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THE ELECTROLYTIC DISSOCIATION OF METHYLENE SUCCINIC ACID

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Abstract: The work deals with the analysis of regularities of the electrolytic dissociation of alkene derivative of the succinic acid (methylene succinic acid) in their dilute (0.0001-0.01M) solutions carried out by means of a new method of determination of dissociation parameters of weak multibasic organic acids with “overlapping equilibriums” effect previously described by the authors. Values of usual and “partial” degrees of dissociation, concentrations of all anions, hydrogen ions and undissociated acid molecules, as well as activity coefficients of all charged dissociation products were calculated. The concentration intervals of predominance of various charged and uncharged substances in the dilute solutions of the above mentioned acid were determined. Together with accurate equations, there were also suggested simple empirical equations for quick approximate determination of various dissociation parameters.

Keywords: dissociation constants, degree of dissociation, weak organic acids, equations, dissociation step.

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Introduction

Previously we described an original method for determination of various dissociation parameters of weak multibasic organic acids with close values of stepwise dissociation constants (effect of “overlapping equilibriums”) [1-4]. This method was widely used for an analysis of various weak organic acids with different basicity in their dilute solutions. A term the “partial” degree of dissociation was also suggested [2] and used for more detailed analysis of complex equilibriums typical for dissolution processes of such acids. In this work our method is

applied for the research into peculiarities of electrolytic dissociation of alkene derivative of the succinic acid (methylene succinic acid) in their dilute (0.0001-0.01M) solutions. Succinic acid and its various derivatives are widely used in the organic synthesis and polymer industry, take part in biologically important Krebs cycle. Methylene succinic acid is widely used in the production of polyacrylonitrile and polyacrylic fiber. The useful properties of these acids are directly connected with peculiarities of their electrolytic dissociation.

The Equations

In case of weak dibasic organic acid H_2A the mass action equations for both dissociation steps may be written as follows [1-4]:

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

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

where K_1 and K_2 are the thermodynamic dissociation constants of first and second steps, α_1 and α_2 are usual degrees of dissociation of the corresponding steps, α_2' is the "partial" degree of dissociation for second step, c is the total concentration of acid, F_1 and F_2 are the quotients of the activity coefficients:

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

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

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

$$\alpha_2' = \frac{1}{2} \left[-\left(1 + \frac{K_2}{\alpha_1 cF_2}\right) + \sqrt{\left(1 + \frac{K_2}{\alpha_1 cF_2}\right)^2 + \frac{4K_2}{\alpha_1 cF_2}} \right] \quad (7)$$

Values of "partial" degrees of dissociation may be calculated with the help of the following equations:

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

or with the help of the more complex equation as set forth in [2].

Note that values of activity coefficients can be approximated by the Debye-Huckel equation:

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

where a_i is the cation-anion distance of closest approach, A and B are constants depending on properties of water at a given temperature, z_i is the charge of ion. The ionic strength is $I = c(\alpha_1 + 2\alpha_2) = c\alpha_1(1 + 2\alpha_2')$. Note that values of a_i , A and B at 25°C were taken

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

Degrees of dissociation α_1 , α_2 and α_2' may be evaluated successively by iterative solution of the following quadratic equations:

from [5]. The activity coefficient of undissociated acid is assumed to be unity. Values of dissociation constants of methylene succinic acid at 25°C necessary for calculations were taken from [6-7]: $K_1 = 1.41 \times 10^{-4}$; $K_2 = 3.55 \times 10^{-6}$.

Using the above mentioned dissociation parameters, we can determine equilibrium concentrations of hydrogen ions, mono and dianions and undissociated acid molecules:

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

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

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

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

With the aid of the Eqs. (10)-(13), we can determine intervals of the acid concentration where various charged or uncharged substances dominate. This is possible due to equations below that express equality conditions of various products of dissociation:

$$[H^+] = [H_2A]: \alpha_1 = \frac{1 - \alpha_2}{2} = \frac{1}{\alpha_2' + 2} \quad (14)$$

$$[HA^-] = [H_2A]: \alpha_1 = \frac{1 + \alpha_2}{2} = \frac{1}{2 - \alpha_2'} \quad (15)$$

$$[A^{2-}] = [H_2A]: \alpha_1 = 1 - \alpha_2 = \frac{1}{\alpha_2' + 1} \quad (16)$$

$$[A^{2-}] = [HA^-]: \alpha_1 = 2\alpha_2 \quad (17)$$

$$\alpha_2' = 0.5 \quad (18)$$

In line with concentration conditions, the equality of dominance areas of mono and dianions and undissociated acid molecules may be formulated.

The results and discussion

In Table 1, the α_1 , α_2 , α_2' and pH values for dilute solutions (0.0001-0.01M) of analyzed acid are presented.

Table 1. Values of dissociation parameters of dilute solutions of methylene succinic acid at 25°C

Acid concentration, M	α_1	α_2	α_2'	pH
0.0001	0.6796	0.03222	0.04741	4.152
0.0002	0.5625	0.01753	0.03116	3.941
0.0004	0.4481	0.009069	0.02024	3.745
0.0006	0.3864	0.006145	0.01590	3.635
0.0008	0.3460	0.004659	0.01347	3.560
0.001	0.3167	0.003758	0.01187	3.503
0.002	0.2376	0.001925	0.008102	3.330
0.004	0.1755	0.000986	0.005620	3.164
0.006	0.1463	0.000667	0.004561	3.068
0.008	0.1283	0.000506	0.003942	3.002
0.01	0.1158	0.000408	0.003524	2.950

The comparison of the α_2 and α_2' values goes to show that values of the "partial" degree of dissociation (which more correctly characterize the completeness of dissociation at second step) exceed appreciably those of the usual degree of dissociation (especially in higher acid concentrations).

With the aid of the equations (14)-(18), areas of predominance of various charged and uncharged forms in the dilute solutions of methylene succinic acid were identified. Calculations show that the monoanion concentration exceeds the $[H_2A]$ value when $c < 0.0003M$. In all these cases the inequalities:

$$\alpha_1 > \frac{1 + \alpha_2}{2} \quad \text{and} \quad \alpha_1 > \frac{1}{2 - \alpha_2'}$$

Regions of prevailing $[H^+]$ values in comparison with the $[H_2A]$ values are also: $c < 0.0003M$. In

all these cases the inequalities: $\alpha_1 > \frac{1 - \alpha_2}{2}$ and

$$\alpha_1 > \frac{1}{2 + \alpha_2}$$

were fulfilled. As a whole, analyzed concentration interval the $[HA^-]$ and $[H^+]$ values exceed the $[A^{2-}]$ values.

To sum up, allowing for the comparative complexity of calculations by

means of equations (5)-(7), we suggest simple empirical equations for quick approximate determination of values of usual and “partial”

degrees of dissociation and pH in the dilute solutions of methylene succinic acid.

Methylene succinic acid

$$\alpha_1 = \lg(0.17742c^{-0.355}) \quad (\text{up to } 0.0001\text{M}) \quad (19)$$

$$\alpha_2 = 5.7544 \cdot 10^{-6} c^{-0.939} \quad (\text{up to } 0.006\text{M}) \quad (20)$$

$$\alpha_2' = 1.85353 \cdot 10^{-4} c^{-0.602} \quad (\text{up to } 0.004\text{M}) \quad (21)$$

$$\text{pH} = 1.575 - 0.641 \lg c \quad (\text{up to } 0.01\text{M}) \quad (22)$$

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METİLENKƏHRƏBA TURŞUSUNUN ELEKTROLİTİK DİSSOSİASİYASI

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Çoxəsaslı zəif üzvi turşuların dissosiasiya parametrlərinin yeni təyin metodu ilə metilenkəhrəba turşusunun duru məhlullarda (0.0001-0.01 M) elektrolitik dissosiasiyasının qanunauyğunluğu təhlil edilmişdir. Dissosiasiya parametrlərinin təyini üçün dəqiq tənliklərlə yanaşı sadə empirik tənliklər təklif olunur.

Açar sözlər : metilenkəhrəba turşusu, elektrolitik dissosiasiya, zəif üzvi turşular, tənlik

ЭЛЕКТРОЛИТИЧЕСКАЯ ДИССОЦИАЦИЯ МЕТИЛЕНЯНТАРНОЙ КИСЛОТЫ**Е.Р. Кварацхелия и Р.Р. Куртанидзе**

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В данной работе проведен анализ закономерностей электролитической диссоциации алкенпроизводной янтарной кислоты (метиленянтарной кислоты) в ее разбавленных (0.0001-0.01M) растворах с помощью нового метода определения параметров диссоциации слабых многоосновных органических кислот с эффектом «перекрывающихся равновесий», ранее описанным авторами. Были рассчитаны значения обычных и «парциальных» степеней диссоциации, концентрации всех анионов, ионов водорода и недиссоциированных молекул кислот, коэффициенты активности всех заряженных продуктов диссоциации. Также рассчитаны концентрационные интервалы преобладания различных заряженных и незаряженных частиц в разбавленных растворах указанной кислоты. Вместе с точными уравнениями были также предложены простые эмпирические уравнения для быстрого приближённого расчёта значений параметров диссоциации.

Ключевые слова: константы диссоциации, степень диссоциации, слабые органические кислоты, уравнения, ступени диссоциации.