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The Regularities of Electrolytic Dissociation of Diphenyladipic Acids

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ABSTRACT. The original method for an analysis and determination of the parameters of the processes of electrolytic dissociation of weak multibasic organic acids with the "overlapping equilibria" effect was used for a study of the peculiarities of the dilute solutions of diphenyladipic acids. Values of the usual and "partial" degrees of dissociation for both steps, 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 mono and dianions were determined. The intervals of acid concentration with the predominance of various charged and uncharged products of dissociation were also determined with the aid of original equations. The simple empirical equations for fast approximate calculation of the dissociation parameters of the studied derivatives of adipic acid were also suggested. © *2014 Bull. Georg. Natl. Acad. Sci.*

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

The isomeric diphenyladipic acids (together with the phenyl and diphenyl derivatives of other higher saturated dibasic acids) are used for manufacture of novel synthetic linear copolyamides. In this work the regularities of the processes of electrolytic dissociation of α,α′-diphenyladipic and β,β′-diphenyladipic acids in their dilute (0.0001-0.01M) solutions are analyzed with the aid of an original method suggested and used by the authors for 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 can be expressed as follows:

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

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

where K_1 and K_2 denote the thermodynamic dissociation constants for the first and second dissociation steps, α_1 and α_2 are the usual degrees of dissociation for the corresponding steps, α'_2 is the "partial" degree of dissociation for the second step, c is the total (analytical) concentration of acid, F_1 and F_2 are the quotients of the activity coefficients for both steps:

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

Acid concentration, M	α_1	α_2	α'_2	pH
0.0001	0.5558	0.0364	0.0655	4.231
0.0002	0.4412	0.0192	0.0434	4.041
0.0004	0.3398	0.0100	0.0293	3.860
0.0006	0.2884	0.0068	0.0234	3.758
0.0008	0.2557	0.0051	0.0201	3.688
0.001	0.2325	0.0041	0.0178	3.633
0.002	0.1714	0.0021	0.0124	3.469
0.004	0.1250	0.0011	0.0087	3.308
0.006	0.1036	0.0007	0.0071	3.215
0.008	0.0906	0.0006	0.0061	3.150
0.01	0.0815	0.0004	0.0055	3.099

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

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

According to the equations (1) and (2), the values of the dissociation degrees may be evaluated successively by iterative solution of the following quadratic equations:

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

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

The values of the "partial" degrees of dissociation may be evaluated by iterative solution of the following quadratic equations:

$$\alpha_1 = \frac{1}{2}\left\{\left[-\frac{K_1}{cF_1[H_2A]} + \sqrt{\left\{\frac{K_1}{cF_1[H_2A]}\right\}^2 + \frac{4K_1}{cF_1[H_2A]}}\right]\right\}, \quad (7)$$

$$\alpha'_2 = \frac{1}{2}\left[-\left(1 + \frac{K_2}{\alpha_1 cF_2}\right) + \sqrt{\left(1 + \frac{K_2}{\alpha_1 cF_2}\right)^2 + \frac{4K_2}{\alpha_1 cF_2}}\right]. \quad (8)$$

Using the α_1, α_2 and α'_2 values we may determine the equilibrium concentrations of hydrogen ions, mono and dianions and undissociated acid:

$$[H^+] = c(\alpha_1 + \alpha_2) = c\alpha_1(1 + \alpha'_2), \quad (9)$$

$$[HA^-] = c(\alpha_1 - \alpha_2) = c\alpha_1(1 - \alpha'_2), \quad (10)$$

$$[A^{2-}] = c\alpha_2 = c\alpha_1\alpha'_2, \quad (11)$$

$$[H_2A] = c(1 - \alpha_1) = c\left(1 - \frac{\alpha_2}{\alpha'_2}\right). \quad (12)$$

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

$$\lg f_i = -\frac{z_i^2 A\sqrt{I}}{1 + a_i B\sqrt{I}}, \quad (13)$$

where a_i is the cation-anion distance of the closest approach, A and B are constants depending on the properties of water at the 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.

The equations (5)-(8) were used for the calculation of α_1, α_2 and α'_2 values for α,α′-diphenyladipic and β,β′-diphenyladipic acids in their dilute (0.0001-0.01M) solutions. The K_1 and K_2 values for the studied acids at 25°C were taken from [5]: $K_1 = 6.8 \times 10^{-5}$; $K_2 = 4.0 \times 10^{-6}$ (α,α′isomer): $K_1 = 6.04 \times 10^{-5}$; $K_2 = 6.39 \times 10^{-6}$ (β,β′ isomer). The values of the constants of equation (13) at 25°C were taken from [6]. The calculated values of α_1, α_2, α'_2 and pH at 25°C are presented in Tables 1 and 2.

The equations (9)-(12) allow the determination of the intervals of acid concentration, in which various charged and uncharged forms of acid prevail. The

Table 2. The values of the dissociation parameters of β,β′ -diphenyladipic acid at 25°C

Acid concentration, M	α_1	α_2	α'_2	pH
0.0001	0.5365	0.0541	0.1009	4.233
0.0002	0.4231	0.0291	0.0688	4.048
0.0004	0.3241	0.0153	0.0473	3.873
0.0006	0.2745	0.0105	0.0382	3.774
0.0008	0.2431	0.0080	0.0328	3.704
0.001	0.2208	0.0065	0.0292	3.651
0.002	0.1624	0.0033	0.0205	3.488
0.004	0.1182	0.0017	0.0145	3.330
0.006	0.0979	0.0012	0.0118	3.238
0.008	0.0855	0.0009	0.0103	3.173
0.01	0.0770	0.0007	0.0092	3.123

conditions of equality of these concentrations are:

$$[HA^-]=[H_2A]:\alpha_1=\frac{1+\alpha_2}{2}=\frac{1}{2-\alpha'_2}, \quad (14)$$

$$[H^+]=[H_2A]:\alpha_1=\frac{1-\alpha_2}{2}=\frac{1}{\alpha'_2+2}, \quad (15)$$

$$[A^{2-}]=[H_2A]:\alpha_1=1-\alpha_2=\frac{1}{\alpha'_2+1}, \quad (16)$$

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

$$\alpha'_2=0.5. \quad (18)$$

These equations and data presented in Tables 1 and 2 show that the monoanion concentration exceeds the concentration of undissociated acid only when c ≤ 0.0001M for both studied acids (the inequalities $\alpha_1>\frac{1+\alpha_2}{2}$ and $\alpha_1>\frac{1}{2-\alpha'_2}$ are fulfilled). The $[H^+]$ value exceeds the $[H_2A]$ value also when c ≤ 0.0001M for both acids (the inequalities $\alpha_1>\frac{1-\alpha_2}{2}$ and $\alpha_1>\frac{1}{\alpha'_2+2}$ are fulfilled). The dianion concentration is less than the $[H_2A]$ value in all the studied intervals of acid concentration (the inequalities $\alpha_1<1-\alpha_2$ and $\alpha_1<\frac{1}{\alpha'_2+1}$ are fulfilled). The monoanion concentration exceeds the dianion concentration for all c values (the inequalities $\alpha_1>2\alpha_2$ and $\alpha'_2<0.5$ are fulfilled).

Taking into account the comparative complexity of the calculations with the aid of equations (5)-(8), we suggest also the simple empirical equations for fast approximate determination of the dissociation parameters of α,α′ -diphenyladipic and β,β′ -diphenyladipic acids in their dilute solutions.

α,α′ -Diphenyladipic acid

$$\alpha_1=0.016256c^{-0.385} \quad (19)$$

(c = 0.0001-0.002M),

$$\alpha_2=6.0534\times10^{-6}c^{-0.945} \quad (20)$$

(c = 0.0001-0.01M),

$$\alpha'_2=3.7239\times10^{-4}c^{-0.56} \quad (21)$$

(c = 0.0001-0.004M),

$$pH=1.854-0.593\lg c \quad (22)$$

(c = 0.0001-0.01M),

β,β′ -Diphenyladipic acid

$$\alpha_1=0.016032c^{-0.381} \quad (23)$$

(c = 0.0001-0.002M),

$$\alpha_2=1.1246\times10^{-5}c^{-0.921} \quad (24)$$

(c = 0.0001-0.01M),

$$\alpha'_2=7.0146\times10^{-4}c^{-0.54} \quad (25)$$

(c = 0.0001-0.006M),

$$pH=1.901-0.582\lg c \quad (26)$$

(c = 0.0001-0.01M).

In all indicated intervals of acid concentration the values of the relative error for all these equations do not exceed 5-6%.

We suggest also the universal general empirical equation for the approximate calculation of the pH values of dilute solutions of weak dibasic organic acids:

$$pH = 1.489 + 0.8\,pK_1 - (1.185 - 0.14\,pK_1)\lg c \quad (27)$$

This equation is applicable in the c values interval 0.0001-0.01M. In case of the studied diphenyl derivatives of adipic acid the values of the relative error do not exceed 1.66%.

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