

The “Overlapping Equilibria” Effect in the Processes of the Electrolytic Dissociation of Weak Multibasic Organic Acids

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Abstract

The “overlapping equilibria” effect observed in the processes of electrolytic dissociation of many weak multibasic organic acids determines the character of these processes. In this communication, the degree of “overlapping equilibria” in case of weak dibasic organic acids is quantitatively characterized by the values of “partial” degree of dissociation for second step and ratio of the concentrations of dianion and monoanion. It has been shown that these dissociation parameters are directly connected with the values of the second dissociation constant. It has been also shown that the contribution of third dissociation step in the “overlapping equilibria” effect is especially appreciable in case of penta and hexabasic weak organic acids causing the double “overlapping” phenomenon.

Keywords

Dissociation Constant, Dissociation Degree, “Overlapping Equilibria” Effect, Weak Organic Acids

1. Introduction

Organic acids and specifically weak multibasic organic acids play the great role in the existence of living organisms and in everyday life of humankind. Many multibasic organic acids are widely used in medicine, pharmacology, organic synthesis, food and cosmetic industry, analytical chemistry and many other branches. Oxaloacetic, citric, isocitric, cis-aconitic, oxalosuccinic, α -ketoglutaric, succinic, *L*-malic and fumaric acids participate in the complex fermentative process (the cycle of tricarboxylic acids or Krebs cycle); with the aid of this process in vital organisms, the oxidation of the main intermediate products of the cleavage of carbohydrates, fats and

proteins is near completion.

The wide use of above-mentioned acids in many branches causes a great interest to their chemical behavior because their ability for reactions in various areas, the effects connected with the peculiarities of their solutions form the basis of use of these acids in the various fields. For example, an analysis of the electrolytic dissociation processes of weak multibasic organic acids gives an opportunity for conclusions about the peculiarities of formation of the hydrogen ions concentration in their solutions; this is important for the discussion of the peculiarities and possibility of the various chemical processes proceeding in these solutions.

In this communication, the effect of “overlapping equilibria” which determines the chemical behaviour (and, in particular, the peculiarities of the electrolytic dissociation) of weak multibasic organic acids is considered and analyzed.

2. Results and Discussion

2.1. The Effect of “Overlapping Equilibria” and Methods of Its Investigation

It is well known in the literature that an analysis of the processes of electrolytic dissociation of weak multibasic organic acids is complicated by participating of two or more dissociation steps in the formation of total hydrogen ions concentration in the acid solution. When this occurs the process is said to be overlapping. The analysis of such cases demands the use of iterative techniques, a powerful weapon in the more complex (overlapping two or more dissociation steps) situations. As a rule, the “overlapping equilibria” effect is explained in the literature by the closeness of the dissociation constant values of the adjacent steps. But the results of our investigations convince us that this explanation is not only one-sided but erroneous.

The suggested by us original method for a calculation of the main parameters of the complex processes of electrolytic dissociation of weak multibasic organic acids with the “overlapping equilibria” effect [1]-[3] was used for the investigation of these processes for a big amount of such acids with the various basicities in their dilute solutions [4]-[7]. The general mass action equations suggested by us for m dissociation step of weak multibasic organic acid H_nA with the close values of dissociation constants of separate steps is written as follows:

$$K_m = \frac{c(\alpha_m - \alpha_{m+1}) \sum_{m=1}^n \alpha_m}{\alpha_{m-1} - \alpha_m} F_m = \frac{c\alpha'_m (1 - \alpha'_{m+1}) \sum_{m=1}^n \alpha'_m \alpha_{m-1}}{1 - \alpha'_m} F_m \quad (1)$$

where K_m is the thermodynamic dissociation constant of m step, α_m , α_{m+1} and α_{m-1} are the usual degrees of dissociation of corresponding steps (they are equal to the ratio of the number of moles of H^+ ions formed in a given dissociation step to the total number of moles of acid), α'_m , α'_{m+1} and α'_{m-1} are the corresponding “partial” degrees of dissociation (they are equal to the ratio of the number of moles of anion dissociated at a given step to the number of moles of this anion formed in the previous step; for first step the concepts of usual and “partial” degrees of dissociation coincide), c is a total concentration of acid, F_m is the quotient of the activity coefficients for m step:

$$F_m = \frac{f_{H^+} f_{H_{n-m}A^{m-}}}{f_{H_{n-(m-1)}A^{(m-1)-}}} \quad (2)$$

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

$$\lg f_i = - \frac{z_i^2 A \sqrt{I}}{1 + a_i B \sqrt{I}} \quad (3)$$

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 $I = c \sum_{m=1}^n m \alpha_m = c \sum_{m=1}^n m \alpha'_m \alpha_{m-1}$. The usual and “partial” degrees of dissociation may be evaluated successively by iterative solution of the quadratic equations obtained from Equation (1) for the adjacent dissociation steps of weak organic acids with any basicity [1]-[7]. The values of the degrees of dissociation may be used for a calculation of the concentrations of the hydrogen ions, all anions and undissociated acids.

The degree of “overlapping equilibria” may be also characterized by the values of the different dissociation parameters connected with the second dissociation step: the contribution of this step to the formation of the hydrogen ions concentration $[H^+]$ (denoted by us before as x_2 [1] [2]), the concentration of dianion $[A^{2-}]$ (the values of these two parameters are equal), the ratio of the concentrations of dianion and monoanion $[A^{2-}]/[HA^-]$, the regular dissociation degree of second step α_2 and the “partial” degree of this step α_2' (this term was suggested by us before [3]). These parameters are connected by the following dependences:

$$[A^{2-}] = x_2 = c\alpha_2 = c\alpha_1\alpha_2' \quad (4)$$

$$\alpha_2' = \frac{x_2}{x_1} = \frac{\alpha_2}{\alpha_1} \quad (5)$$

$$\frac{[A^{2-}]}{[HA^-]} = \frac{\alpha_2}{\alpha_1 - \alpha_2} = \frac{x_2}{x_1 - x_2} = \frac{\alpha_2'}{1 - \alpha_2'} \quad (6)$$

2.2. The Weak Dibasic Organic Acids

In **Table 1**, the values of the ratio of the first and second dissociation constants K_1/K_2 , the ratio of the concentrations of dianion and monoanion $[A^{2-}]/[HA^-]$ and the “partial” degree of dissociation for second step α_2' are presented for 57 weak dibasic organic acids (the values of the dissociation constants were taken from [8]-[12]). The analysis of the data of **Table 1** testifies that any convincing dependence between the K_1/K_2 , values and the $[A^{2-}]/[HA^-]$ and α_2' parameters which quantitatively characterize the degree of “overlapping equilibria” is absent. One can see from **Table 1** that the values of $[A^{2-}]/[HA^-]$ which are equal to or exceed unity (and the α_2' values which are equal to or exceed 0.5) are observed only for the first 11 acids. It is necessary to note that the K_2 values for these acids have the order $10^{-4} - 10^{-3}$; for other acids presented in **Table 1**, these values have the order $10^{-6} - 10^{-5}$. Consequently, we can conclude that the condition $[A^{2-}] \geq [HA^-]$ is observed in the interval of the K_2 values $10^{-4} - 10^{-3}$ only (without any dependence on the K_1/K_2 values). This fact convincingly confirms that the degree of “overlapping equilibria” depends on the K_2 values and does not connect with the closeness of the K_1 and K_2 values.

In **Figure 1** and **Figure 2**, the dependence of the $[A^{2-}]/[HA^-]$ and α_2' values on the K_2 values is shown for the weak dibasic organic acids with the K_2 values $10^{-4} - 10^{-3}$. Taking into account that these acids have the high α_1 values, the quantity of α_2' is very close to the value of the regular dissociation degree of second step α_2 . It is also necessary to note that the dependence of $[A^{2-}]$ and x_2 on K_2 are analogous to the dependence of α_2' and α_2 on K_2 (according to the Equation (4)). The same dependence is also observed for x_2/x_1 (according to the Equation (5)).

Taking into account the mass action equation for the second dissociation step:

$$K_2 = \frac{[H^+][A^{2-}]}{[HA^-]} \quad (7)$$

We may conclude that the linear dependences between the $[A^{2-}]/[HA^-]$ and K_2 values shown in **Figure 1** correspond to the following equation:

$$\frac{[A^{2-}]}{[HA^-]} = \frac{1}{[H^+]} K_2 \quad (8)$$

With the aid of this Equation we can explain the fact of the intense “overlapping equilibria” effect in the interval of K_2 values $10^{-4} - 10^{-3}$. This Equation shows that the $[A^{2-}]/[HA^-]$ value equal to unity is achieved (under the acid concentration $c = 0.0001 \text{ mol}\cdot\text{dm}^{-3}$ when the $[H^+]$ value is also close to $0.0001 \text{ mol}\cdot\text{dm}^{-3}$) when $K_2 = 10^{-4}$. It is clear that with the further increase of the K_2 value the $[A^{2-}]/[HA^-]$ quantity will also appreciably rise. When the concentration of acid increases, the “overlapping equilibria” effect weakens, but the $[A^{2-}]/[HA^-]$ values remain sufficiently high (**Figure 1**).

The dependence of α_2' on K_2 shown in **Figure 2** also characterizes the “overlapping equilibria” effect. One can see from **Figure 2** that an increase of the K_2 values causes the sharp rise of the α_2' values for all shown acid concentration quantities. These dependences may be described by following equation:

Table 1. The values of the ratio of first and second dissociation constants, ratio of the concentrations of dianion and monoanion and the “partial” dissociation degrees of weak dibasic organic acids with the “overlapping equilibria” effect ($c = 0.0001 \text{ mol} \cdot \text{dm}^{-3}$).

| Acid | K_1/K_2 | $[A^{2-}]/[HA^-]$ | α_2 |
|--|-----------|-------------------|------------|
| Chloromaleic | 138.04 | 0.987 | 0.497 |
| Chlorofumaric | 107.17 | 1.091 | 0.5217 |
| Bromofumaric | 128.79 | 1.763 | 0.638 |
| <i>DL</i> -1,2-Dichlorosuccinic | 31.62 | 3.959 | 0.798 |
| <i>meso</i> -1,2-Dichlorosuccinic | 31.63 | 3.488 | 0.777 |
| <i>DL</i> -2,3-Dichlorosuccinic | 23.98 | 8.808 | 0.898 |
| <i>meso</i> -2,3-Dichlorosuccinic | 30.19 | 6.209 | 0.861 |
| <i>DL</i> -2,3-Dibromosuccinic | 6.46 | 31.577 | 0.969 |
| <i>meso</i> -2,3-Dibromosuccinic | 15.85 | 10.986 | 0.917 |
| Squaric | 758.08 | 2.114 | 0.679 |
| Croconic | 27.55 | 31.573 | 0.969 |
| Succinic | 26.91 | 0.0424 | 0.0406 |
| Glutaric | 12.59 | 0.0742 | 0.0691 |
| Adipic | 10.00 | 0.081 | 0.0749 |
| Pimelic | 7.41 | 0.0711 | 0.0664 |
| Suberic | 7.92 | 0.0869 | 0.0799 |
| Azelaic | 6.30 | 0.1055 | 0.0954 |
| Sebacic | 10.00 | 0.063 | 0.0592 |
| Isophthalic | 7.94 | 0.2896 | 0.224 |
| Terephthalic | 6.31 | 0.4569 | 0.314 |
| Methylsuccinic | 32.36 | 0.0401 | 0.0386 |
| Methylenesuccinic | 39.72 | 0.0498 | 0.0474 |
| β -Methylglutaric | 14.35 | 0.0726 | 0.0676 |
| β -Ethylglutaric | 11.06 | 0.0882 | 0.081 |
| β -Propylglutaric | 11.95 | 0.0791 | 0.0733 |
| β -Isopropylglutaric | 16.40 | 0.0598 | 0.0564 |
| 2,2-Diphenylglutaric | 29.50 | 0.0624 | 0.0587 |
| Benzylsuccinic | 33.70 | 0.03976 | 0.0382 |
| α,α' -Diphenyladipic | 17.00 | 0.07006 | 0.0654 |
| β,β' -Diphenyladipic | 9.45 | 0.1122 | 0.101 |
| Fumaric | 22.90 | 0.376 | 0.273 |
| Mesaconic | 45.71 | 0.179 | 0.152 |
| Itaconic | 39.80 | 0.0518 | 0.0492 |
| <i>L</i> -Tartaric | 22.91 | 0.419 | 0.295 |
| <i>DL</i> -Tartaric | 21.88 | 0.385 | 0.278 |
| α,α' -Diphenylpimelic | 12.80 | 0.0774 | 0.0718 |
| α,α' -Diphenylsuberic | 12.17 | 0.0786 | 0.0729 |
| Thioacetoacetic | 15.85 | 0.312 | 0.238 |
| Dithioacetoacetic | 13.34 | 0.540 | 0.351 |
| Methylenedithiodiacetic | 10.84 | 0.425 | 0.298 |
| Ethylenedithiodiacetic | 9.33 | 0.430 | 0.301 |
| Trimethylenedithiodiacetic | 8.86 | 0.407 | 0.289 |
| Tetramethylenedithiodiacetic | 9.10 | 0.380 | 0.275 |
| Pentamethylenedithiodiacetic | 8.47 | 0.389 | 0.280 |
| β -Thiodipropionic | 9.77 | 0.133 | 0.117 |
| γ -Thiodibutyric | 8.07 | 0.108 | 0.0971 |
| <i>trans</i> -1,2-Cyclopropanedicarboxylic | 30.20 | 0.0946 | 0.0864 |
| <i>trans</i> -1,3-Cyclobutanedicarboxylic | 29.52 | 0.0352 | 0.0340 |
| <i>cis</i> -1,3-Cyclobutanedicarboxylic | 18.62 | 0.0783 | 0.0726 |
| 1,1-Cyclopentanedicarboxylic | 7.11 | 0.699 | 0.412 |
| 1,1-Cyclohexanedicarboxylic | 4.49 | 0.699 | 0.411 |
| <i>cis</i> -1,3-Cyclopentanedicarboxylic | 17.78 | 0.0584 | 0.0552 |
| <i>trans</i> -1,3-Cyclopentanedicarboxylic | 12.59 | 0.0742 | 0.0691 |
| <i>cis</i> -1,3-Cyclohexanedicarboxylic | 22.91 | 0.0585 | 0.0553 |
| <i>trans</i> -1,3-Cyclohexanedicarboxylic | 26.31 | 0.0372 | 0.0359 |
| <i>cis</i> -1,2-Cyclohexanedicarboxylic | 10.72 | 0.0748 | 0.0696 |
| <i>trans</i> -1,2-Cyclohexanedicarboxylic | 10.97 | 0.0774 | 0.0719 |

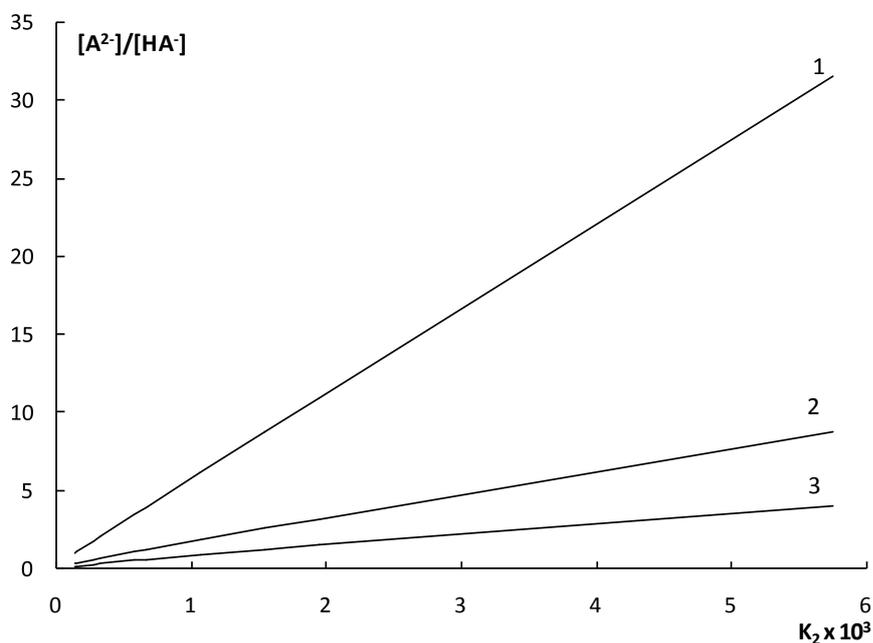


Figure 1. The dependence of the ratio of the concentrations of dianion and monoanion on the K_2 values for weak dibasic organic acids. 1 - $c = 0.0001 \text{ mol}\cdot\text{dm}^{-3}$; 2 - $c = 0.0004 \text{ mol}\cdot\text{dm}^{-3}$; 3 - $c = 0.001 \text{ mol}\cdot\text{dm}^{-3}$.

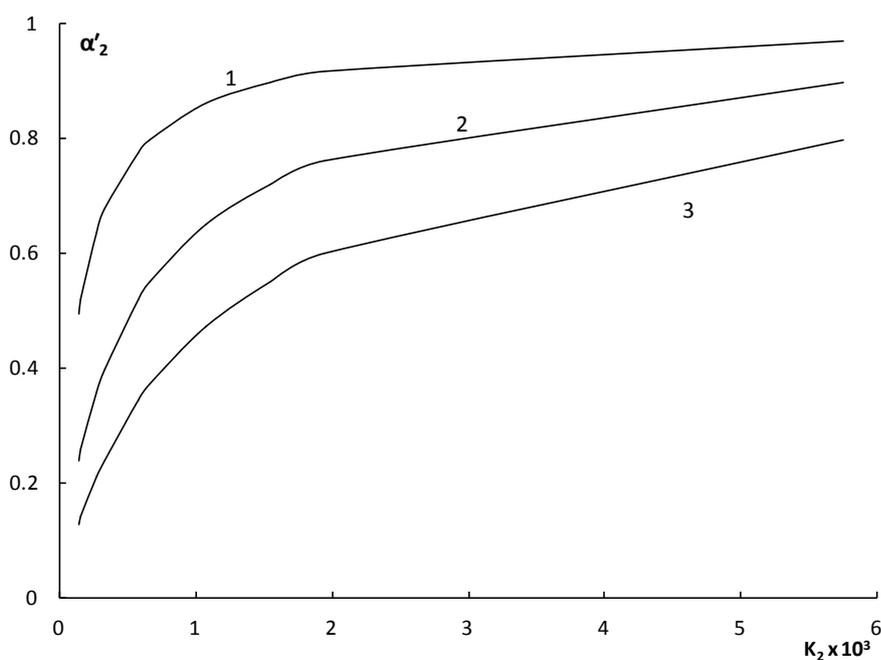


Figure 2. The dependence of the "partial" degrees of dissociation for second step on the K_2 values for weak dibasic organic acids. 1 - $c = 0.0001 \text{ mol}\cdot\text{dm}^{-3}$; 2 - $c = 0.0004 \text{ mol}\cdot\text{dm}^{-3}$; 3 - $c = 0.001 \text{ mol}\cdot\text{dm}^{-3}$.

$$\alpha'_2 = \frac{K_2}{K_2 + [H^+]} \quad (9)$$

This equation shows that, when $c = 0.0001 \text{ mol}\cdot\text{dm}^{-3}$, the α'_2 value equal to 0.5 is achieved, when $K_2 = 10^{-4}$.

We can conclude that an interval of the K_2 values 10^{-4} - 10^{-3} may be named as the region of strong “overlapping equilibria”.

Two main dissociation parameters characterizing the degree of the “overlapping equilibria” effect are connected with each other by the Equation (6). This dependency is shown in **Figure 3**. One can see from the Equation (6) and **Figure 3** that the $[A^{2-}]/[HA^-]$ value equal to unity is achieved when $\alpha_2' = 0.5$.

In case of weak dibasic organic acids with the K_2 values order 10^{-6} - 10^{-5} is also observed the linear dependence described by Equation (8). As the α_2' values in this interval of K_2 are appreciably less than 0.5, the $[A^{2-}]/[HA^-]$ values are also less than 1. This interval of the K_2 values may be named as the region of weak “overlapping equilibria” effect.

In **Table 2**, the intervals of the K_2 values corresponding to the different degrees of the “overlapping equilibria” effect are presented.

2.3. The Weak Multibasic Organic Acids

The “overlapping equilibria” effect is also observed in the processes of electrolytic dissociation of weak multibasic organic acids. In this case this effect has some specific peculiarities which will be considered below. In **Table 3** and **Table 4** the various dissociation parameters for weak tri, tetra, penta and hexabasic organic acids are presented. In **Figure 4** and **Figure 5** the dependences of the ratio of the anions concentrations and α_2' on the K_2 values are shown (the dissociation constants values were taken from [9]).

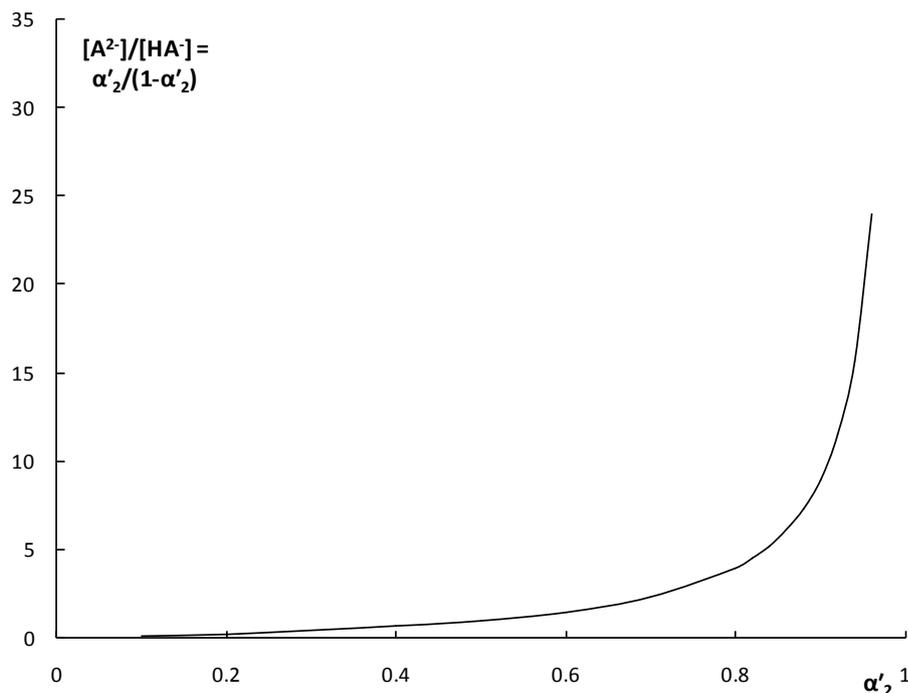


Figure 3. The dependence of the ratio of the concentrations of dianion and monoanion on the “partial” degrees of dissociation for second step for weak dibasic organic acids. $c = 0.0001 \text{ mol}\cdot\text{dm}^{-3}$.

Table 2. The intervals of the degree of the “overlapping equilibria” effect in the dilute solutions of weak dibasic organic acids ($c = 0.0001 \text{ mol}\cdot\text{dm}^{-3}$).

| “Overlapping equilibria” effect | K_2 | $[A^{2-}]/[HA^-]$ | α_2' |
|---------------------------------|------------|-------------------|-------------|
| Strong | $>10^{-4}$ | >1.0 | ≥ 0.5 |
| Medium | $>10^{-5}$ | >0.1 | >0.1 |
| | $<10^{-4}$ | <1.0 | <0.5 |
| Weak | $<10^{-5}$ | <0.1 | <0.1 |

Table 3. The values of the ratio of the dissociation constants for different steps, ratio of the concentrations of dianion and monoanion, trianion and dianion and the “partial” dissociation degrees for second and third steps of weak tri and tetrabasic organic acids with the “overlapping equilibria” effect ($c = 0.0001 \text{ mol}\cdot\text{dm}^{-3}$).

| Acid | K_1/K_2 | K_2/K_3 | $\frac{[\text{dianion}]}{[\text{monoanion}]}$ | $\frac{[\text{trianion}]}{[\text{dianion}]}$ | α_2 | α_3 |
|-------------------------|-----------|-----------|---|--|------------|------------|
| Tribasic acids | | | | | | |
| Trimellitic | 20.90 | 22.90 | 1.022 | 0.046 | 0.517 | 0.044 |
| Trimesic | 6.09 | 5.50 | 0.825 | 0.156 | 0.488 | 0.135 |
| Hemimellitic | 25.04 | 46.74 | 0.521 | 0.011 | 0.345 | 0.011 |
| Propanetricarboxylic | 15.86 | 32.35 | 0.165 | 0.005 | 0.142 | 0.005 |
| Citric | 42.65 | 43.66 | 0.163 | 0.004 | 0.140 | 0.004 |
| Tetrabasic acids | | | | | | |
| Butanetetracarboxylic | 14.13 | 18.61 | 0.273 | 0.015 | 0.217 | 0.015 |
| Pyromellitic | 8.96 | 41.87 | 7.162 | 0.178 | 0.894 | 0.153 |
| Prehnic | 13.55 | 8.61 | 1.858 | 0.224 | 0.695 | 0.184 |
| Mellophanic | 15.85 | 30.22 | 3.296 | 0.142 | 0.786 | 0.100 |

Table 4. The values of the dissociation parameters for weak penta and hexabasic organic acids with the “overlapping equilibria” effect ($c = 0.0001 \text{ mol}\cdot\text{dm}^{-3}$).

| The values of the dissociation parameters | Benzenepentacarboxylic acid | Mellitic acid |
|---|-----------------------------|---------------|
| K_1/K_2 | 8.55 | 33.87 |
| K_2/K_3 | 16.9 | 15.42 |
| K_3/K_4 | 19.57 | 49.2 |
| $\frac{[\text{dianion}]}{[\text{monoanion}]}$ | 8.94 | 25.94 |
| $\frac{[\text{trianion}]}{[\text{dianion}]}$ | 0.55 | 1.75 |
| $\frac{[\text{tetraanion}]}{[\text{trianion}]}$ | 0.029 | 0.037 |
| α_2 | 0.933 | 0.986 |
| α_3 | 0.360 | 0.645 |
| α_4 | 0.029 | 0.036 |

One can see from the data presented in tables that there is not the clear dependence between the values of the parameters which determine the degree of “overlapping equilibria” (the ratios of the concentrations of various anions and the “partial” degrees of dissociation) and the values of the ratios of the dissociation constants of adjacent steps. At the same time one can see from **Figure 4** and **Figure 5** that the functional dependence exists between the values of these parameters and the K_2 values. It is interesting to note that the linear dependence between the $[A^{2-}]/[HA^-]$ values and K_2 observed in case of dibasic acids (**Figure 1**) is preserved for tri and tetrabasic acids only at the lesser K_2 values; with the further rise of the latter this dependence is deflected from linearity (**Figure 4**). This phenomenon is connected with the following circumstances. The $[A^{2-}]/[HA^-]$ value for dibasic acids is expressed by the following equation:

$$\frac{[A^{2-}]}{[HA^-]} = \frac{\alpha_2}{\alpha_1 - \alpha_2} \quad (9)$$

and for tri and tetrabasic acids as follows:

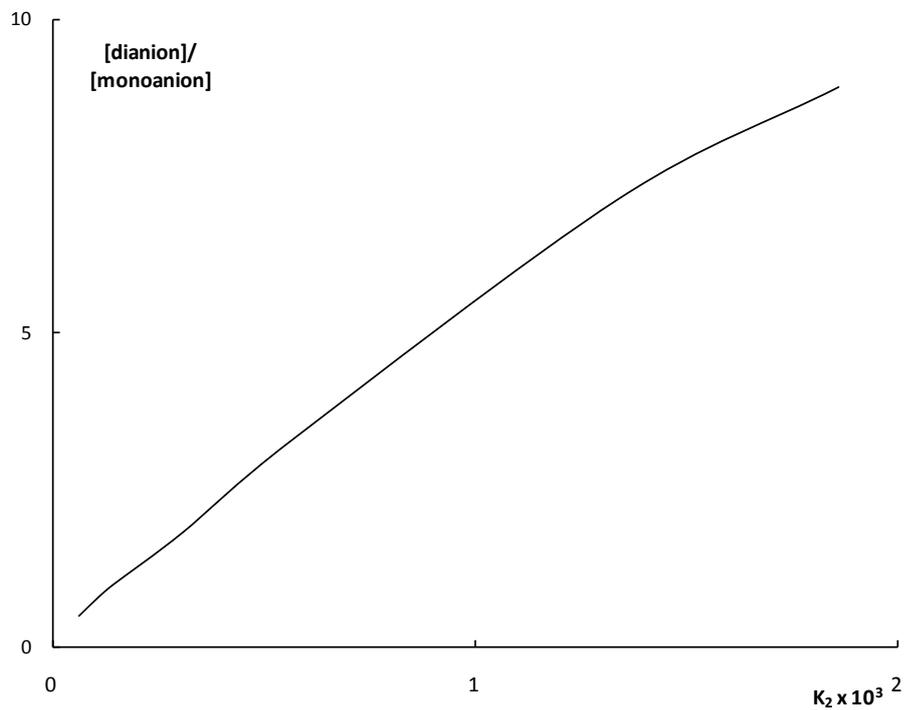


Figure 4. The dependence of the ratio of the anions concentrations on the K_2 values for weak multibasic organic acids. $c = 0.0001 \text{ mol}\cdot\text{dm}^{-3}$.

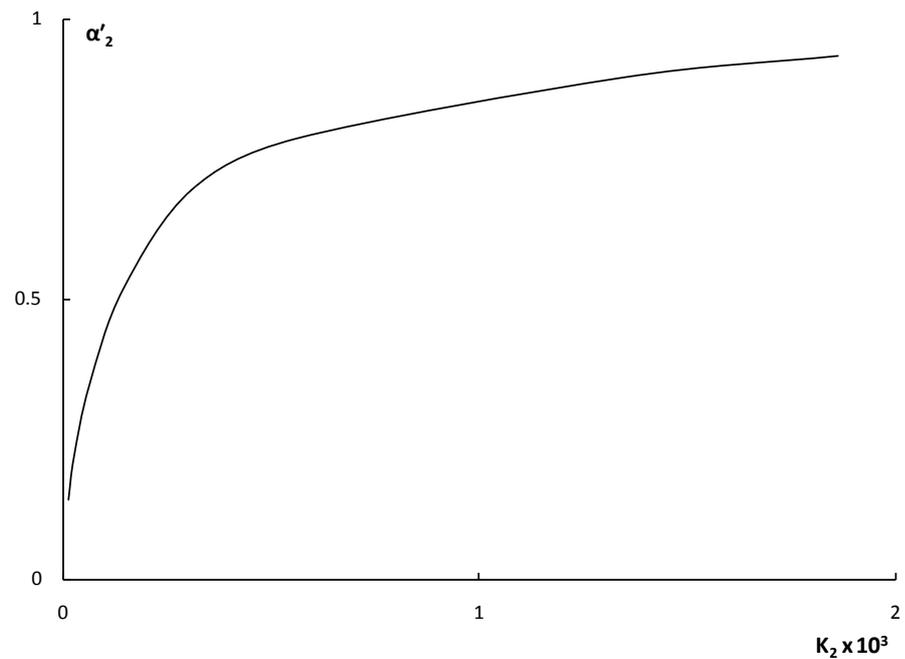


Figure 5. The dependence of the "partial" degrees of dissociation for second step on the K_2 values for weak multibasic organic acids. $c = 0.0001 \text{ mol}\cdot\text{dm}^{-3}$.

$$\frac{[\text{dianion}]}{[\text{monoanion}]} = \frac{\alpha_2 - \alpha_3}{\alpha_1 - \alpha_2} \quad (10)$$

Under the small K_2 values the K_3 and α_3 values are also small and the α_3 quantity in the Equation (6) may be

neglected; in these conditions the Equation (10) becomes analogous to the Equation (6). With the rise of the K_2 values the K_3 and α_3 values also increase and the dependence between the ratio of the concentrations of dianion and monoanion is deflected from linearity.

The data presented in **Table 3** testify that in case of weak tri and tetrabasic organic acids third dissociation step does not appreciably contribute to the “overlapping equilibria” effect. This fact is confirmed by the small values of the ratio of the concentrations of trianion and dianion and “partial” degree of dissociation for third step. One can see from **Table 3** that these values at the small K_3 values are very close to each other. Taking into account the following expression:

$$\frac{[\text{trianion}]}{[\text{dianion}]} = \frac{\alpha_3}{\alpha_2 - \alpha_3} \quad (11)$$

and the very small α_3 values, the Equation (11) may be presented as follows:

$$\frac{[\text{trianion}]}{[\text{dianion}]} = \frac{\alpha_3}{\alpha_2} = \alpha_3' \quad (12)$$

The different picture is observed in case of weak organic acids with highest acidity. One can see from **Table 4** that in case of benzenepentacarboxylic acid the values of the ratio of the trianion and dianion and the α_3' quantity achieve 0.55 and 0.36, respectively. This fact testifies about the appreciable contribution of third step in the “overlapping equilibria” effect which is connected with the sufficiently high K_3 value ($1.1 \cdot 10^{-4}$). At the same time the contribution of fourth step in the above mentioned effect is negligible.

Even more clearly the “overlapping equilibria” effect is observed in case of hexabasicmellitic acid. Thanks to the higher K_3 value ($4 \cdot 10^{-4}$) the quantity of the ratio of trianion and dianion concentrations achieves 1.75; that is, the trianion concentration exceeds the concentrations of dianion and monoanion (the ratio $[H_4A^{2-}]/[H_5A^-]$ is equal to 25.94 despite the high value of the K_1/K_2 ratio). The α_3' value also achieves the high quantity: 0.645. Thus, in this case takes place the double “overlapping equilibria” effect when two dissociation steps contribute to this phenomenon.

3. Conclusion

If the “overlapping equilibria” effect is observed in the processes of electrolytic dissociation of weak multibasic organic acid H_nA , the degree of this phenomenon is determined by the dissociation parameters of the responsible m dissociation step and is not directly connected with the K_{m-1}/K_m value. These dissociation parameters are the ratio of the concentrations of anions:

$$\frac{[H_{n-m}A^{m-}]}{[H_{n-(m-1)}A^{(m-1)-}]} = \frac{\alpha_m - \alpha_{m+1}}{\alpha_{m-1} - \alpha_m}$$

and the “partial” degree of dissociation for m step α_m' . The interconnection between these dissociation parameters may be presented as follows:

$$\frac{[H_{n-m}A^{m-}]}{[H_{n-(m-1)}A^{(m-1)-}]} = \frac{\alpha_m'}{1 - \alpha_m'}$$

This conclusion is confirmed by the results of the thorough analysis of the processes of dissociation of 57 weak dibasic organic acids and 11 weak organic acids with the higher acidity.

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