The Electrolytic Dissociation of 1,2-Cyclopentanedicarboxylic Acids

E. Kvaratskhelia, R. Kvaratskhelia and R. Kurtanidze
R. Agladze Institute of Inorganic Chemistry and Electrochemistry,
Iv. Javakhishvili Tbilisi State University
11 Mindely str., Tbilisi, 0186, Georgia

Cyclopentanedicarboxylic acids are widely used in industry as pharmaceutical intermediates. Their useful properties are closely connected with the peculiarities of their behaviour in solutions and, consequently, with the regularities of their electrolytic dissociation which determine the distribution of biopharmaceutically active and inactive forms in their solutions. In this communication the analysis of the complex equilibria in the processes of electrolytic dissociation of isomeric cis and trans-1,2-cyclopentanedicarboxylic acids is carried out with the aid of original method suggested by authors for case of weak multibasic organic acids.

For weak dibasic organic acids the law of dilution for both dissociation steps may be expressed as follows:

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

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

where K_1 and K_2 are the thermodynamic dissociation constants of first and second steps, α_1 and α_2 are the usual degrees of dissociation of these 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. The values of the activity coefficients of hydrogen ions and mono and dianions may be approximated by the Debye-Huckel equation:

$$\lg f_i = -\frac{z_i^2 A\sqrt{I}}{1+a_i B\sqrt{I}} \qquad [3]$$

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

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

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

$$\alpha_2 = \frac{1}{2}\left[-\left(\frac{K_2}{cF_2}+\alpha_1\right) + \sqrt{\left(\frac{K_2}{cF_2}+\alpha_1\right)^2 + \frac{4K_2\alpha_1}{cF_2}}\right] \qquad [5]$$

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

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

$$[H^+] = c(\alpha_1+\alpha_2) = c\alpha_1(1+\alpha_2') \qquad [7]$$

$$[HA^-] = c(\alpha_1-\alpha_2) = c\alpha_1(1-\alpha_2') \qquad [8]$$

$$[A^{2-}] = c\alpha_2 = c\alpha_1\alpha_2' \qquad [9]$$

$$[H_2A] = c(1-\alpha_1) \qquad [10]$$

The dissociation constants for cis-acid have the following values: $K_1=3.715\times10^{-5}$; $K_2=2.14\times10^{-7}$. The corresponding values for trans isomer are: $K_1=1.096\times10^{-4}$; $K_2=1.413\times10^{-6}$ (all values – for 25ºC).

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-1,2-cyclopentanedicarboxylic acid at 25ºC

Concentration, M	α_1	α_2	α_2'	pH
0.0001	0.4539	0.002187	0.004818	4.344
0.0002	0.3507	0.001105	0.003151	4.157
0.0004	0.2645	0.0005585	0.002112	3.980
0.0006	0.2223	0.0003746	0.001685	3.880
0.0008	0.1960	0.0002824	0.001441	3.810
0.001	0.1775	0.0002268	0.001278	3.757
0.002	0.1295	0.0001148	0.0008865	3.594
0.004	0.09374	$5.828\cdot10^{-5}$	0.0006217	3.435
0.006	0.07740	$3.922\cdot10^{-5}$	0.0005067	3.343
0.008	0.06751	$2.963\cdot10^{-5}$	0.0004389	3.278
0.01	0.06069	$2.384\cdot10^{-5}$	0.0003928	3.228

Table II. The values of the dissociation parameters for the dilute solutions of trans-1,2-cyclopentanedicarboxylic acid at 25ºC

Concentration, M	α_1	α_2	α_2'	pH
0.0001	0.6369	0.01404	0.02204	4.191
0.0002	0.5194	0.007204	0.01387	3.983
0.0004	0.4085	0.003678	0.009004	3.789
0.0006	0.3502	0.002480	0.007082	3.682
0.0008	0.3125	0.001875	0.006000	3.607
0.001	0.2853	0.001509	0.005289	3.551
0.002	0.2126	0.0007690	0.003617	3.380
0.004	0.1563	0.0003923	0.002510	3.215
0.006	0.1300	0.0002649	0.002038	3.120
0.008	0.1138	0.0002004	0.001761	3.054
0.01	0.1027	0.0001617	0.001574	3.002

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

Cis-1,2-cyclopentanedicarboxylic acid

$$\alpha_1 = 0.010765\, c^{-0.408} \quad \text{(up to 0.002M)} \qquad [11]$$

$$\alpha_2 = 2.53513\times10^{-7}\, c^{-0.984} \quad \text{(up to 0.01M)} \qquad [12]$$

$$\alpha_2' = 2.15278\times10^{-5}\, c^{-0.588} \quad \text{(up to 0.002M)} \qquad [13]$$

$$pH = 1.983 - 0.588\lg c \quad \text{(up to 0.01M)} \qquad [14]$$

Trans-1,2-cyclopentanedicarboxylic acid

$$\alpha_1 = 0.024266\, c^{-0.359} \quad \text{(up to 0.002M)} \qquad [15]$$

$$\alpha_2 = 1.8578\times10^{-6}\, c^{-0.969} \quad \text{(up to 0.01M)} \qquad [16]$$

$$\alpha_2' = 6.76083\times10^{-5}\, c^{-0.628} \quad \text{(up to 0.002M)} \qquad [17]$$

$$pH = 1.609 - 0.644\lg c \quad \text{(up to 0.01M)} \qquad [18]$$