THE FORMS OF THE LAW OF DILUTION FOR WEAK MULTIBASIC ORGANIC ACIDS IN CASE OF OVERLAPPING EQUILIBRIA

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The weak multibasic organic acids are widely used in pharmacology, medicine, food industry, organic synthesis; participate in various processes proceeding in vital organisms. In this communication the regularities of electrolytic dissociation of tri-, tetra- and pentabasic weak organic acids are considered.

We suggest new general mass action equation (the law of dilution) for the process of dissociation of weak multibasic organic acid H_nA with the close values of dissociation constants of various steps (the m dissociation step is considered):

$$\mathrm{K}_m = \frac{[\mathrm{H}^+](x_m - x_{m+1})}{x_{m-1} - x_m} F_m = \frac{[\mathrm{H}^+](\alpha_m - \alpha_{m+1})}{\alpha_{m-1} - \alpha_m} F_m \quad [1]$$

where K_m is the dissociation constant for m step, $[H^+]$ is the total hydrogen ion concentration, x_m, x_{m+1} and x_{m-1} are the parts of $[H^+]$ value obtained at the corresponding dissociation steps, α_m, α_{m+1} and α_{m-1} are the degrees of dissociation of these steps, F_m is the quotient of the activity coefficients for the m step. The values of the latters are approximated by the Debye-Huckel equation:

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

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. Ionic strength $I = c\sum_{m=1}^{n} m\alpha_m$.

<u>Tribasic acids.</u> Taking into account that $[H^+] = x_1 + x_2 + x_3 = c(\alpha_1 + \alpha_2 + \alpha_3)$, we obtain the expressions for the law of dilution for tribasic weak organic acids (case of overlapping dissociation equilibria):

$$\mathrm{K}_1 = \frac{(\alpha_1 + \alpha_2 + \alpha_3)(\alpha_1 - \alpha_2)c}{1 - \alpha_1} F_1 \quad [3]$$

$$\mathrm{K}_2 = \frac{(\alpha_1 + \alpha_2 + \alpha_3)(\alpha_2 - \alpha_3)c}{\alpha_1 - \alpha_2} F_2 \quad [4]$$

$$\mathrm{K}_3 = \frac{(\alpha_1 + \alpha_2 + \alpha_3)\alpha_3 c}{\alpha_2 - \alpha_3} F_3 \quad [5]$$

From these equations the expressions for all three degrees of dissociation are obtained:

$$\alpha_1 = \frac{1}{2}\left\{-\left(\frac{K_1}{cF_1} + \alpha_3\right) + \sqrt{\left(\frac{K_1}{cF_1} + \alpha_3\right)^2 + 4\left(\alpha_2^2 + \alpha_2\alpha_3 + \frac{K_1}{cF_1}\right)}\right\} \quad [6]$$

$$\alpha_2 = \frac{1}{2}\left\{-\left(\frac{K_2}{cF_2} + \alpha_1\right) + \sqrt{\left(\frac{K_2}{cF_2} + \alpha_1\right)^2 + 4\left(\alpha_3^2 + \alpha_1\alpha_3 + \frac{K_2}{cF_2}\alpha_1\right)}\right\} \quad [7]$$

$$\alpha_3 = \frac{1}{2}\left\{-\left(\frac{K_3}{cF_3} + \alpha_1 + \alpha_2\right) + \sqrt{\left(\frac{K_3}{cF} + \alpha_1 + \alpha_2\right)^2 + \frac{4K_3}{cF_3}\alpha_2}\right\} \quad [8]$$

The examples of such acids are citric, isocitric, aconitic, benzenetricarboxylic (hemimellitic, trimellitic and trimesic) acids.

<u>Tetrabasic acids.</u> The law of dilution in this case have the following forms:

$$\mathrm{K}_1 = \frac{\left(c\sum_{m=1}^{4}\alpha_m\right)(\alpha_1 - \alpha_2)}{1 - \alpha_1} F_1 \quad [9]$$

$$\mathrm{K}_2 = \frac{\left(c\sum_{m=1}^{4}\alpha_m\right)(\alpha_2 - \alpha_3)}{\alpha_1 - \alpha_2} F_2 \quad [10]$$

$$\mathrm{K}_3 = \frac{\left(c\sum_{m=1}^{4}\alpha_m\right)(\alpha_3 - \alpha_4)}{\alpha_2 - \alpha_3} F_3 \quad [11]$$

$$\mathrm{K}_4 = \frac{\left(c\sum_{m=1}^{4}\alpha_m\right)\alpha_4}{\alpha_3 - \alpha_4} F_4 \quad [12]$$

The examples of such acids are three benzenetetracarboxylic (pyromellitic, prehnitic and mellophanic) acids.

<u>Pentabasic acids.</u> Here are the following equations:

$$\mathrm{K}_1 = \frac{\left(c\sum_{m=1}^{5}\alpha_m\right)(\alpha_1 - \alpha_2)}{1 - \alpha_1} F_1 \quad [13]$$

$$\mathrm{K}_2 = \frac{\left(c\sum_{m=1}^{5}\alpha_m\right)(\alpha_2 - \alpha_3)}{\alpha_1 - \alpha_2} F_2 \quad [14]$$

$$\mathrm{K}_3 = \frac{\left(c\sum_{m=1}^{5}\alpha_m\right)(\alpha_3 - \alpha_4)}{\alpha_2 - \alpha_3} F_3 \quad [15]$$

$$\mathrm{K}_4 = \frac{\left(c\sum_{m=1}^{5}\alpha_m\right)(\alpha_4 - \alpha_5)}{\alpha_3 - \alpha_4} F_4 \quad [16]$$

$$\mathrm{K}_5 = \frac{\left(c\sum_{m=1}^{5}\alpha_m\right)\alpha_5}{\alpha_4 - \alpha_5} F_5 \quad [17]$$

The example of such acid is benzenepentacarboxylic acid.