

Physical Chemistry

The Regularities of the Electrolytic Dissociation of 1,1-Cyclopentane and 1,1-Cyclohexanedicarboxylic Acids

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ABSTRACT. The parameters of electrolytic dissociation of 1,1-Cyclopentane and 1,1-Cyclohexanedicarboxylic acids in their dilute (0.0001-0.01M) solutions were determined with the aid of original accurate and empirical equations suggested by the authors. ©2012 Bull. Georg. Natl. Acad. Sci.

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Cyclopentane and cyclohexanedicarboxylic acids are used as pharmaceutical intermediates and also in such demanding markets as automotive, transportation, maintenance and aerospace. They are also the members of positive resist radiation-sensitive and coating resinous compositions. It should be noted that their useful properties are directly connected with the peculiarities of electrolytic dissociation of these acids.

In this communication the regularities of dissociation of 1,1-cyclopentanedicarboxylic (CPCA) and 1,1-cyclohexanedicarboxylic (CHCA) acids are determined with the aid of an original method suggested by the authors for analysis of the complex equilibria of dissociation of weak multibasic organic acids with the “overlapping” equilibria effect [1-3].

It was shown by us that the mass action law equations for the m dissociation step of weak multibasic organic acid H_nA may be written as follows:

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

where K_m is the thermodynamic dissociation constant of m step, c is a total (analytical) concentration of acid, α_m , α_{m+1} and α_{m-1} are the usual degrees of dissociation of corresponding steps, α'_m , α'_{m+1} and α'_{m-1} are the “partial” degrees of dissociation (this term was first suggested by the authors [3]), F_m is the quotient of the activity coefficients for m step:

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

In the case of dibasic CPCA and CHCA the equations for the law of dilution for both dissociation steps may be presented as follows (according to equation (1)):

$$K_1 = \frac{c(\alpha_1^2 - \alpha_2^2)}{1 - \alpha_1} F_1 = \frac{c\alpha_1^2[1 - (\alpha_2')^2]}{1 - \alpha_1} F_1, \quad (3)$$

$$K_2 = \frac{c\alpha_2(\alpha_1 + \alpha_2)}{\alpha_1 - \alpha_2} F_2 = \frac{c\alpha_1\alpha_2'(1 + \alpha_2')}{1 - \alpha_2'} F_2. \quad (4)$$

According to equations (3) and (4) the degrees of dissociation, α_1 , α_2 and α_2' can be evaluated successively by iterative solution of following quadratic equations:

$$\alpha_1 = \frac{1}{2} \left[-\frac{K_1}{cF_1} + \sqrt{\left(\frac{K_1}{cF_1}\right)^2 + 4\left(\alpha_2' + \frac{K_1}{cF_1}\right)} \right], \quad (5)$$

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

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

The values of the “partial” degree of dissociation α_2' may be also determined with the aid of α_1 and α_2 values:

$$\alpha_2' = \frac{\alpha_2}{\alpha_1}. \quad (8)$$

The values of the activity coefficient of hydrogen ions and mono- and dianions may be approximated with the aid of the Debye-Huckel equation:

$$\lg f_i = -\frac{z_i^2 A \sqrt{I}}{1 + a_i B \sqrt{I}}, \quad (9)$$

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

of undissociated acid is assumed to be unity.

With the aid of the dissociation degree values we may also calculate the values of concentration of all dissociated and undissociated forms of both acids:

$$[H^+] = c(\alpha_1 + \alpha_2) = c\alpha_1(1 + \alpha_2'), \quad (10)$$

$$[HA^-] = c(\alpha_1 - \alpha_2) = c\alpha_1(1 - \alpha_2'), \quad (11)$$

$$[A^{2-}] = c\alpha_2 = c\alpha_1\alpha_2', \quad (12)$$

$$[H_2A] = c(1 - \alpha_1). \quad (13)$$

The equations (5)-(8) were used for the calculation of the values of usual and “partial” degrees of dissociation for CPCA and CHCA in their dilute (0.0001-0.01M) solutions. The K_1 and K_2 values were taken from [4]: $K_1 = 5.9 \cdot 10^{-4}$; $K_2 = 8.3 \cdot 10^{-5}$ (CPCA); $K_1 = 3.5 \cdot 10^{-4}$; $K_2 = 7.8 \cdot 10^{-5}$ (CHCA). The values of the constants of equation (9) were taken from [5]. The calculated values of α_1 , α_2 , α_2' and pH at 25°C are presented in Tables 1 (CPCA) and 2 (CHCA).

The equations (10)-(13) allow the determination of the intervals of the acid concentration in which various charged and uncharged forms of acid prevail. The conditions of equality of these concentrations are:

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

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

$$[H^+] = [H_2A]: \alpha_1 = \frac{1 - \alpha_2}{2} = \frac{1}{\alpha_2' + 2}, \quad (16)$$

$$[HA^-] = [A^{2-}]: \alpha_1 = 2\alpha_2', \quad (17)$$

$$\alpha_2' = 0.5. \quad (18)$$

The data of Table 1 show that in the $c \leq 0.001M$ interval the $[HA^-]$ value in the CPCA solutions exceeds the $[H_2A]$ value (the inequality $\alpha_1 > \frac{1 + \alpha_2}{2}$ is fulfilled). Up to $c = 0.0002M$ the $[A^{2-}]$ value also

Table 1. The parameters of electrolytic dissociation of 1,1-cyclopentanedicarboxylic acid in its dilute solutions at 25°C

Acid concentration, M	α_1	α_2	α'_2	pH
0.0001	0.8903	0.3665	0.4117	3.907
0.0002	0.8053	0.2407	0.2989	3.687
0.0004	0.6971	0.1475	0.2116	3.481
0.0006	0.6280	0.1079	0.1718	3.366
0.0008	0.5782	0.08566	0.1481	3.286
0.001	0.5399	0.07129	0.1320	3.226
0.002	0.4269	0.03949	0.09250	3.045
0.004	0.3283	0.02161	0.06582	2.871
0.006	0.2788	0.01486	0.05330	2.773
0.008	0.2474	0.01145	0.04628	2.704
0.01	0.2251	$9.34 \cdot 10^{-3}$	0.04151	2.651

exceeds $[H_2A]$ value (the inequality $\alpha_1 > 1 - \alpha_2$ is fulfilled). Up to $c = 0.0015M$ the $[H^+]$ value exceeds $[H_2A]$ value (the inequality $\alpha_1 > \frac{1 - \alpha_2}{2}$ is fulfilled). In all studied regions of the CPCA concentration monoanion remains the predominant anion (the inequalities $\alpha_1 > 2\alpha_2$ and $\alpha'_2 < 0.5$ are fulfilled).

According to the data of Table 2 in the solutions of CHCA up to $c = 0.0005M$ the $[HA^-]$ value exceeds the $[H_2A]$ value (inequality $\alpha_1 > \frac{1 + \alpha_2}{2}$ are fulfilled). Up to $c \approx 0.0002M$ the inequality $\alpha_1 > 1 - \alpha_2$ is fulfilled (the $[A^{2-}]$ value exceeds the $[H_2A]$ value). The $[H^+]$ value exceeds the $[H_2A]$ value up to $c = 0.0009M$

(inequality $\alpha_1 > \frac{1 - \alpha_2}{2}$ is fulfilled). In the CHCA solutions monoanion also remains the predominant anion (the inequalities $\alpha_1 > 2\alpha_2$ and $\alpha'_2 < 0.5$ are fulfilled in all studied regions of the c values).

Taking into account the comparative complexity of calculations with the aid of equations (5)-(7), we suggest also simple empirical equations for fast approximate calculation of the α_1 , α_2 , α'_2 and pH values in the dilute solutions of CPCA and CHCA.

1,1-cyclopentanedicarboxylic acid

$$\alpha_1 = 0.10888c^{-0.235}, \quad (19)$$

$$\alpha_2 = 4.742 \cdot 10^{-4} c^{-0.729}, \quad (20)$$

Table 2. The parameters of electrolytic dissociation of 1,1-cyclohexanedicarboxylic acid in its dilute solutions at 25°C

Acid concentration, M	α_1	α_2	α'_2	pH
0.0001	0.8366	0.3441	0.4113	3.934
0.0002	0.7305	0.2226	0.3047	3.727
0.0004	0.6099	0.1351	0.2215	3.535
0.0006	0.5387	0.09852	0.1829	3.428
0.0008	0.4897	0.07809	0.1595	3.353
0.001	0.4531	0.06494	0.1433	3.297
0.002	0.3496	0.03595	0.1028	3.126
0.004	0.2639	0.01949	0.07385	2.961
0.006	0.2222	0.01353	0.06089	2.867
0.008	0.1961	0.01043	0.05319	2.800
0.01	0.1777	$8.51 \cdot 10^{-3}$	0.04787	2.750

$$\alpha'_2 = 4.3551 \cdot 10^{-3} c^{-0.494}, \quad (21) \qquad \alpha'_2 = 6.0954 \cdot 10^{-3} c^{-0.458}, \quad (25)$$

$$pH = 1.188 - 0.677 \lg c. \quad (22) \qquad pH = 1.367 - 0.64 \lg c. \quad (26)$$

1,1-cyclohexanedicarboxylic acid

$$\alpha_1 = 0.07261 c^{-0.269}, \quad (23)$$

$$\alpha_2 = 4.4259 \cdot 10^{-4} c^{-0.727}, \quad (24)$$

The equations for α_1 and α_2 may be used in the interval $c=0.0001-0.001M$; the equations for α'_2 and pH may be used in the interval $c=0.0001-0.01M$.

ფიზიკური ქიმია

1,1-ციკლოპენტან- და 1,1-ციკლოპექსანდიკარბონმჟავების ელექტროლიტური დისოციაციის კანონზომიერებები

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ავტორების მიერ შემოთავაზებული ორიგინალური განტოლებების დახმარებით გათვლილია 1,1-ციკლოპენტან- და 1,1-ციკლოპექსანდიკარბონმჟავების ელექტროლიტური დისოციაციის ორივე საფეხურის ჩვეულებრივი და “პარციალური” ხარისხების, pH-ის, მონო- და დიანიონებისა და არადისოცირებული მჟავას მოლეკულების კონცენტრაციების სიდიდეები ორივე მჟავას განზავებული ხსნარების კონცენტრაციის ინტერვალში 0.0001-0.01M. დადგენილია სხვადასხვა დამუხტული და დაუმუხტავი ნაწილაკების დომინირების კონცენტრაციული უბნები. შემოთავაზებულია აგრეთვე მარტივი ემპირიული განტოლებები დისოციაციის ხარისხებისა და ხსნართა pH-ის მნიშვნელობების სწრაფი მიახლოებითი გათვლისათვის.

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