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Physical Chemistry

The Regularities of Electrolytic Dissociation of Camphoric Acid

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ABSTRACT. The parameters of dissociation of camphoric acid in its dilute (0.0001-0.01M) solutions were determined with the aid of original exact and approximate equations. *© 2010 Bull. Georg. Natl. Acad. Sci.*

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

Camphoric acid (1,2,2-trimethyl-1,3-cyclopentanedicarboxylic acid) is one of the important representatives of the group of cycloalkanedicarboxylic acids (these acids and their derivatives are widely used in pharmaceutical industry). Taking into account that the majority of drugs are weak acids or bases and their dissociation parameters have a strong influence on the biopharmaceutical properties of drugs and their intermediates, knowledge of these parameters is very important. In this work the regularities of the electrolytic dissociation of biologically active camphoric acid were determined with the aid of original equations suggested by us for the calculation of the dissociation parameters of weak multibasic organic acids with "overlapping" equilibria [1-9].

In the case of dibasic weak organic acid with "overlapping" equilibria the mass action equations may be presented as follows:

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

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

where 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, α_2' is the "partial" degree of dissociation of the second step (this term was first suggested by us [8,9]), c is the total 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 the 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 value of the "partial" degree of dissociation α_2' according to equation (2) can be determined 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 calculated with the aid of the Debye-Huckel expression:

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

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 $I = c(\alpha_1 + 2\alpha_2) = c\alpha_1(1+2\alpha_2')$.

With the aid of equations (5), (6) and (8) the values of the "usual" and "partial" degrees of dissociation for dilute (0.0001-0.01M) solutions of D-camphoric acid have been calculated. The K_1 and K_2 values for this acid (K_1=2.7x10^{-5}; K_2=8x10^{-6}) were taken from [10]. The α_1, α_2, α_2' and pH values for the dilute solutions of D-camphoric acid at 25ºC are presented in Table 1. The concentrations of dissociated and undissociated forms may be determined with the aid of the following equations:

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

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

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

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

Taking into account the comparative complexity of calculations with the aid of equations (5) and (6), we obtained simple empirical equations for fast approximate calculation of the α_1, α_2, α_2' and pH values for the dilute solutions of D-camphoric acid (concentration range c=0.0001-0.01M):

$$\alpha_1 = 0.008531c^{-0.42} \quad (14)$$

$$\alpha_2 = 1.5488\times10^{-5}c^{-0.9} \quad (15)$$

$$\alpha_2' = 1.8155\times10^{-3}c^{-0.48} \quad (16)$$

$$pH = 2.177 - 0.538\lg c \quad (17)$$

The difference between the results obtained with the aid of these equations and the accurate values presented in Table 1 does not exceed 10%.

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Table 1.

The parameters of dissociation of D-camphoric acid in dilute solutions at 25º

Concentration of acid, M	α_1	α_2	α_2'	pH
0.0001	0.4075	0.06105	0.1498	4.333
0.0002	0.3100	0.03350	0.1081	4.167
0.0003	0.2616	0.02331	0.0891	4.073
0.0004	0.2312	0.01794	0.0776	4.007
0.0005	0.2096	0.01462	0.0697	3.956
0.0006	0.1934	0.01236	0.0639	3.914
0.0007	0.1805	0.01071	0.0593	3.879
0.0008	0.1700	0.00946	0.0556	3.849
0.0009	0.1611	0.00847	0.0526	3.823
0.001	0.1536	0.00768	0.0500	3.799
0.002	0.1115	0.00399	0.0358	3.644
0.004	0.0804	0.00206	0.0256	3.490
0.006	0.0663	0.00140	0.0212	3.401
0.008	0.0578	0.00106	0.0184	3.338
0.01	0.0519	0.00086	0.0165	3.289

ფიზიკური ქიმია

ქაფურის მჟავას ელექტროლიტური დისოციაციის კანონზომიერებები

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** რ. აგლაძის არაორგანული ქიმიისა და ელექტროქიმიის ინსტიტუტი, თბილისი*

(წარმოდგენილია აკადემიის წევრის გ. ცინცაძის მიერ)

ავტორების მიერ შემოთავაზებული ორიგინალური განტოლებების დახმარებით გათვლილია ბიოლოგიურად აქტიური D-ქაფურის მჟავას ელექტროლიტური დისოციაციის ორივე საფეხურის ჩვეულებრივი და "პარციალური" ხარისხები და pH-ის სიდიდეები მჟავას განზავებული ხსნარების კონცენტრაციის ინტერვალში 0.0001-0.01M. მიღებულია აგრეთვე მარტივი ემპირიული განტოლებები დისოციაციის ხარისხებისა და ხსნართა pH-ის მნიშვნელობების სწრაფი მიახლოებითი გათვლისათვის მჟავას კონცენტრაციის აღნიშნულ ინტერვალში.

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