

*Physical Chemistry*

## The Electrolytic Dissociation of Isomeric 4-Cyclohexene-1,2-Dicarboxylic Acids

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**ABSTRACT.** Isomeric 4-cyclohexene-1,2-dicarboxylic acids (cis- and trans-isomers) are widely used in various photosensitive, curable and thermostable enzyme compositions. It should be noted that their useful properties are directly connected with the peculiarities of the electrolytic dissociation of these acids. In this work an analysis of the regularities of the electrolytic dissociation of the cis- and trans-isomers of 4-cyclohexene-1,2-dicarboxylic acid in their dilute (0.0001 – 0.01M) solutions were carried out with the aid of an original method of determination of the dissociation parameters of weak multibasic organic acids with “overlapping” equilibria previously described by the authors. Values of the usual and “partial” degrees of dissociation (the “partial” degree term was first suggested by the authors) for all dissociation steps, and the values of the concentrations of various ionized and non-ionized forms of these acids, were calculated. With the aid of Debye-Huckel equation the activity coefficients of hydrogen ions and various anions were determined. The intervals of acid concentration in which various charged and uncharged products of dissociation (hydrogen ions, monoanions, dianions and undissociated acid molecules) prevail were also determined with the aid of an original method. We suggest also simple empirical equations for fast approximate calculation of the  $\alpha_1$ ,  $\alpha_2$ ,  $\alpha_2'$  and pH values in the dilute (0.0001 – 0.01M) solutions of the cis- and trans isomers of 4-cyclohexene-1,2-dicarboxylic acids. © 2013 Bull. Georg. Natl. Acad. Sci.

**Key words:** dissociation constant, degree of dissociation, dissociation step, hydrogen ion, monoanion, dianion, concentration.

Isomeric 4-cyclohexene-1,2-dicarboxylic acids (cis- and trans-isomers) are widely used in various photosensitive, curable and thermostable enzyme compositions. It should be noted that their useful properties are directly connected with the peculiarities of the electrolytic dissociation of these acids. In this communication the regularities of corresponding dissociation processes in the dilute (0.0001-

0.01M) solutions of cis- and trans-4-cyclohexene-1,2-dicarboxylic acids are analyzed with the aid of an original method suggested and used by the authors for the investigation of the complex equilibria of dissociation of weak multibasic organic acids with the “overlapping” equilibria effect [1-4].

It has been shown in [1,3] that the law of dilution for both dissociation steps of weak dibasic organic

acid may be expressed as follows:

$$K_1 = \frac{c(\alpha_1^2 - \alpha_2^2)}{1 - \alpha_1} F_1 = \frac{\alpha_1^2 [1 - (\alpha_2')^2] c}{1 - \alpha_1} F_1 = \frac{x_1^2 - x_2^2}{c - x_1} F_1 \quad (1)$$

$$\begin{aligned} K_2 &= \frac{c\alpha_2(\alpha_1 + \alpha_2)}{\alpha_1 - \alpha_2} F_2 = \frac{\alpha_1\alpha_2'(1 + \alpha_2')c}{1 - \alpha_2'} F_2 = \\ &= \frac{x_2(x_1 + x_2)}{x_1 - x_2} F_2, \end{aligned} \quad (2)$$

where  $K_1$  and  $K_2$  are the thermodynamic dissociation constants for both dissociation steps,  $\alpha_1$  and  $\alpha_2$  are the "usual" degrees of dissociation for the first and second steps,  $\alpha_2'$  is the "partial" degree of dissociation for the second step,  $x_1$  and  $x_2$  are the contributions of the corresponding steps to the  $[H^+]$  value,  $c$  is the total (analytical) concentration of acid,  $F_1$  and  $F_2$  are the quotients of the activity coefficients for the corresponding steps:

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

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

According to the equations (1) and (2),  $\alpha_1$ ,  $\alpha_2$ ,  $\alpha_2'$ ,  $x_1$  and  $x_2$  values can be evaluated successively by iterative solution of the following quadratic equations:

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

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

$$\alpha_2' = \frac{1}{2} \left[ -\left(1 + \frac{K_2}{\alpha_1 c F_2}\right) + \sqrt{\left(1 + \frac{K_2}{\alpha_1 c F_2}\right)^2 + \frac{4K_2}{\alpha_1 c F_2}} \right] \quad (7)$$

$$x_1 = \frac{1}{2} \left[ -\frac{K_1}{F_1} + \sqrt{\left(\frac{K_1}{F_1}\right)^2 + 4\left(x_2^2 + \frac{K_1 c}{F_1}\right)} \right] \quad (8)$$

$$x_2 = \frac{1}{2} \left[ -\left(\frac{K_2}{F_2} + x_1\right) + \sqrt{\left(\frac{K_2}{F_2} + x_1\right)^2 + \frac{4K_2 x_1}{F_2}} \right] \quad (9)$$

Using the  $\alpha_1$ ,  $\alpha_2$ ,  $\alpha_2'$ ,  $x_1$  and  $x_2$  values we may determine the equilibrium concentrations of hydrogen ions, mono- and dianions and undissociated acid molecules:

$$[H^+] = c(\alpha_1 + \alpha_2) = c\alpha_1(1 + \alpha_2') = x_1 + x_2 \quad (10)$$

$$[HA^-] = c(\alpha_1 - \alpha_2) = c\alpha_1(1 - \alpha_2') = x_1 - x_2 \quad (11)$$

$$[A^{2-}] = c\alpha_2 = c\alpha_1\alpha_2' = x_2 \quad (12)$$

$$[H_2A] = c(1 - \alpha_1) = c\left(1 - \frac{\alpha_2}{\alpha_2'}\right) = c - x_1 \quad (13)$$

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

$$\lg f_i = -\frac{z_i^2 A \sqrt{I}}{1 + a_i B \sqrt{I}} \quad (14)$$

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  $I = c(\alpha_1 + 2\alpha_2) = c\alpha_1(1 + 2\alpha_2') = x_1 + 2x_2$ . The activity coefficient of undissociated acid is assumed to be unity.

The  $\alpha_1$ ,  $\alpha_2$ ,  $\alpha_2'$ ,  $x_1$  and  $x_2$  are mutually connected by the following equations:

$$\alpha_2' = \frac{\alpha_2}{\alpha_1} = \frac{x_2}{x_1} \quad (15)$$

$$\alpha_1 = \frac{x_1}{c} \quad (16)$$

$$\alpha_2 = \frac{x_2}{c} \quad (17)$$

**Table 1.** The dissociation parameters of trans-4-cyclohexene-1,2-dicarboxylic acid in its dilute solutions at 20°C

Acid concentration, M	$\alpha_1$	$\alpha_2$	$\alpha'_2$	pH
0.0001	0.6409	0.01533	0.02392	4.187
0.0002	0.5233	0.007875	0.01505	3.979
0.0004	0.4121	0.004024	0.009765	3.785
0.0006	0.3534	0.002713	0.007677	3.677
0.0008	0.3154	0.002051	0.006503	3.603
0.001	0.2880	0.001651	0.005733	3.546
0.002	0.2147	0.000841	0.003919	3.375
0.004	0.1579	0.000429	0.002719	3.210
0.006	0.1314	0.000290	0.002207	3.115
0.008	0.1151	0.000220	0.001908	3.049
0.01	0.1038	0.000177	0.001705	2.998

The equations (5)-(9) and (15)-(17) were used for the calculation of the values of usual and “partial” degrees of dissociation and the  $x_1$  and  $x_2$  values for cis and trans 4-cyclohexene-1,2-dicarboxylic acids in their dilute (0.0001-0.01M) solutions. The  $K_1$  and  $K_2$  values for these acids at 20°C were taken from [5]:  $K_1=1.122 \times 10^{-4}$ ;  $K_2=1.549 \times 10^{-6}$  (trans isomer);  $K_1=1.288 \times 10^{-4}$ ;  $K_2=1.62 \times 10^{-7}$  (cis isomer). The values of the constants of equation (14) at 20°C were taken from [6]. The calculated values of  $\alpha_1$ ,  $\alpha_2$ ,  $\alpha'_2$  and pH at 20°C are presented in Tables 1 (trans isomer) and 2 (cis isomer).

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

$$[HA^-] = [H_2A]: \alpha_1 = \frac{1 + \alpha_2}{2} = \frac{1}{2 - \alpha'_2} \quad (18)$$

$$c = 2x_1 - x_2 \quad (19)$$

$$[H^+] = [H_2A]: \alpha_1 = \frac{1 - \alpha_2}{2} = \frac{1}{\alpha'_2 + 2} \quad (20)$$

$$c = 2x_1 + x_2 \quad (21)$$

$$[A^{2-}] = [H_2A]: \alpha_1 = 1 - \alpha_2 = \frac{1}{\alpha'_2 + 1} \quad (22)$$

$$c = x_1 + x_2 = [H^+] \quad (23)$$

$$[HA^-] = [A^{2-}]: \alpha_1 = 2\alpha_2 \quad (24)$$

$$\alpha'_2 = 0.5 \quad (25)$$

$$x_1 = 2x_2 \quad (26)$$

The data of Table 1 show that in the acid concentration region  $c \leq 0.0002M$  the  $[HA^-]$  value in the solutions of trans- and cis- isomers exceeds the  $[H_2A]$  value: the inequalities  $\alpha_1 > \frac{1 + \alpha_2}{2}$ ,  $\alpha_1 > \frac{1}{2 - \alpha'_2}$  and  $c < 2x_1 - x_2$  are fulfilled. The dianion concentration is less than the  $[H_2A]$  value in all studied intervals of acid concentration (the inequalities  $\alpha_1 < 1 - \alpha_2$ ,  $\alpha_1 < \frac{1}{\alpha'_2 + 1}$  and  $c > [H^+]$  are fulfilled). The  $[H^+]$  values exceed  $[H_2A]$  values also in the acid concentration interval  $c \leq 0.0002M$  (the inequalities  $\alpha_1 > \frac{1 - \alpha_2}{2}$ ,  $\alpha_1 > \frac{1}{\alpha'_2 + 2}$  and  $c < 2x_1 + x_2$  are fulfilled). The monoanion concentration exceeds the dianion concentration in all studied intervals of concentrations of both isomers of 4-cyclohexene-1,2-dicarboxylic acid (the inequalities  $\alpha_1 > 2\alpha_2$ ,  $\alpha'_2 < 0.5$  and  $x_1 > 2x_2$  are fulfilled).

**Table 2.** The dissociation parameters of cis-4-cyclohexene-1,2-dicarboxylic acid in its dilute solutions at 20°C

Acid concentration, M	$\alpha_1$	$\alpha_2$	$\alpha'_2$	pH
0.0001	0.6640	0.00100	0.001596	4.181
0.0002	0.5467	0.000846	0.001548	3.966
0.0004	0.4334	0.000429	0.000989	3.767
0.0006	0.3730	0.000288	0.000773	3.657
0.0008	0.3336	0.000216	0.000648	3.581
0.001	0.3050	0.000175	0.000573	3.524
0.002	0.2282	0.000089	0.000389	3.351
0.004	0.1683	0.000045	0.000269	3.184
0.006	0.1401	0.000031	0.000218	3.089
0.008	0.1229	0.000023	0.000188	3.022
0.01	0.1109	0.000019	0.000168	2.970

Taking into account the comparative complexity of calculations with the aid of equations (5)-(9), we suggest also simple empirical equations for fast approximate determination of the dissociation parameter values in the dilute solutions of both studied acids.

**Trans-4-cyclohexene-1,2-dicarboxylic acid**

$$\alpha_1 = 0.0257c^{-0.351} \quad (27)$$

(up to  $c = 0.002\text{M}$ )

$$\alpha_2 = 2.06063 \times 10^{-6} c^{-0.968} \quad (28)$$

(up to  $c = 0.01\text{M}$ )

$$\alpha'_2 = 8.10961 \times 10^{-5} c^{-0.614} \quad (29)$$

(up to  $c = 0.002\text{M}$ )

$$pH = 1.62 - 0.639 \lg c \quad (30)$$

(up to  $c = 0.01\text{M}$ )

**Cis-4-cyclohexene-1,2-dicarboxylic acid**

$$\alpha_1 = 0.031405c^{-0.333} \quad (31)$$

(up to  $c = 0.001\text{M}$ )

$$pH = 1.535 - 0.658 \lg c \quad (32)$$

(up to  $c = 0.01\text{M}$ )

In all specified intervals of acid concentration the values of relative error for the presented empirical equations do not exceed 6%.

ფიზიკური ქიმია

## იზომერული 4-ციკლოჰექსენ-1,2-დიკარბონმჟავების ელექტროლიტური დისოციაცია

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(წარმოდგენილია აკადემიის წევრის გ. ცინცაძის მიერ)

ავტორების მიერ შემოთავაზებული ორიგინალური განტოლებების დახმარებით გათვლილია 4-ციკლოჰექსენ-1,2-დიკარბონმჟავას ცის- და ტრანს-იზომერების ელექტროლიტური დისოციაციის ორივე საფეხურის ჩვეულებრივი და “პარციალური” ხარისხების, pH-ის, მონო- და დიანიონებისა და არადისოცირებული მჟავას მოლეკულების კონცენტრაციების სიდიდეები ორივე იზომერის განზავებულ ხსნარებში (0.0001-0.01M) 20°C-ზე. დადგენილია სხვადასხვა დამუხტული და დაუმუხტავი ნაწილაკების დომინირების კონცენტრაციული უბნები. შემოთავაზებულია აგრეთვე მარტივი ემპირიული განტოლებები დისოციაციის სხვადასხვა პარამეტრის მნიშვნელობების სწრაფი მიახლოებითი გათვლისათვის.

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