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THE PECULIARITIES OF ELECTROLYTIC DISSOCIATION OF HALOGEN DERIVATIVES OF MALEIC AND FUMARIC ACIDS

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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 halogen derivatives of maleic and fumaric acids: chloromaleic, bromomaleic, chlorofumaric and bromofumaric acids have been calculated. The areas of dominance of various charged and uncharged forms of these acids in connection with the values of usual and "partial" degrees of dissociation have been formulated. Simple empirical equations for fast approximate calculation of the dissociation parameters values in the dilute solutions of studied acids have also been suggested.

Keywords: *Maleic acid; Fumaric acid; Degrees of Dissociation; Halogen; Hydrogen Ion; Monoanion; Dianion.*

1. Introduction

Halogen derivatives of unsaturated dicarboxylic acids (maleic, fumaric, mesaconic, itaconic) are widely used in industry for preparation the room-temperature curing agents for epoxidized oils, unsaturated polyester resins, fire-retardant compositions, scorch-inhibited elastomeric compositions, heat resistant thermoplastic copolymers, ink compositions, curable mixtures and cured resins. They are also the pharmaceutical intermediates. Many useful properties of these acids are directly connected with the interesting peculiarities of behavior of these acids in the solutions and, in particular, with the regularities of their electrolytic dissociation. In this communication an analysis of the processes of dissociation of chloromaleic, bromomaleic, chlorofumaric and bromofumaric acids in their dilute (0.0001-0.01M) solutions is carried out with the aid of an original method suggested and used by authors for determination of main dissociation parameters of weak multibasic organic acids with the effect of "overlapping" equilibria [1-13].

2. The results and discussion

All acids studied in this work are the vivid examples of weak dibasic organic acids with "overlapping" equilibria. The evidence to this fact are the values of the dissociation constants of these acids presented in Table 1.

Table 1. The values of the dissociation constants of maleic and fumaric acids and their halogen derivatives

Acid	K_1	K_2	t, ºC	Reference
Maleic	1.202×10^{-2}	5.888×10^{-7}	25	[14]
Chloromaleic	1.905×10^{-2}	1.380×10^{-4}	25	[14]
Bromomaleic	3.548×10^{-2}	2.399×10^{-5}	25	[14]
Fumaric	9.550×10^{-4}	4.169×10^{-5}	25	[14]
Chlorofumaric	1.660×10^{-2}	1.549×10^{-4}	25	[14]
Bromofumaric	3.467×10^{-2}	2.292×10^{-4}	25	[14]

The data presented in Table 1 show that putting the halogen atoms into the molecules of maleic and fumaric acids causes the appreciable increase of the K_1 and K_2 values. Thanks to this fact the halogen derivatives of unsaturated dicarboxylic acids are among the group of weak organic acids with the comparatively high acidity.

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

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

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

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 the contributions of first and second steps to the $[H^+]$ value ($[H^+] = x_1 + x_2$), c is the total (analytical) concentration of acid, $F_1$and F_2 are the quotients of the activity coefficients:

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

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

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 following equations:

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

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

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

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

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

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

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

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

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

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

Taking into account these equations, we can formulate the conditions of an equality of the concentrations of the ionized and non-ionized forms:

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

$$c = 2x_1 + x_2 \tag{15}$$

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

$$c=2x_1-x_2 \tag{17}$$

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

$$c=x_1+x_2 \tag{19}$$

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

$$\alpha_2^{'}=0.5 \tag{21}$$

$$x_1=2x_2 \tag{22}$$

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

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

$$\lg f_i=-\frac{z_i^2A\sqrt{I}}{1+a_iB\sqrt{I}} \tag{23}$$

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 $I=c(\alpha_1+2\alpha_2)=c\alpha_1(1+2\alpha_2^{'})=x_1+2x_2$. The values of a_i, A and B at 25ºC were taken from [15]. The activity coefficient of undissociated acid is assumed to be unity.

In Tables 2-5 the α_1, α_2, $\alpha_2^{'}$ and pH values for the dilute solutions of studied halogen derivatives of maleic and fumaric acids are presented.

Table 2. The values of the dissociation parameters of chloromaleic acid at 25ºC

Acid concentration, M	α_1	α_2	$\alpha_2^{'}$	pH
0.0001	0.9961	0.4947	0.4966	3.833
0.0002	0.9913	0.3546	0.3577	3.579
0.0004	0.9818	0.2354	0.2398	3.324
0.0006	0.9728	0.1793	0.1843	3.174
0.0008	0.9643	0.1460	0.1514	3.066
0.001	0.9561	0.1237	0.1294	2.983
0.002	0.9198	0.07176	0.07802	2.723
0.004	0.8626	0.04044	0.04688	2.468
0.006	0.8179	0.02870	0.03509	2.324
0.008	0.7818	0.02246	0.02873	2.224
0.01	0.7512	0.01856	0.02471	2.149

Table 3. The values of the dissociation parameters of bromomaleic acid at 25ºC

Acid concentration, M	α_1	α_2	α'_2	pH
0.0001	0.9974	0.1768	0.1773	3.936
0.0002	0.9947	0.1043	0.1049	3.666
0.0004	0.9895	0.05856	0.05918	3.388
0.0006	0.9845	0.04116	0.04181	3.223
0.0008	0.9797	0.03192	0.03258	3.105
0.001	0.9751	0.02618	0.02685	3.014
0.002	0.9534	0.01409	0.01478	2.733
0.004	0.9166	0.00760	0.00829	2.458
0.006	0.8857	0.00532	0.00600	2.303
0.008	0.8591	0.00414	0.00481	2.195
0.01	0.8357	0.00343	0.00410	2.113

Table 4. The values of the dissociation parameters of chlorofumaric acid at 25ºC

Acid concentration, M	α_1	α_2	α'_2	pH
0.0001	0.9957	0.5195	0.5217	3.827
0.0002	0.9902	0.3774	0.3811	3.572
0.0004	0.9794	0.2539	0.2592	3.318
0.0006	0.9692	0.1947	0.2009	3.169
0.0008	0.9595	0.1592	0.1659	3.063
0.001	0.9504	0.1353	0.1424	2.980
0.002	0.9101	0.07913	0.08695	2.724
0.004	0.8477	0.04481	0.05286	2.473
0.006	0.8001	0.03185	0.03081	2.332
0.008	0.7618	0.02494	0.03274	2.234
0.01	0.7299	0.02061	0.02824	2.160

Table 5. The values of the dissociation parameters of bromofumaric acid at 25ºC

Acid concentration, M	α_1	α_2	α'_2	pH
0.0001	0.9983	0.6370	0.6381	3.794
0.0002	0.9958	0.4947	0.4968	3.535
0.0004	0.9905	0.3559	0.3593	3.281
0.0006	0.9854	0.2836	0.2878	3.133
0.0008	0.9804	0.2379	0.2427	3.027
0.001	0.9756	0.2059	0.2111	2.944
0.002	0.9533	0.1267	0.1329	2.687
0.004	0.9157	0.07458	0.08145	2.430
0.006	0.8843	0.05399	0.06105	2.281
0.008	0.8573	0.04277	0.04989	2.177
0.01	0.8335	0.03564	0.04276	2.098

The data presented in Tables 2-5 show that halogen derivatives of unsaturated carboxylic acids have the comparatively high values of the dissociation degrees of second step (the analogous picture is observed in case of halogen derivatives of succunic acid [13]). This fact testifies to the appreciable contribution of second dissociation step to a formation of the hydrogen ions concentration in the dilute solutions of given acids.

With the aid of the equations (14)-(22) the areas of a predominance of various charged and uncharged forms in the dilute solutions of the halogen derivatives of maleic and fumaric acids have been determined. The fulfilment of an equality $\alpha_1 < 2\alpha_2$ or $\alpha_2^{'} > 0.5$ in the concentration interval c < 0.0001M (chloroderivatives of maleic and fumaric acids) and c < 0.0002M (bromofumaric acids) shows that in these intervals of acid concentration the $[A^{2-}]$ value exceeds the $[HA^{-}]$ value (in case of bromomaleic acid in all studied concentration interval the inequality $\alpha_1 > 2\alpha_2$ is fulfilled). The inequalities $\alpha_1 > \frac{1+\alpha_2}{2}$ and $\alpha_1 > \frac{1-\alpha_2}{2}$ are fulfilled in all concentration interval; this fact shows that the concentrations of monoanion and hydrogen ion always exceed the undissociated acid concentration. The inequality $\alpha_1 > 1-\alpha_2$ is fulfilled when c < 0.001M (bromomaleic acid), c < 0.002M (chloroderivatives of maleic and fumaric acids) and c < 0.004M (bromofumaric acid); consequently, in these concentration intervals the $[A^{2-}]$ values exceed the $[H_2A]$ values.

Taking into account the comparative complexity of calculations with the aid of the equations (5)-(9), we suggest also the simple empirical equations for fast approximate determination of the α_1, α_2, α'_2 and pH values in the dilute solutions of the halogen derivatives of maleic and fumaric acids.

Chloromaleic acid

$$\alpha_1 = 0.99988 - 44.111c \qquad (24)$$

(up to c = 0.004M)

$$\alpha_2 = 2.037\times10^{-3}c^{-0.6} \qquad (25)$$

(up to c = 0.001M)

$$\alpha_2^{'} = 2.414\times10^{-3}c^{-0.58} \qquad (26)$$

(up to c = 0.001M)

$$pH = 0.433 - 0.85\lg c \qquad (27)$$

(up to c = 0.01M)

Bromomaleic acid

$$\alpha_1 = 0.99988 - 24.7778c \qquad (28)$$

(up to c = 0.006M)

$$\alpha_2 = 8.2604\times10^{-5}c^{-0.835} \qquad (29)$$

(up to c = 0.002M)

$$\alpha_2^{'} = 8.98388\times10^{-5}c^{-0.828} \qquad (30)$$

(up to c = 0.01M)

$$pH = 0.248 - 0.922\lg c \qquad (31)$$

(up to c = 0.01M)

Chlorofumaric acid

$$\alpha_1 = 1.00029 - 49.888c \tag{32}$$

(up to c = 0.004M)

$$\alpha_2 = 2.45471 \times 10^{-3} c^{-0.585} \tag{33}$$

(up to c = 0.001M)

$$\alpha_2' = 2.71363 \times 10^{-3} c^{-0.575} \tag{34}$$

(up to c = 0.001M)

$$pH = 0.439 - 0.847 \lg c \tag{35}$$

(up to c = 0.01M)

Bromofumaric acid

$$\alpha_1 = 1.00082 - 25.222c \tag{36}$$

(up to c = 0.008M)

$$\alpha_2 = \lg(0.081283 c^{-0.429}) \tag{37}$$

(up to c = 0.001M)

$$\alpha_2' = \lg(0.082696 c^{-0.428}) \tag{38}$$

(up to c = 0.001M)

$$pH = 0.394 - 0.85 \lg c \tag{39}$$

(up to c = 0.01M)

The values of the relative error for these equations in the specified intervals of acid concentration do not exceed 7%.

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ОСОБЕННОСТИ ЭЛЕКТРОЛИТИЧЕСКОЙ ДИССОЦИАЦИИ ГАЛОГЕНПРОИЗВОДНЫХ МАЛЕИНОВОЙ И ФУМАРОВОЙ КИСЛОТ

Е.Р.Кварацхелия, Р.К.Кварацхелия и Р.Р.Куртанидзе

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 галогенпроизводных малеиновой и фумаровой кислот: хлормалеиновой, броммалеиновой, хлорфумаровой и бромфумаровой кислот были рассчитаны с помощью предложенных авторами методов. Были также определены области доминирования различных заряженных и незаряженных форм этих кислот в зависимости от значений обычных и «парциальных» степеней диссоциации. Были также предложены простые эмпирические уравнения для быстрого приближённого расчёта значений параметров диссоциации в разбавленных растворах изученных кислот.

Ключевые слова: *малеиновая кислота; фумаровая кислота; степени диссоциации; галоген; ион водорода; моноанион; дианион.*

MALEİN VƏ FUMAR TURŞULARININ HALOGEN TÖRƏMƏLƏRİNİN ELEKTROLİTİK DİSSOSİASİYASININ XÜSUSİYYƏTLƏRİ

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Müəlliflər tərəfindən təklif olunan metodla malein və fumar turşularının halogen törəmələrinin (xlormalein, brommalein, xlorfumar və bromfumar) 0.0001-0.01M duru məhlullarında dissosiasiya dərəcəsi, ionlaşmış və ionlaşmamış formaların konsentrasiyası, hidrogen ionunun və mono- və dianionların aktivliyi hesablanmışdır. Tədqiq olunan turşuların duru məhlullarında dissosiasiya parametrlərini təxmini təyin etmək üçün sadə empirik düstürlar təklif olunub.

Açar sözlər: *malein turşusu, fumar turşusu, dissosiasiya dərəcəsi, halogen, monoanion, dianion.*

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