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The Regularities of the Electrolytic Dissociation of 1,3-Cyclohexanedicarboxylic Acids

Elene Kvaratskhelia[1], Ramaz Kvaratskhelia[1] and Rusudan Kurtanidze[1]

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[1] Ivane Javakhishvili Tbilisi State University

Abstract

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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

Cyclohexanedicarboxylic acids are widely used as the members of the positive resist radiation-sensitive composition, the coating resinous compositions, for production the high-solid polyurethane coatings for such demanding markets as automotive, transportation, maintenance, and aerospace. In this communication the regularities of electrolytic dissociation of cis and trans-1,3-cyclohexanedicarboxylic acids are studied by the suggested by authors original method for calculation the parameters of dissociation of weak multibasic organic acids with the "overlapping" equilibria effect.

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

[1]

[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:

[3]

[4]

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

[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'_2can be evaluated successively by iterative solution of following two quadratic equations:

[6]

[7]

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[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:

[9]

[10]

[11]

[12]

The dissociation constants of cis-acid have the following values: $K_1=7.943\times10^{-5}$; $K_2=3.467\times10^{-6}$. The corresponding values for trans-acid are: $K_1=4.898\times10^{-5}$; $K_2=1.862\times10^{-6}$.

In Tables I and II the values of α_1, α_2, $\alpha'_2$and pH for the dilute solutions of both acids are presented.

Table I. The values of the dissociation parameters

of cis-1,3-cyclohexanedicarboxylic acid

at 16ºC

Concentration, M	α_1
0.00010.00020.00040.00060.00080.0010.0020.0040.0060.0080.01	0.58220.46600.36120.30750.27320.24870.18390.13440.11150.097530.08785 0.032180.016860.0087230.0059

Table II. The values of the dissociation parameters

of trans-1,3-cyclohexanedicarboxylic acid

at 19ºC

Concentration, M	α_1	c
0.00010.00020.00040.00060.00080.0010.0020.0040.0060.0080.01	0.49950.39040.29710.25080.22160.20100.14730.10700.088450.077220.06945	0.017910.0092480.0047390.00 $^{4}5.05\cdot10^{-4}3.40\cdot10^{-4}2.57\cdot10^{-4}2.$

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

Cis-1,3-cyclohexanedicarboxylic acid

[13]

[14]

[15]

[16]

Trans-1,3-cyclohexanedicarboxylic acid

[17]

[18]

[19]

[20]

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R. Agladze Institute of Inorganic Chemistry
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Iv. Javakhishvili Tbilisi State University
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Cyclohexanedicarboxylic acids are widely used as the members of the positive resist radiation-sensitive composition, the coating resinous compositions, for production the high-solid polyurethane coatings for such demanding markets as automotive, transportation, maintenance, and aerospace. In this communication the regularities of electrolytic dissociation of cis and trans-1,3-cyclohexanedicarboxylic acids are studied by the suggested by authors original method for calculation the parameters of dissociation of weak multibasic organic acids with the "overlapping" equilibria effect.

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

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

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

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:

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

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

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

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 two quadratic equations:

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

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

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

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:

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

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

$$[A^{2-}] = c\alpha_2 \quad [11]$$

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

The dissociation constants of cis-acid have the following values: $K_1=7.943\times10^{-5}$; $K_2=3.467\times10^{-6}$. The corresponding values for trans-acid are: $K_1=4.898\times10^{-5}$; $K_2=1.862\times10^{-6}$.

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.

Table I. The values of the dissociation parameters of cis-1,3-cyclohexanedicarboxylic acid at 16°C

Concentration, M	α_1	α_2	α'_2	pH
0.0001	0.5822	0.03218	0.05527	4.215
0.0002	0.4660	0.01686	0.03618	4.020
0.0004	0.3612	0.008723	0.02415	3.836
0.0006	0.3075	0.005912	0.01923	3.732
0.0008	0.2732	0.004482	0.01641	3.661
0.001	0.2487	0.003614	0.01453	3.606
0.002	0.1839	0.001849	0.01005	3.439
0.004	0.1344	0.000945	0.007030	3.277
0.006	0.1115	0.000639	0.005728	3.184
0.008	0.09753	0.000484	0.004958	3.118
0.01	0.08785	0.000390	0.004437	3.068

Table II. The values of the dissociation parameters of trans-1,3-cyclohexanedicarboxylic acid at 19°C

Concentration, M	α_1	α_2	α'_2	pH
0.0001	0.4995	0.01791	0.03586	4.290
0.0002	0.3904	0.009248	0.02369	4.102
0.0004	0.2971	0.004739	0.01595	3.924
0.0006	0.2508	0.003198	0.01275	3.823
0.0008	0.2216	0.002418	0.01091	3.753
0.001	0.2010	0.001946	0.009682	3.699
0.002	0.1473	$9.91\cdot10^{-4}$	0.006730	3.536
0.004	0.1070	$5.05\cdot10^{-4}$	0.004720	3.376
0.006	0.08845	$3.40\cdot10^{-4}$	0.003849	3.284
0.008	0.07722	$2.57\cdot10^{-4}$	0.003333	3.219
0.01	0.06945	$2.07\cdot10^{-4}$	0.002986	3.169

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

Cis-1,3-cyclohexanedicarboxylic acid

$$\alpha_1 = 0.019588c^{-0.371} \quad \text{(up to 0.002M)} \quad [13]$$

$$\alpha_2 = 4.93174\times10^{-6}c^{-0.955} \quad \text{(up to 0.01M)} \quad [14]$$

$$\alpha_2' = 2.61216\times10^{-4}c^{-0.581} \quad \text{(up to 0.002M)} \quad [15]$$

$$pH = 1.801 - 0.601\lg c \quad \text{(up to 0.01M)} \quad [16]$$

Trans-1,3-cyclohexanedicarboxylic acid

$$\alpha_1 = 0.013366c^{-0.395} \quad \text{(up to 0.002M)} \quad [17]$$

$$\alpha_2 = 2.48313\times10^{-6}c^{-0.964} \quad \text{(up to 0.01M)} \quad [18]$$

$$\alpha_2' = 1.8578\times10^{-4}c^{-0.571} \quad \text{(up to 0.002M)} \quad [19]$$

$$pH = 1.919 - 0.592\lg c \quad \text{(up to 0.01M)} \quad [20]$$

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