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Electrochemistry

The Electrolytic Dissociation of Trans- and Cis-Epoxysuccinic Acids

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ABSTRACT. In this work an analysis of the regularities of the electrolytic dissociation of alkene derivatives of the succinic acid (trans and cis-epoxysuccinic acids) in their dilute (0.0001-0.01M) solutions was carried out with the aid of a new method of determination the dissociation parameters of weak multibasic organic acids with the "overlapping equilibria" effect previously described by authors. Values of the usual and "partial" degrees of dissociation, the concentrations of all anions, hydrogen ions and undissociated acid molecules, the activity coefficients of all charged dissociation products were calculated. Together with the accurate equations were also suggested the simple empirical equations for fast approximate determination of the various dissociation parameters. *© 2019 Bull. Georg. Natl. Acad. Sci.*

Key words: dissociation constants, degree of dissociation, weak organic acids, equations, dissociation step

Succinic acid and its various derivatives are widely used in the organic synthesis and polymer industry, participate in the biologically important Krebs cycle. Trans and cis-epoxysuccinic acids are used for producing mezo and L-tartaric acids and they are also involved in various microbiological transformations. The useful properties of these acids are directly connected with the peculiarities of their electrolytic dissociation.

Previously we described the original method for determination of various dissociation parameters of weak multibasic organic acids with the close values of stepwise dissociation constants (the effect of "overlapping equilibria") [1-5]. The term of the "partial" degree of dissociation was also suggested [2] and used for a more detailed analysis of the complex equilibria existing in the processes of dissociation of such acids. In this work our method is applied for the study of the peculiarities of electrolytic dissociation of the alkene derivatives of succinic acid: trans and cis-epoxysuccinic acids in their dilute (0.0001-0.01M) solutions.

In case of weak dibasic organic acid H_2A the mass action equations for both dissociation steps may be written as follows [1,2]:

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

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

where K_1 and K_2 are the thermodynamic dissociation constants of the first and second steps, α_1 and α_2 are the 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:

$$F_1 = \frac{f_{H^+} f_{HA^-}}{f_{H_2A}} \tag{3}$$

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

The degrees of dissociation α_1, α_2 and α'_2 may be evaluated successively by iterative solution of the following quadratic equations:

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

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

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

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

$$\alpha_2' = \alpha_2 / \alpha_1 \tag{8}$$

or with the aid of the more complex equation presented in [2].

The values of the activity coefficients were approximated by the Debye-Huckel equation (12):

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

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 values of a_i, A and B at 25ºC were taken from [6]. The activity coefficient of undissociated acid is assumed to be unity. The values of the dissociation constants of alkene derivatives of succinic acid at 25ºC necessary for calculations were taken from [7,8]: trans-epoxysuccinic acid: K_1=0.01175; K_2=5.623×10^{-4}, cis-epoxysuccinic acid: K_1=0.01148; K_2=1.202×10^{-4}.

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

$$[H^+] = c(\alpha_1 + \alpha_2) = c\alpha_1(1 + \alpha_2') \tag{10}$$

$$[HA^-] = c(\alpha_1 - \alpha_2) = c\alpha_1(1 - \alpha_2') \tag{11}$$

$$[A^{2-}] = c\alpha_2 = c\alpha_1\alpha_2' \tag{12}$$

$$[H_2A] = c(1 - \alpha_1) \tag{13}$$

With the aid of these equations we can determine the intervals of the acid concentration in which the various charged or uncharged substances dominate. This is possible according to the following equations expressed the conditions of equality of the various products of dissociation:

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

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

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

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

$$\alpha_2' = 0.5 \tag{18}$$

In Tables 1 and 2 the values of α_1, α_2, α'_2 and pH for the dilute solutions of both acids are presented.

Table 1. The values of the dissociation parameters of trans-epoxysuccinic acid at 25ºC

Acid concentration, M	α_1	α_2	α'_2	pH
0.0001	0.9966	0.7711	0.7737	3.760
0.0002	0.9905	0.6476	0.6538	3.495
0.0004	0.9768	0.5057	0.5177	3.240
0.0006	0.9632	0.4222	0.4383	3.095
0.0008	0.9503	0.3656	0.3847	2.994
0.001	0.9380	0.3241	0.3455	2.917
0.002	0.8853	0.2129	0.2405	2.681
0.004	0.8085	0.1317	0.1629	2.452
0.006	0.7531	0.09731	0.1292	2.323
0.008	0.7102	0.07791	0.1097	2.233
0.01	0.6753	0.06534	0.09676	2.166

Table 2. The values of the dissociation parameters of cis-epoxysuccinic acid at 25ºC

Acid concentration, M	α_1	α_2	α'_2	pH
0.0001	0.9934	0.4645	0.4678	3.843
0.0002	0.9854	0.3271	0.3319	3.590
0.0004	0.9702	0.2134	0.2200	3.336
0.0006	0.9561	0.1610	0.1684	3.187
0.0008	0.9430	0.1303	0.1382	3.081
0.001	0.9307	0.1099	0.1181	2.998
0.002	0.8783	0.06298	0.07171	2.745
0.004	0.8021	0.03513	0.04380	2.501
0.006	0.7469	0.02479	0.03319	2.364
0.008	0.7041	0.01932	0.02744	2.270
0.01	0.6693	0.01591	0.02377	2.198

With the aid of the equations (14)-(18) the areas of a predominance of various charged and uncharged forms in the dilute solutions of studied alkene derivatives of succinic acid have been determined. For both acids in whole studied concentration interval the $[HA^-]$ and $[H^+]$ values exceed the $[H_2A]$ values. In case of trans isomer the concentration of dianion exceeds the $[H_2A]$ values when $c \leq 0.003$M; in case of cis isomer the $[A^{2-}]$ values exceed the $[H_2A]$ values when $c \leq 0.0015$M. In case of trans isomer with the high K_2 value concentration of dianion exceeds the $[HA^-]$ values up to $c \leq 0.0005$M; in case of cis isomer with the lesser K_2 value the monoanion concentration exceeds the $[A^{2-}]$ values in all studied acid concentration interval.

In conclusion, taking into account the comparative complexity of calculations with the aid of the equations (5)-(7), we suggest also the simple empirical equations for fast approximate determination of the values of usual and "partial" degrees of dissociation and pH in the dilute solutions of all studied derivatives of succinic acid.

Trans-epoxysuccinic acid

$$\alpha_1 = 1.00454 - 67.444c \quad \text{(up to 0.004M)} \tag{18}$$

$$\alpha_2 = lg\left(0.09016c^{-0.456}\right) \quad \text{(up to 0.0001M)} \tag{19}$$

$$\alpha_2{}' = lg\left(0.1135c^{-0.43}\right) \quad \text{(up to 0.0002M)} \tag{20}$$

$$pH = 0.407 - 0.836lgc \quad \text{(up to 0.01M)} \tag{21}$$

Cis-epoxysuccinic acid

$$\alpha_1 = 0.9995 - 70c \quad \text{(up to 0.002M)} \tag{22}$$

$$\alpha_2 = lg\left(0.10617c^{-0.354}\right) \quad \text{(up to 0.0001M)} \tag{23}$$

$$\alpha_2{}' = lg\left(0.11429c^{-0.348}\right) \quad \text{(up to 0.0004M)} \tag{24}$$

$$pH = 0.463 - 0.845lgc \quad \text{(up to 0.01M)} \tag{25}$$

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