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Physical Chemistry

The Regularities of Electrolytic Dissociation of Phthalic Acid

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ABSTRACT. An analysis of the regularities of the dissociation of phthalic (benzenedicarboxylic) acid was carried out with the aid of a method previously described by the authors. The values of the degrees of dissociation for both steps, and the concentrations of various ionized and non-ionized forms of this acid were determined. Empirical equations are also suggested for easy approximate calculation of the degrees of dissociation and pH values of dilute solutions of phthalic acid. *© 2009 Bull. Georg. Natl. Acad. Sci.*

Key words: *degree of dissociation, dissociation step, dissociation constant, hydrogen ion concentration, phthalic acid.*

Phthalic (benzenedicarboxylic) acid is an important representative of benzenepolycarboxylic acids. This acid is widely used in the manufacture of dyes, perfumes, pharmaceuticals, and synthetic fibers. The derivatives of phthalic acid (phthalates) are used in plastics, especially PVC (where they act as plasticizers) and are also present in a wide range of industrial, household and consumer products, including personal care products, such as pipes, vinyl wall and floor coverings, roofing materials, safety glass, car parts, lubricating oils, detergents, food packaging, adhesives, paints, inks, medical tubing, blood bags, pharmaceuticals, footwear, electrical cables, nail polish, hair sprays, soaps, shampoos, perfumes, moisturizers and toys. It is interesting to note that an unusually large percentage of phthalic acid was found in fatty acids during an analysis of the lipids of the deep sea jellyfish *Atolla.*

In this work, with the aid of the method suggested by us for the determination of the degrees of dissociation and other dissociation parameters of weak multibasic organic acids with close values for the stepwise dissociation constants [1], an analysis is carried out of the regularities of dissociation of phthalic acid in its dilute solutions. Because of the very low solubility of the meta- and para-isomers of phthalic acid only the dissociation of ortho-phthalic acid is considered.

In our previous communication [1] we suggested original equations for the law of dilution for weak dibasic organic acids with close values of the dissociation constants of both steps (case of "overlapping" dissociation equilibria):

$$\mathrm{K}_1 = \frac{c(\alpha_1^2 - \alpha_2^2)}{1 - \alpha_1} F_1 \tag{1}$$

$$\mathrm{K}_2 = \frac{c\alpha_2(\alpha_1 + \alpha_2)}{\alpha_1 - \alpha_2} F_2 \tag{2}$$

where K_1 and K_2 are the dissociation constants of the corresponding steps, α_1 and α_2 are the degrees of dissociation of these steps, c is the total (analytical) concentration of acid, F_1 and F_2 are the corresponding quotients of activity coefficients:

$$F_1 = \frac{f_{H^+} f_{HA^-}}{f_{H_2A}} \tag{3}$$

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

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

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

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

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

$$\log f_i = -\frac{z_i^2 A\sqrt{I}}{1 + a_i B\sqrt{I}}, \qquad (7)$$

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 $I = c(\alpha_1 + 2\alpha_2)$. The activity coefficient of undissociated phthalic acid was assumed to be unity.

The various dissociation parameters can be expressed by the following equations:

$$[HA^-] = c(\alpha_1 - \alpha_2) \qquad (8)$$

$$[A^{2-}] = c\alpha_2 \qquad (9)$$

$$[H_2A] = c(1 - \alpha_1) \qquad (10)$$

$$[H^+] = c(\alpha_1 + \alpha_2) \qquad (11)$$

Taking into account that

$$\alpha_1 = \frac{x}{c} \qquad (12)$$

$$\alpha_2 = \frac{y}{c} \qquad (13)$$

(where x and y are the contributions of first and second dissociation steps to the equilibrium concentration of hydrogen ions $[H^+]$) we may express the laws of dilution also by the following equations:

$$\mathrm{K}_1 = \frac{x^2 - y^2}{c - x} \qquad (14)$$

$$\mathrm{K}_2 = \frac{y(x + y)}{x - y}. \qquad (15)$$

According to these equations the values of x and y can be evaluated successively by iterative solution of two quadratic equations:

$$x = \frac{1}{2}\left[-\frac{K_1}{F_1} + \sqrt{\left(\frac{K_1}{F_1}\right)^2 + 4\left(y^2 + \frac{K_1 c}{F_1}\right)}\right] \qquad (16)$$

$$y = \frac{1}{2}\left[-\left(\frac{K_2}{F_2} + x\right) + \sqrt{\left(\frac{K_2}{F_2} + x\right)^2 + \frac{4K_2 x}{F_2}}\right]. \qquad (17)$$

The equilibrium concentrations of ionized and nonionized forms may be expressed by the following equations:

$$[HA^-] = x - y \qquad (18)$$

$$[A^{2-}] = y \qquad (19)$$

$$[H_2A] = c - x \qquad (20)$$

$$[H^+] = x + y \qquad (21)$$

An analysis of the process of electrolytic dissociation of phthalic acid (and also of any weak dibasic organic acid with the "overlapping" dissociation equilibria) can be carried out with the aid of the set of equations (5), (6), (8)-(11) as well as the equations (16)-(21).

In Table 1 the values of the degrees of dissociation and pH for the dilute solutions of phthalic acid at 25°C are presented. Table 2 contains the values of the equilibrium concentrations of mono- and dianions and undissociated molecules of phthalic acid in analogous solutions. The K_1 and K_2 values of phthalic acid necessary for the calculations were taken from the CRC Handbook [2] (these values are: $K_1 = 1.14\times10^{-3}$; $K_2 = 3.698\times10^{-6}$). The values of a_i, A and B for the equation (7) at 25°C were taken from [3, 4].

Taking into account the comparative complexity of the calculations with the aid of the equations (5), (6),

Table 1.

The values of α_1, α_2 and pH for the dilute solutions of phthalic acid at 25°C

$c \cdot 10^3$ mol · dm^{-3}	α_1	α_2	pH
0.1	0.9265	0.03583	4.022
0.2	0.8710	0.01883	3.756
0.3	0.8266	0.01285	3.607
0.4	0.7898	0.009778	3.504
0.5	0.7585	0.007911	3.426
0.6	0.7314	0.006653	3.364
0.7	0.7076	0.005742	3.312
0.8	0.6863	0.005060	3.268
0.9	0.6672	0.004523	3.230
1.0	0.6499	0.004090	3.197
2.0	0.5340	0.002115	2.985
4.0	0.4235	0.001096	2.789
6.0	0.3648	0.0007461	2.680
8.0	0.3266	0.0005692	2.604
10.0	0.2989	0.0004630	2.548

Table 2.

The values of [HA$^-$], [A^{2-}] and [H$_2$A] for the dilute solutions of phthalic acid at 25°C

$c \cdot 10^3$ mol·dm^{-3}	[HA$^-$] mol·dm^{-3}	[A^{2-}] mol·dm^{-3}	[H$_2$A] mol·dm^{-3}
0.1	$8.907 \cdot 10^{-5}$	$3.583 \cdot 10^{-6}$	$7.350 \cdot 10^{-6}$
0.2	$1.704 \cdot 10^{-4}$	$3.766 \cdot 10^{-6}$	$2.580 \cdot 10^{-5}$
0.3	$2.441 \cdot 10^{-4}$	$3.855 \cdot 10^{-6}$	$5.202 \cdot 10^{-5}$
0.4	$3.120 \cdot 10^{-4}$	$3.911 \cdot 10^{-6}$	$8.408 \cdot 10^{-5}$
0.5	$3.753 \cdot 10^{-4}$	$3.956 \cdot 10^{-6}$	$1.207 \cdot 10^{-4}$
0.6	$4.348 \cdot 10^{-4}$	$3.992 \cdot 10^{-6}$	$1.612 \cdot 10^{-4}$
0.7	$4.913 \cdot 10^{-4}$	$4.019 \cdot 10^{-6}$	$2.047 \cdot 10^{-4}$
0.8	$5.450 \cdot 10^{-4}$	$4.048 \cdot 10^{-6}$	$2.510 \cdot 10^{-4}$
0.9	$5.964 \cdot 10^{-4}$	$4.071 \cdot 10^{-6}$	$2.995 \cdot 10^{-4}$
1.0	$6.458 \cdot 10^{-4}$	$4.090 \cdot 10^{-5}$	$3.501 \cdot 10^{-4}$
2.0	$1.064 \cdot 10^{-3}$	$4.230 \cdot 10^{-6}$	$9.320 \cdot 10^{-4}$
4.0	$1.690 \cdot 10^{-3}$	$4.384 \cdot 10^{-6}$	$2.306 \cdot 10^{-3}$
6.0	$2.184 \cdot 10^{-3}$	$4.477 \cdot 10^{-6}$	$3.811 \cdot 10^{-3}$
8.0	$2.608 \cdot 10^{-3}$	$4.554 \cdot 10^{-6}$	$5.387 \cdot 10^{-3}$
10.0	$2.984 \cdot 10^{-3}$	$4.630 \cdot 10^{-6}$	$7.011 \cdot 10^{-3}$

(7), (16) and (17), we suggest the following simple empirical equations for fast approximate calculations of the α_1, α_2 and pH values in the phthalic acid concentration interval from 0.0001 to 0.001 mol·dm^{-3}:

$$\alpha_1 = 0.23552c^{-0.151} \tag{22}$$

$$\alpha_2 = 5.808 \cdot 10^{-6} c^{-0.949} \tag{23}$$

$$pH = 0.706 - 0.827 \lg c \tag{24}$$

The reliability of these equations is confirmed by the values of their relative errors which don't exceed 3% (the relative error is the ratio of the difference between the approximate value and corresponding accurate value, divided by the approximate value, and converted to percent).

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ავტორების მიერ ადრე აღწერილი მეთოდით ჩატარებულია ფტალის მჟავას (ბენზოლდიკარბონმჟავას) დისოციაციის კანონზომიერებების ანალიზი. განსაზღვრულია ამ მჟავას დისოციაციის ორივე საფეხურის ხარისხებისა და სხვადასხვა იონიზებული და არაიონიზებული ფორმების კონცენტრაციების სიდიდეები. შემოთავაზებულია აგრეთვე ემპირიული განტოლებები ფტალის მჟავას დისოციაციის ხარისხებისა და მისი განზავებული ხსნარების pH-ის მნიშვნელობათა მარტივი მიახლოებითი გათვლისათვის.

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