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**THE ELECTROLYTIC DISSOCIATION OF METHYL DERIVATIVES OF
SUCCINIC ACID**

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Using the authors' suggested methods, 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 methyl derivatives of succinic acid: methyl succinic, DL-1,2-dimethylsuccinic and meso-1,2-dimethylsuccinic acids have been calculated. Concentration intervals of predominance of various charged and uncharged substances in the dilute solutions of all the acids mentioned above have been identified. Simple empirical equations for fast approximate calculation of the dissociation parameters have also been suggested.

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 actively involved in the biologically important Krebs cycle. Many useful properties of these acids are directly connected with interesting peculiarities of these acids' behavior in the solutions and, in particular, with regularities of their electrolytic dissociation. The paper focuses on the analysis

of regularities of the electrolytic dissociation of methylsuccinic, DL-1,2-dimethylsuccinic and meso-1,2-dimethylsuccinic acids in their dilute (0.0001-0.01M) solutions through the use of a new method of the establishment of dissociation parameters of weak multi-basic organic acids by "overlapping" equilibriums previously described by authors[1-4].

2. THE EQUATIONS

All acids analyzed in the paper are vivid values of dissociation constants of the acids examples of weak dibasic organic acids with presented in Table 1. "overlapping" equilibriums. Evidence to this are

Table 1. The dissociation constants of methyl derivatives of succinic acid

Acid	K_1	K_2	Reference
Methyl succinic	7.413×10^{-5}	2.291×10^{-6}	[5]
DL-1,2-Dimethylsuccinic	1.175×10^{-4}	1.000×10^{-6}	[6]
meso-1,2- Dimethyl succinic	1.698×10^{-4}	4.365×10^{-6}	[6]

Regularities of the dilution for both dissociation steps of weak dibasic organic acid with the effect of “overlapping” equilibria may be expressed by the following equations:

$$K_1 = \frac{c(\alpha_1^2 - \alpha_2^2)}{1 - \alpha_1} F_1 = \frac{\alpha_1^2 [1 - (\alpha_2')^2] c}{1 - \alpha_1} F_1 = \frac{x_1^2 - x_2^2}{c - x_1} F_1 \quad (1)$$

$$K_2 = \frac{c\alpha_2(\alpha_1 + \alpha_2)}{\alpha_1 - \alpha_2} F_2 = \frac{\alpha_1 \alpha_2' (1 + \alpha_2') c}{1 - \alpha_2'} F_2 = \frac{x^2 (x_1 + x_2)}{x_1 - x_2} F_2 \quad (2)$$

where K_1 and K_2 are the thermodynamic dissociation constants for first and second steps, α_1 and α_2 are the usual degrees of dissociation for these steps, α_2' is the “partial” degree of dissociation for the second step, x_1 and x_2 are contributions of the first and second steps to the $[H^+]$ value ($[H^+] = x_1 + x_2$), where c is the total (analytical) concentration of acid, F_1 and F_2 are the quotients of the activity coefficients:

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

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

According to the equations (1) and (2), the α_1 , α_2 , α_2' , x_1 and x_2 values may be evaluated successively by iterative solution of the following equations:

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

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

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

$$x_1 = \frac{1}{2} \left[-\frac{K_1}{F_1} + \sqrt{\left(\frac{K_1}{F_1}\right)^2 + 4\left(x_2^2 + \frac{K_1 c}{F_1}\right)} \right] \quad (8)$$

$$x_2 = \frac{1}{2} \left[-\left(\frac{K_2}{F_2} + x_1\right) + \sqrt{\left(\frac{K_2}{F_2} + x_1\right)^2 + \frac{4K_2 x_1}{F_2}} \right] \quad (9)$$

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

$$[H^+] = c(\alpha_1 + \alpha_2) = c\alpha_1(1 + \alpha_2') = x_1 + x_2 \quad (10)$$

$$[HA^-] = c(\alpha_1 - \alpha_2) = c\alpha_1(1 - \alpha_2') = x_1 - x_2 \quad (11)$$

$$[A^{2-}] = c\alpha_2 = c\alpha_1\alpha_2' = x_2 \quad (12)$$

$$[H_2A] = c(1 - \alpha_1) = c\left(\frac{\alpha_2' - \alpha_2}{\alpha_2'}\right) = c - x_1 \quad (13)$$

In considering the equations above, we can formulate conditions for equality of concentrations of the ionized and non-ionized forms:

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

$$c = 2x_1 + x_2 \quad (15)$$

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

$$c = 2x_1 - x_2 \quad (17)$$

$$[A^{2-}] = [H_2A]: \alpha_1 = 1 - \alpha_2 = \frac{1}{\alpha_2' + 1} \quad (18)$$

$$c = x_1 + x_2 \quad (19)$$

$$[A^{2-}] = [HA^-]: \alpha_1 = 2\alpha_2 \quad (20)$$

$$\alpha_2' = 0.5 \quad (21)$$

$$x_1 = 2x_2 \quad (22)$$

Pursuant to these conditions of the concentrations equality, the areas of dominance of mono and dianions and undissociated acid molecules may be identified.

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

$$\lg f_i = -\frac{z_i^2 A \sqrt{I}}{1 + a_i B \sqrt{I}} \quad (23)$$

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, and z_i is the charge of ion. The ionic effect is $I = c(\alpha_1 + 2\alpha_2) = c\alpha_1(1 + 2\alpha_2') = x_1 + 2x_2$. The values of a_i , A and B at 25°C were taken from [7]. The activity coefficient of undissociated acid is assumed to be single.

3. THE RESULTS AND DISCUSSION

Tables 2-4 presents the α_1 , α_2 , α_2' and pH values for the dilute solutions (0.0001-0.01M) of analyzed methyl derivatives of succinic acid.

Table 2. The values of the dissociation parameters for the dilute solutions of methyl succinic acid at 25°C

Acid concentration, M	α_1	α_2	α_2'	pH
0.0001	0.5701	0.02199	0.03857	4.231
0.0002	0.4548	0.01139	0.02504	4.035
0.0004	0.3515	0.00585	0.01665	3.851
0.0006	0.2989	0.00396	0.01323	3.747
0.0008	0.2653	0.00299	0.01129	3.676
0.001	0.2414	0.00241	0.00998	3.621
0.002	0.1783	0.00123	0.00690	3.454
0.004	0.1302	0.00063	0.00482	3.292
0.006	0.1080	0.00042	0.00393	3.199
0.008	0.0944	0.00032	0.00340	3.133
0.01	0.0850	0.00026	0.00304	3.083

The comparison of the α_2 and α_2' values shows that the values of the “partial” degree of dissociation (which more correctly characterize the completeness of dissociation at the second step) exceed appreciably those of the usual degree of dissociation (especially in case of the low K_1 values and higher acid concentrations).

With the help of the equations (14)-(22), the areas of predominance of various charged and uncharged forms in the dilute solutions of analyzed methyl derivatives of

succinic acid have been determined. The calculations show that the monoanion concentration exceeds the $[H_2A]$ value when $c \leq 0.0001M$ (methyl succinic acid) and $c < 0.0003M$ (DL-1,2-dimethylsuccinic and meso-1,2-dimethylsuccinic acids). In all the cases above, the inequalities: $\alpha_1 > \frac{1-\alpha_2}{2}$, $\alpha_1 > \frac{1}{2+\alpha_2}$ and $c < 2x_1 + x_2$ are carried out.

Table 3. The values of the dissociation parameters for the dilute solutions of DL-1,2-dimethylsuccinic acid at 25°C

Acid concentration, M	α_1	α_2	α_2'	pH
0.0001	0.6487	0.01007	0.01552	4.185
0.0002	0.5312	0.00514	0.00968	3.975
0.0004	0.4192	0.00262	0.00625	3.779
0.0006	0.3600	0.00177	0.00490	3.671
0.0008	0.3215	0.00133	0.00415	3.596
0.001	0.2937	0.00107	0.00365	3.539
0.002	0.2193	0.00055	0.00249	3.367
0.004	0.1614	0.00028	0.00173	3.201
0.006	0.1343	0.00019	0.00140	3.106
0.008	0.1177	0.00014	0.00121	3.026
0.01	0.1062	0.00011	0.00108	2.988

Table 4. The values of the dissociation parameters for the dilute solutions of meso-1,2-dimethylsuccinic acid at 25°C

Acid concentration, M	α_1	α_2	α_2'	pH
0.0001	0.7101	0.04056	0.05712	4.827
0.0002	0.5947	0.02139	0.03597	3.915
0.0004	0.4783	0.01111	0.02323	3.715
0.0006	0.4146	0.00754	0.01819	3.604
0.0008	0.3723	0.00573	0.01538	3.528
0.001	0.3415	0.00462	0.01353	3.470
0.002	0.2575	0.00237	0.00921	3.295
0.004	0.1911	0.00122	0.00637	3.127
0.006	0.1595	0.00082	0.00517	3.031
0.008	0.1401	0.00063	0.00446	2.964
0.01	0.1266	0.00050	0.00399	2.912

Areas of prevailing $[H^+]$ values in comparison with the $[H_2A]$ values are as follows: $c < 0.0002M$ (methylsuccinic acid), $c < 0.0003M$ (DL-1,2-dimethylsuccinic acid) and $c < 0.0004M$ (meso-1,2-dimethylsuccinic acid). In all the cases above, the inequalities: $\alpha_1 > \frac{1-\alpha_2}{2}$, $\alpha_1 > \frac{1}{2+\alpha_2}$ and $c < 2x_1 + x_2$ are carried out.

To conclude, in considering the comparative complexity of calculations made with the help of the equations (5)-(9), we also suggest simple empirical equations for prompt approximate identification of the values of usual and "partial" degrees of dissociation and pH in the dilute solutions of all analyzed derivatives of succinic acid.

Methylsuccinic acid

$$\alpha_1 = 0.018156 c^{-0.375} \quad (24)$$

(up to c = 0.002M)

$$\alpha_2 = 3.177 \times 10^{-6} c^{-0.96} \quad (25)$$

(up to c = 0.01M)

$$\alpha_2' = 1.7498 \times 10^{-4} c^{-0.585} \quad (26)$$

(up to c = 0.002M)

$$pH = 1.795 - 0.606 \lg c \quad (27)$$

(up to c = 0.01M)

DL-1,2-Dimethylsuccinic acid

$$\alpha_1 = \lg(0.16827 c^{-0.354}) \quad (28)$$

(up to c = 0.001M)

$$\alpha_2 = 1.30317 \times 10^{-6} c^{-0.972} \quad (29)$$

(up to c = 0.01M)

$$\alpha_2' = 4.57088 \times 10^{-5} c^{-0.632} \quad (30)$$

(up to c = 0.002M)

$$pH = 1.595 - 0.645 \lg c \quad (31)$$

(up to c = 0.01M)

meso-1,2-Dimethylsuccinic acid

$$\alpha_1 = \lg(0.17498 c^{-0.365}) \quad (32)$$

(up to c = 0.001M)

$$\alpha_2 = 6.85488 \times 10^{-6} c^{-0.943} \quad (33)$$

(up to c = 0.01M)

$$\alpha_2' = 1.72584 \times 10^{-4} c^{-0.628} \quad (34)$$

(up to c = 0.002M)

$$pH = 1.499 - 0.655 \lg c \quad (35)$$

(up to c = 0.01M)

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**ЭЛЕКТРОЛИТИЧЕСКАЯ ДИССОЦИАЦИЯ МЕТИЛПРОИЗВОДНЫХ
ЯНТАРНОЙ КИСЛОТЫ**

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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 метилпроизводных янтарной кислоты: метилянтарной, DL-1,2-диметилянтарной и мезо-1,2-диметилянтарной кислот были рассчитаны с помощью предложенных авторами методов. Рассчитаны концентрационные интервалы преобладания различных заряженных и незаряженных частиц в разбавленных растворах указанных кислот. Предложены также простые эмпирические уравнения для быстрого приближённого расчёта значений параметров диссоциации.

Ключевые слова: *слабые органические кислоты, константа диссоциации, степень диссоциации, концентрация ионов водорода, уравнения.*

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