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PECULIARITIES OF ELECTROLYTIC DISSOCIATION OF ETHYL DERIVATIVES OF SUCCINIC ACID

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The original method suggested by authors for the analysis of processes of electrolytic dissociation of weak multibasic organic acids was used for the calculation of dissociation parameters of ethyl derivatives of succinic acids: DL-2,3-diethylsuccinic and meso-2,3-diethylsuccinic acids. The values of dissociation degrees of separate steps (including "partial" dissociation degrees of the second step), concentrations of various ionized and non-ionized forms, activity coefficients of hydrogen ions and mono and dianions in the dilute (0.0001-0.01M) solutions of these acids have been calculated. The concentration intervals of predominance of various charged and uncharged substances in the dilute solutions of the above mentioned acids determined. Also suggested are simple empirical equations for fast approximate calculation of the dissociation parameters.

Keywords: *weak organic acids, dissociation constant, dissociation step ,hydrogen ions concentration, equations*

1. INTRODUCTION

Succinic acid and its various derivatives are widely used in the organic synthesis and polymer industry and involved in the biologically important Krebs cycle. Many useful properties of these acids are directly connected with interesting peculiarities of behavior of these acids in the solutions and, in particular, with regularities of their electrolytic dissociation. The paper provides an analysis of regularities in the electrolytic dissociation of DL-2,3-diethylsuccinic and meso-2,3-diethylsuccinic acids in the diluted (0.0001-0.01M) solutions which was carried out with the help of a new method of determination of dissociation parameters of weak multibasic organic acids with the "overlapping "equilibriums previously described by the authors[1-5].

2. 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]:

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

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

(2)

where K_1 and K_2 are thermodynamic dissociation constants of first and second steps; and α_1 and α_2 are usual degrees of dissociation of corresponding steps; $\alpha_2^{'}$ is "partial" degree of dissociation for second step; c is total concentration of the acid; F_1 and F_2 are quotients of activity coefficients:

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

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

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

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

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

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

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

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

or with the aid of the more complex equation presented in [3].

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

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

where a_i is cation-anion distance of the closest approach; A and B are constants depending on the properties of water at given temperature; z_i is ion charge with the ionic strength $I = c(\alpha_1 + 2\alpha_2) = c\alpha_1(1 + 2\alpha_2')$. Note that the values of a_i, A and B at 25ºC have been taken from [6], while the activity coefficient of undissociated acid is assumed to make up integrity. The values of dissociation constants of ethyl derivatives of succinic acid at 25ºC needed for calculations were taken from [7-8]: DL-2,3-diethylsuccinic acid: K_1=2.34×10^{-4}; K_2=7.47×10^{-7}, meso-2,3-diethylsuccinic acid: K_1=2.88×10^{-4}; K_2=2.57×10^{-7}.

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

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

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

$$[H^+] = c(\alpha_1 + \alpha_2) = c\alpha_1(1 + \alpha_2') \; (12) \; [H_2A] = c(1 - \alpha_1) \qquad (13)$$

With the help 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 the following equations that disclose equality conditions of the various products of dissociation:

$$[H^{+}]=[H_{2}A]:\alpha_{1}=\frac{1-\alpha_{2}}{2}=\frac{1}{\alpha_{2}^{'}+2} \qquad (14)$$

$$[HA^{-}]=[H_{2}A]:\alpha_{1}=\frac{1+\alpha_{2}}{2}=\frac{1}{2-\alpha_{2}^{'}} \qquad (15)$$

$$[A^{2-}]=[H_{2}A]:\alpha_{1}=1-\alpha_{2}=\frac{1}{\alpha_{2}^{'}+1} \qquad (16)$$

$$[A^{2-}]=[HA^{-}]:\alpha_{1}=2\alpha_{2} \qquad (17)$$

$$\alpha_{2}^{'}=0.5 \qquad (18)$$

Pursuant to the conditions of concentrations equality, areas of dominance of mono and dianions, as well as undissociated acid molecules may be formulated.

3. RESULTS AND DISCUSSION

Tables 1 and 2 provide the α_1, α_2, $\alpha_2^{'}$ and pH values for the diluted solutions (0.0001-0.01M) of the reviewed ethyl derivatives of succinic acid.

Table 1. Values of dissociation parameters for the diluted solutions of DL-2,3-diethylsuccinic acid at 25ºC

Acid concentration, M	**α_1**	**α_2**	**$\alpha_2^{'}$**	**pH**
0.0001	0.7588	0.003579	0.004717	4.112
0.0002	0.6491	0.001818	0.002801	3.891
0.0004	0.5320	0.000924	0.001736	3.678
0.0006	0.4655	0.000622	0.001337	3.561
0.0008	0.4203	0.000470	0.001118	3.482
0.001	0.3871	0.000378	0.000977	3.421
0.002	0.2950	0.000193	0.000654	3.240
0.004	0.2206	0.000099	0.000447	3.068
0.006	0.1848	0.000067	0.000361	2.970
0.008	0.1627	0.000051	0.000311	2.902
0.01	0.1472	0.000041	0.000277	2.849

Table 2. Values of dissociation parameters for the diluted solutions of meso-2,3-diethylsuccinic acid at 25ºC

Acid concentration, M	**α_1**	**α_2**	**α'_2**	**pH**
0.0001	0.7885	0.002660	0.003373	4.106
0.0002	0.6838	0.001350	0.001974	3.869
0.0004	0.5676	0.000686	0.001209	3.651
0.0006	0.4997	0.000462	0.000925	3.531
0.0008	0.4533	0.000349	0.000771	3.449
0.001	0.4186	0.000281	0.000672	3.388
0.002	0.3214	0.000144	0.000447	3.204
0.004	0.2417	0.000074	0.000304	3.029
0.006	0.2031	0.000050	0.000245	2.930
0.008	0.1790	0.000038	0.000210	2.861
0.01	0.1621	0.000031	0.000189	2.808

The comparison of the α_2 and α'_2 values shows that the values of "partial" degree of dissociation (which more correctly characterizes the completeness of dissociation at the second step) exceed appreciably the values of usual degree of dissociation (especially in case of lower K_1 values and higher acid concentrations).

With the help of the equations (14)-(18) areas of a predominance of various charged and uncharged forms in the diluted solutions of the reviewed methyl derivatives of succinic acid were determined. Calculations go to show that the monoanion concentration exceeds the $[H_2A]$ value where c ≤ 0.0005M (for both acids). In all cases the in equalities: $\alpha_1 > \frac{1+\alpha_2}{2}$ and $\alpha_1 > \frac{1}{2-\alpha'_2}$ are fulfilled. Areas of prevailing $[H^+]$ values in comparison with the $[H_2A]$ values are as follows: c < 0.0005M (DL-2,3-diethylsuccinic acid) and c < 0.0006M(meso-2,3-diethylsuccinic acid). In all cases the inequalities: $\alpha_1 > \frac{1-\alpha_2}{2}$ and $\alpha_1 > \frac{1}{2+\alpha'_2}$ are fulfilled.

To conclude, when adjusted for the comparative complexity of calculations through the use of the equations (5)-(7), we suggest simple empirical equations for the prompt approximate determination of the values of usual and "partial" degrees of dissociation and pH in the diluted solutions of all reviewed derivatives of succinic acid.

DL-2,3-diethylsuccinic acid

$$\alpha_1 = \lg(0.18664c^{-0.372}) \qquad (19)$$

(up to c = 0.002M)

$$\alpha_2 = 4.46684\times10^{-7}c^{-0.976} \qquad (20)$$

(up to c = 0.01M)

$$\alpha'_2 = 9.0365\times10^{-6}c^{-0.675} \qquad (21)$$

(up toc = 0.001M)

$$pH = 1.324 - 0.6971\lg c \qquad (22)$$

(up to c = 0.01M)

Meso-2,3-diethylsuccinic acid

$$\alpha_1 = \lg(0.19953c^{-0.372}) \qquad (23)$$

(up to c = 0.002M)

$$\alpha_2 = 3.31894\times10^{-7}c^{-0.976} \qquad (24)$$

(up to c = 0.01M)

$$\alpha_2' = 5.19996\times10^{-6}c^{-0.7} \qquad (25)$$

(up to c = 0.003M)

$$pH = 1.221 - 0.7191\lg c \qquad (26)$$

(up to c = 0.001M)

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ОСОБЕННОСТИ ЭЛЕКТРОЛИТИЧЕСКОЙ ДИССОЦИАЦИИ ЭТИЛПРОИЗВОДНЫХ ЯНТАРНОЙ КИСЛОТЫ

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Оригинальный метод, предложенный авторами для анализа процессов электролитической диссоциации слабых многоосновных органических кислот, был использован для расчета параметров диссоциации этилпроизводных янтарной кислоты: DL-2,3-диэтилянтарной и мезо-2,3-диэтилянтарной кислот. Были рассчитаны значения степеней диссоциации отдельных ступеней (включая «парциальные» степени диссоциации второй ступени), концентраций различных ионизированных и *неионизированных форм, коэффициентов активности ионов водорода и моно- и дианионов в разбавленных (0.0001-0.01M) растворах данных кислот. Также рассчитаны концентрационные интервалы преобладания различных заряженных и незаряженных частиц в разбавленных растворах указанных кислот. Предложены простые эмпирические уравнения для быстрого приближённого расчёта значений параметров диссоциации.*

Ключевые слова: *слабые органические кислоты, константы диссоциации, степени диссоциации, концентрация ионов водорода, уравнения.*

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