation of tartronic acid for its dilute (0.0001-0.1M) solutions. The K_1 and K_2 values for this acid (K_1=3.8x10^{-3}; K_2=2.88x10^{-5}) were taken from [7]. The calculated values of α_1, α_2, α_2' and pH at 25ºC are presented in Table 1.

The concentrations of dissociated and undissociated forms in the dilute solutions of tartronic acid can be determined with the aid of the following equations:

Table 2.

The concentrations of the anions and undissociated acid in dilute solutions of tartronic acid at 25ºC

Concentration of acid, M	$[HA^-]$, M	$[A^{2-}]$, M	$[H_2A]$, M
0.0001	$7.76\cdot10^{-5}$	$2.00\cdot10^{-5}$	$2.35\cdot10^{-6}$
0.0002	$1.67\cdot10^{-4}$	$2.40\cdot10^{-5}$	$9.12\cdot10^{-6}$
0.0004	$3.39\cdot10^{-4}$	$2.72\cdot10^{-5}$	$3.36\cdot10^{-5}$
0.0006	$5.04\cdot10^{-4}$	$2.88\cdot10^{-5}$	$6.70\cdot10^{-5}$
0.0008	$6.54\cdot10^{-4}$	$2.98\cdot10^{-5}$	$1.16\cdot10^{-4}$
0.001	$8.00\cdot10^{-4}$	$3.05\cdot10^{-5}$	$1.70\cdot10^{-4}$
0.002	$1.44\cdot10^{-3}$	$3.27\cdot10^{-5}$	$5.26\cdot10^{-4}$
0.004	$2.48\cdot10^{-3}$	$3.47\cdot10^{-5}$	$1.49\cdot10^{-3}$
0.006	$3.33\cdot10^{-3}$	$3.60\cdot10^{-5}$	$2.64\cdot10^{-3}$
0.008	$4.07\cdot10^{-3}$	$3.69\cdot10^{-5}$	$3.89\cdot10^{-3}$
0.01	$4.74\cdot10^{-3}$	$3.77\cdot10^{-5}$	$5.22\cdot10^{-3}$
0.02	$7.46\cdot10^{-3}$	$4.01\cdot10^{-5}$	$1.25\cdot10^{-2}$
0.04	$1.15\cdot10^{-2}$	$4.29\cdot10^{-5}$	$2.85\cdot10^{-2}$
0.06	$1.46\cdot10^{-2}$	$4.47\cdot10^{-5}$	$4.53\cdot10^{-2}$
0.08	$1.73\cdot10^{-2}$	$4.61\cdot10^{-5}$	$6.26\cdot10^{-2}$
0.1	$1.97\cdot10^{-2}$	$4.73\cdot10^{-5}$	$8.02\cdot10^{-2}$

$$[HA^-] = c(\alpha_1 - \alpha_2) = c\alpha_1(1 - \alpha_2^{'}) \qquad (10)$$

$$[A^{2-}] = c\alpha_2 = c\alpha_1\alpha_2^{'} \qquad (11)$$

$$[H^+] = c(\alpha_1 + \alpha_2) = c\alpha_1(1 + \alpha_2^{'}) \qquad (12)$$

$$[H_2A] = c(1 - \alpha_1) \qquad (13)$$

The values of the equilibrium concentrations of anions and undissociated acid are presented in Table 2.

Taking into account the comparative complexity of calculations with the aid of equations (5) and (6), we suggest also simple empirical equations for fast approximate calculation of the α_1, α_2, $\alpha_2^{'}$ and pH values for the dilute solutions of tartronic acid (concentration range c=0.0001-0.001M):

$$\alpha_1 = 0.5188c^{-0.07} \qquad (14)$$

$$\alpha_2 = 1.122 \times 10^{-4} c^{-0.816} \qquad (15)$$

$$\alpha_2^{'} = 2.1627 \times 10^{-4} c^{-0.746} \qquad (16)$$

$$pH = 0.527 - 0.85 \lg c. \qquad (17)$$

The difference between the results obtained with the aid of these equations and the accurate values presented in Table 1 does not exceed 5%.

ფიზიკური ქიმია

ტარტრონის მჟავას ელექტროლიტური დისოციაცია

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ავტორების მიერ შემოთავაზებული ორიგინალური განტოლებების დახმარებით გათვლილია ჰიდროქსიკარბონმჟავების ჯგუფის მნიშვნელოვანი წარმომადგენლის – ტარტრონის მჟავას ელექტროლიტური დისოციაციის ორივე საფეხურის ჩვეულებრივი და "პარციალური" ხარისხების, pH-ის, მონო- და დიანიონებისა და არადისოცირებული მჟავას კონცენტრაციების სიდიდეები მჟავას განზავებული ხსნარების კონცენტრაციის ინტერვალში 0.0001-0.1M. შემოთავაზებულია აგრეთვე მარტივი ემპირიული განტოლებები დისოციაციის ხარისხებისა და ხსნართა pH-ის მნიშვნელობების სწრაფი მიახლოებითი გათვლისათვის.

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