The Electrolytic Dissociation of 1,3-Cyclopentanedicarboxylic Acids

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Cyclopentanedicarboxylic acids are widely used in industry as pharmaceutical intermediates. Their biopharmaceutical properties depend on the peculiarities of electrolytic dissociation of these acids which determine the distribution of active and inactive (charged and uncharged) forms in their solutions. In this communication the regularities of the processes of electrolytic dissociation of isomeric cis and trans-1,3-cyclopentanedicarboxylic acids are studied with the aid of the suggested by authors original method for calculation the dissociation parameters of weak multibasic organic acids with the effect of "overlapping" equilibria in their dilute solutions.

The law of dilution for both dissociation steps of weak dibasic organic acid may be expressed as follows:

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

$$K_2 = \frac{c\alpha_2(\alpha_1+\alpha_2)}{\alpha_1-\alpha_2} F_2 = \frac{c\alpha_1\alpha_2'(1+\alpha_2')}{1-\alpha_2'} F_2 \qquad [2]$$

where K_1 and K_2 are the dissociation constants for corresponding steps, α_1 and α_2 are the usual degrees of dissociation for first and second steps, α_2' is the "partial" degree of dissociation of second step, c is the total (analytical) concentration of acid, F_1 and F_2 are the quotients of the activity coefficients for the corresponding steps:

$$F_1 = \frac{f_{H^+} f_{HA^-}}{f_{H_2A}} \qquad [3] \qquad F_2 = \frac{f_{H^+} f_{A^{2-}}}{f_{HA^-}} \qquad [4]$$

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

$$\lg f_i = -\frac{z_i^2 A\sqrt{I}}{1+a_i B\sqrt{I}} \qquad [5]$$

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 $I = c(\alpha_1 + 2\alpha_2) = c\alpha_1(1+2\alpha_2')$.

According to the equations [1] and [2] the degrees of dissociation α_1, α_2 and α_2' can be evaluated successively by iterative solution of the following quadratic equations:

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

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

$$\alpha_2' = \frac{1}{2}\left[-\left(1+\frac{K_2}{\alpha_1 cF_2}\right) + \sqrt{\left(1+\frac{K_2}{\alpha_1 cF_2}\right)^2 + \frac{4K_2}{\alpha_1 cF_2}}\right] \qquad [8]$$

The equilibrium concentrations of the dissociation products: hydrogen ions, mono- and dianions and undissociated acid molecules may be calculated with the aid of the following equations:

$$[H^+] = c(\alpha_1+\alpha_2) = c\alpha_1(1+\alpha_2') \qquad [9]$$

$$[HA^-] = c(\alpha_1-\alpha_2) = c\alpha_1(1-\alpha_2') \qquad [10]$$

$$[A^{2-}] = c\alpha_2 = c\alpha_1\alpha_2' \qquad [11]$$

$$[H_2A] = c(1-\alpha_1) \qquad [12]$$

The dissociation constants for cis-1,3-cyclopentanedicarboxylic acid have the following values: $K_1=5.495\times10^{-5}$; $K_2=3.09\times10^{-6}$. The corresponding values for trans isomer are: $K_1=4.786\times10^{-5}$; $K_2=3.802\times10^{-6}$.

In Tables I and II the values of α_1, α_2, α_2' and pH for the dilute solutions of studied acids at 25ºC are presented.

Table I. The values of the dissociation parameters for the dilute solutions of cis-1,3-cyclopentanedicarboxylic acid at 25ºC

Concentration, M	α_1	α_2	α_2'	pH
0.0001	0.5192	0.02865	0.05518	4.265
0.0002	0.4079	0.01498	0.03672	4.077
0.0004	0.3116	0.007742	0.02485	3.899
0.0006	0.2635	0.005244	0.01990	3.799
0.0008	0.2332	0.003975	0.01705	3.729
0.001	0.2116	0.003204	0.01514	3.675
0.002	0.1554	0.001638	0.01054	3.512
0.004	0.1130	0.0008364	0.007402	3.352
0.006	0.09353	0.0005649	0.006040	3.260
0.008	0.08168	0.0004276	0.005235	3.195
0.01	0.07350	0.0003446	0.004688	3.144

Table II. The values of the dissociation parameters for the dilute solutions of trans-1,3-cyclopentanedicarboxylic acid at 25ºC

Concentration, M	α_1	α_2	α_2'	pH
0.0001	0.4963	0.03427	0.06905	4.279
0.0002	0.3873	0.01806	0.04663	4.096
0.0004	0.2944	0.009401	0.03193	3.921
0.0006	0.2484	0.006370	0.02564	3.822
0.0008	0.2195	0.004835	0.02203	3.753
0.001	0.1990	0.003900	0.01960	3.700
0.002	0.1458	0.001999	0.01371	3.538
0.004	0.1058	0.001022	0.009660	3.379
0.006	0.08751	0.0006903	0.007888	3.287
0.008	0.07639	0.0005227	0.006843	3.223
0.01	0.07304	0.0004216	0.005772	3.146

We suggest also the simple empirical equations for fast approximate calculation of the α_1, α_2, α_2' and pH values for both studied acids:

Cis-1,3-cyclopentanedicarboxylic acid

$$\alpha_1 = 0.014488\ c^{-0.391} \quad \text{(up to 0.002M)} \qquad [13]$$

$$\alpha_2 = 4.4978\times10^{-6} c^{-0.951} \quad \text{(up to 0.01M)} \qquad [14]$$

$$\alpha_2' = 3.13329\times10^{-4} c^{-0.561} \quad \text{(up to 0.004M)} \qquad [15]$$

$$pH = 1.894 - 0.591\lg c \quad \text{(up to 0.01M)} \qquad [16]$$

Trans-1,3-cyclopentanedicarboxylic acid

$$\alpha_1 = 0.012531\ c^{-0.402} \quad \text{(up to 0.002M)} \qquad [17]$$

$$\alpha_2 = 5.74116\times10^{-6} c^{-0.944} \quad \text{(up to 0.01M)} \qquad [18]$$

$$\alpha_2' = 4.4157\times10^{-4} c^{-0.549} \quad \text{(up to 0.004M)} \qquad [19]$$

$$pH = 1.958 - 0.579\lg c \quad \text{(up to 0.01M)} \qquad [20]$$