

Physical Chemistry

The Regularities of Electrolytic Dissociation of 1,1-Cyclopentanediacetic and 1,1-Cyclohexanediacetic Acids

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ABSTRACT. Cycloalcanediacytic acids are the nonaromatic, cyclanic polycarboxylic acids; they are used as the pharmaceutical intermediates. In this communication with the aid of method previously described by the authors an analysis of the regularities of electrolytic dissociation of 1,1-cyclopentanediacetic and 1,1-cyclohexanediacetic acids was carried out. Values of the degrees of dissociation of both steps, the “partial” degrees of dissociation of second step, concentrations of hydrogen ion, monoanion and dianion and undissociated acid were determined for the dilute (0.0001 – 0.01M) solutions of above mentioned acids. The concentration intervals of domination of various charged and uncharged forms of these acids were established. Simple empirical equations were suggested for the fast approximate calculation of α_1 , α_2 , α_2' and pH values for all studied acids. © 2016 Bull. Georg. Natl. Acad. Sci.

Key words: Dissociation constants, degree of dissociation, hydrogen ions, monoanion, dianion, concentration

Cycloalcanediacytic acids are the nonaromatic, cyclanic polycarboxylic acids; they are used as the pharmaceutical intermediates. In this communication the previously suggested by authors original method [1-9] for the determination the parameters of dissociation of weak multibasic organic acids with the “overlapping” equilibria effect was used for an analysis of the processes of electrolytic dissociation of 1,1-cyclopentanediacetic and 1,1-cyclohexanediacetic acids which are not sufficiently investigated.

For weak dibasic organic acids the law of dilution for both dissociation steps may be expressed as follows [1, 2]:

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

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

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:

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

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

The values of the activity coefficients were approximated by the Debye-Huckel equation (12):

$$\lg f_i = -\frac{z_i^2 A \sqrt{I}}{1 + a_i B \sqrt{I}} \quad (5)$$

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 equations (1) and (2) the degrees of dissociation α_1 , α_2 and α_2' can be evaluated successively by iterative solution of following quadratic equations:

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

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

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

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:

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

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

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

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

These equations give the opportunity to estimate the regions of the acid concentration in which the various charged and uncharged forms of acid prevail. The conditions of equality of the concentrations of these particles are:

$$[H^+] = [H_2A]: \alpha_1 = \frac{1 - \alpha_2}{2} = \frac{1}{\alpha_2' + 2} \quad (13)$$

$$[HA^-] = [H_2A]: \alpha_1 = \frac{1 + \alpha_2}{2} = \frac{1}{2 - \alpha_2'} \quad (14)$$

$$[A^{2-}] = [H_2A]: \alpha_1 = 1 - \alpha_2 = \frac{1}{\alpha_2' + 1} \quad (15)$$

$$[HA^-] = [A^{2-}]: \alpha_1 = 2\alpha_2 \quad (16)$$

$$\alpha_2' = 0.5 \quad (17)$$

The dissociation constants of 1,1-cyclopentanediacyetic acid have the following values: $K_1 = 1.585 \times 10^{-4}$; $K_2 = 1.700 \times 10^{-7}$. The corresponding values for 1,1-cyclohexanediacyetic acid are: $K_1 = 3.236 \times 10^{-4}$; $K_2 = 1.1 \times 10^{-7}$ (all values – for 25°C) [10]. The A and B values at 25°C in equation (5) were taken from [11]; the a_i values were estimated according to the data presented in [12]. The activity coefficient of undissociated acid is assumed to be unity.

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

With the aid of the equations (13)-(17) we can determine the regions of concentration of cis and trans-1,3-cyclohexanedicarboxylic acids with the predominance of various charged and uncharged dissociation products. For the cis isomer the $[HA^-]$ value exceeds the $[H_2A]$ value when $c < 0.0002M$ (the inequalities: $\alpha_1 > \frac{1 + \alpha_2}{2}$ and $\alpha_1 > \frac{1}{2 - \alpha_2'}$ are fulfilled

Table 1. The values of the dissociation parameters of 1,1-cyclopentanediacetic acid at 25°C

Acid concentration, M	α_1	α_2	α'_2	pH
0.0001	0.6983	$1.758 \cdot 10^{-3}$	$2.518 \cdot 10^{-3}$	4.159
0.0002	0.5824	$8.904 \cdot 10^{-4}$	$1.529 \cdot 10^{-3}$	3.938
0.0004	0.4668	$4.512 \cdot 10^{-4}$	$9.666 \cdot 10^{-4}$	3.735
0.0006	0.4039	$3.035 \cdot 10^{-4}$	$7.514 \cdot 10^{-4}$	3.623
0.0008	0.3623	$2.291 \cdot 10^{-4}$	$6.323 \cdot 10^{-4}$	3.546
0.001	0.3321	$1.842 \cdot 10^{-4}$	$5.547 \cdot 10^{-4}$	3.487
0.002	0.2499	$9.375 \cdot 10^{-5}$	$3.752 \cdot 10^{-4}$	3.312
0.004	0.1851	$4.783 \cdot 10^{-5}$	$2.584 \cdot 10^{-4}$	3.143
0.006	0.1545	$3.235 \cdot 10^{-5}$	$2.094 \cdot 10^{-4}$	3.047
0.008	0.1356	$2.447 \cdot 10^{-5}$	$1.805 \cdot 10^{-4}$	2.980
0.01	0.1224	$1.973 \cdot 10^{-5}$	$1.612 \cdot 10^{-4}$	2.928

Table 2. The values of the dissociation parameters of 1,1-cyclohexanediacetic acid at 25°C

Acid concentration, M	α_1	α_2	α'_2	pH
0.0001	0.8042	0.001143	0.001421	4.094
0.0002	0.7028	0.0005796	0.0008247	3.858
0.0004	0.5877	0.0002944	0.0005009	3.636
0.0006	0.5193	0.0001983	0.0003819	3.515
0.0008	0.4722	0.0001498	0.0003172	3.432
0.001	0.4369	0.0001206	0.0002760	3.369
0.002	0.3370	0.00006159	0.0001828	3.171
0.004	0.2542	0.00003153	0.0001239	3.007
0.006	0.2139	0.00002134	0.00009958	2.908
0.008	0.1887	0.00001619	0.00008585	2.839
0.01	0.1711	0.00001308	0.00007656	2.785

in this region only). $[H^+]$ value exceeds the $[H_2A]$ value in the same concentration region (the inequalities $\alpha_1 > \frac{1-\alpha_2}{2}$ or $\alpha_1 > \frac{1}{\alpha_2+2}$ are fulfilled). In case of trans isomer the monoanion concentration exceeds the $[H_2A]$ value when $c \leq 0.0001M$ and $[H^+]$ value exceeds the $[H_2A]$ value when $c < 0.0001M$. In all cases the concentration of dianion is lower than the $[H_2A]$ value (the inequalities $\alpha_1 < 1-\alpha_2$ or $\alpha_1 < \frac{1}{\alpha_2+1}$ are fulfilled) and the $[HA^-]$ value.

We suggest also the simple empirical equations for fast approximate calculation of the dissociation parameters of both acids:

1,1-Cyclopentanediacetic acid

$$\alpha_1 = 0.036475c^{-0.0323} \quad (\text{up to } 0.002M) \quad (18)$$

$$\alpha_2 = 2.11349 \times 10^{-7} c^{-0.98} \quad (\text{up to } 0.01M) \quad (19)$$

$$\alpha'_2 = 5.78096 \times 10^{-6} c^{-0.658} \quad (\text{up to } 0.002M) \quad (20)$$

$$pH = 1.469 - 0.667 \lg c \quad (\text{up to } 0.01M) \quad (21)$$

1,1-Cyclohexanediacetic acid

$$\alpha_1 = 0.07187c^{-0.264} \quad (\text{up to } 0.0004M) \quad (22)$$

$$\alpha_2 = 1.404 \times 10^{-7} c^{-0.977} \quad (\text{up to } 0.01M) \quad (23)$$

$$\alpha'_2 = 2.04796 \times 10^{-6} c^{-0.706} \quad (\text{up to } 0.002M) \quad (24)$$

$$pH = 1.173 - 0.728 \lg c \quad (\text{up to } 0.01M) \quad (25)$$

The values of the relative error for all presented empirical equations do not exceed 5-7%.

ფიზიკური ქიმია

1,1-ციკლოპენტანდიმარმჟავასა და 1,1-ციკლოპექსანდიმარმჟავას ელექტროლიტური დისოციაციის კანონზომიერებები

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(წარმოდგენილია აკადემიის წევრის გ. ცინცაძის მიერ)

ავტორების მიერ შემოთავაზებული ორიგინალური მეთოდი, “გადაფარული წონასწორობების” ეფექტის მქონე სუსტი მრავალფუძიანი ორგანული მჟავების ელექტროლიტური დისოციაციის პროცესების ანალიზისათვის და მათი პარამეტრების გათვლისათვის, გამოყენებული იყო 1,1-ციკლოპენტანდიმარმჟავასა და 1,1-ციკლოპექსანდიმარმჟავას განზავებული ხსნარების თავისებურებათა შესასწავლად. გათვლილი იყო დისოციაციის ორივე საფეხურის ჩვეულებრივი და “პარციალური” ხარისხების, მოცემული მჟავების სხვადასხვა დამუხტული და დაუმუხტავი ფორმების კონცენტრაციების მნიშვნელობები. დებაი-ჰიუკელის განტოლების დახმარებით განსაზღვრული იყო წყალბადის იონებისა და მონო- და დიანიონების აქტიურობის კოეფიციენტები. დადგენილი იყო აგრეთვე სხვადასხვა იონიზებული და არაიონიზებული ნაწილაკების დომინირების კონცენტრაციული უბნები. შემოთავაზებულია აგრეთვე მარტივი ემპირიული განტოლებები დისოციაციის სხვადასხვა პარამეტრის მნიშვნელობების სწრაფი მიახლოებითი გათვლისათვის.

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