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):

\[ K_1 = \frac{c(\alpha_1^2 - \alpha_2^2)}{1 - \alpha_1} F_1 \]  \hspace{1cm} (1)

\[ K_2 = \frac{c\alpha_2(\alpha_1 + \alpha_2)}{\alpha_1 - \alpha_2} F_2 \]  \hspace{1cm} (2)

where \( K_1 \) and \( K_2 \) are the dissociation constants of the corresponding steps, \( \alpha_1 \) and \( \alpha_2 \) 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:

\[ F_1 = \frac{f_{H^+}f_{H_2A}}{f_{H_2A}} \]  \hspace{1cm} (3)

According to equations (1) and (2) the degrees of dissociation, \( \alpha_1 \) and \( \alpha_2 \), can be evaluated successively by iterative solution of two quadratic equations:

\[
\alpha_1 = \frac{1}{2} \left( \frac{1}{2} \left( \frac{K_1}{cF_1} + \sqrt{\left( \frac{K_1}{cF_1} \right)^2 + 4 \left( \alpha^2_2 + \frac{K_1}{cF_1} \right)} \right) \right)
\]

\[
\alpha_2 = \frac{1}{2} \left( \frac{1}{2} \left( \frac{K_2}{cF_2} + \alpha_1 \right) + \sqrt{\left( \frac{K_2}{cF_2} + \alpha_1 \right)^2 + 4K_2 \alpha_1} \right) \left( \frac{cF_2}{cF_1} \right)
\]

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

\[
\log f_i = -\frac{z_i^2 A \sqrt{I}}{1 + a_i B \sqrt{I}},
\]

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, and \( z_i \) 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:

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

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

\[
[H_2A] = c(1 - \alpha_1)
\]

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

Taking into account that

\[
\alpha_1 = \frac{x}{c}
\]

\[
\alpha_2 = \frac{y}{c}
\]

(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:

\[
K_1 = \frac{x^2 - y^2}{c - x}
\]

\[
K_2 = \frac{y(x + y)}{x - y}
\]

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

\[
x = \frac{1}{2} \left( \frac{1}{2} \left( \frac{K_1}{cF_1} + \sqrt{\left( \frac{K_1}{cF_1} \right)^2 + 4 \left( \alpha^2_2 + \frac{K_1}{cF_1} \right)} \right) \right)
\]

\[
y = \frac{1}{2} \left( \frac{1}{2} \left( \frac{K_2}{cF_2} + \alpha_1 \right) + \sqrt{\left( \frac{K_2}{cF_2} + \alpha_1 \right)^2 + 4K_2 \alpha_1} \right) \left( \frac{cF_2}{cF_1} \right)
\]

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

\[
[HA^-] = x - y
\]

\[
[A^{2-}] = y
\]

\[
[H_2A] = c - x
\]

\[
[H^+] = x + y
\]

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 25ºC are presented. Table 2 contains the values of the equilibrium concentrations of mono- and dianions and undisassociated 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: \( K_1 = 1.14 \times 10^{-3} \); \( K_2 = 3.698 \times 10^{-6} \)). The values of \( a_i, A \) and \( B \) for the equation (7) at 25ºC were taken from [3, 4].

Taking into account the comparative complexity of the calculations with the aid of the equations (5), (6),
The Regularities of Electrolytic Dissociation of Phthalic Acid


(7), (16) and (17), we suggest the following simple empirical equations for fast approximate calculations of the \( \alpha_1 \), \( \alpha_2 \) and pH values in the phthalic acid concentration interval from 0.0001 to 0.001 mol·dm\(^{-3}\):

\[
\alpha_1 = 0.23552 c^{-0.151} \quad (22)
\]

\[
\alpha_2 = 5.808 \times 10^{-6} c^{-0.949} \quad (23)
\]

\[
pH = 0.706 - 0.8271 \log c \quad (24)
\]

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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### Table 1.

The values of \( \alpha_1 \), \( \alpha_2 \) and pH for the dilute solutions of phthalic acid at 25ºC

<table>
<thead>
<tr>
<th>( c \cdot 10^3 ) mol·dm(^{-3} )</th>
<th>( \alpha_1 )</th>
<th>( \alpha_2 )</th>
<th>pH</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.1</td>
<td>0.9265</td>
<td>0.03583</td>
<td>4.022</td>
</tr>
<tr>
<td>0.2</td>
<td>0.8710</td>
<td>0.01883</td>
<td>3.756</td>
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<td>0.3</td>
<td>0.8266</td>
<td>0.01285</td>
<td>3.607</td>
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<tr>
<td>0.4</td>
<td>0.7898</td>
<td>0.009778</td>
<td>3.504</td>
</tr>
<tr>
<td>0.5</td>
<td>0.7585</td>
<td>0.007911</td>
<td>3.426</td>
</tr>
<tr>
<td>0.6</td>
<td>0.7314</td>
<td>0.006653</td>
<td>3.364</td>
</tr>
<tr>
<td>0.7</td>
<td>0.7076</td>
<td>0.005742</td>
<td>3.312</td>
</tr>
<tr>
<td>0.8</td>
<td>0.6863</td>
<td>0.004523</td>
<td>3.268</td>
</tr>
<tr>
<td>1.0</td>
<td>0.6499</td>
<td>0.004090</td>
<td>3.230</td>
</tr>
<tr>
<td>2.0</td>
<td>0.5340</td>
<td>0.002115</td>
<td>2.985</td>
</tr>
<tr>
<td>4.0</td>
<td>0.4235</td>
<td>0.001096</td>
<td>2.789</td>
</tr>
<tr>
<td>6.0</td>
<td>0.3648</td>
<td>0.0007461</td>
<td>2.680</td>
</tr>
<tr>
<td>8.0</td>
<td>0.3266</td>
<td>0.0005692</td>
<td>2.604</td>
</tr>
<tr>
<td>10.0</td>
<td>0.2989</td>
<td>0.0004630</td>
<td>2.548</td>
</tr>
</tbody>
</table>

### Table 2.

The values of [HA\(^-\)], [A\(^2-\)] and [H\(_2\)A] for the dilute solutions of phthalic acid at 25ºC

<table>
<thead>
<tr>
<th>( c \cdot 10^3 ) mol·dm(^{-3} )</th>
<th>[HA(^-)] mol·dm(^{-3} )</th>
<th>[A(^2-)] mol·dm(^{-3} )</th>
<th>[H(_2)A] mol·dm(^{-3} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.1</td>
<td>8.907 \times 10^{-5}</td>
<td>3.583 \times 10^{-6}</td>
<td>7.350 \times 10^{-6}</td>
</tr>
<tr>
<td>0.2</td>
<td>1.704 \times 10^{-4}</td>
<td>3.766 \times 10^{-6}</td>
<td>2.580 \times 10^{-5}</td>
</tr>
<tr>
<td>0.3</td>
<td>2.441 \times 10^{-4}</td>
<td>3.855 \times 10^{-6}</td>
<td>5.202 \times 10^{-5}</td>
</tr>
<tr>
<td>0.4</td>
<td>3.120 \times 10^{-4}</td>
<td>3.911 \times 10^{-6}</td>
<td>8.408 \times 10^{-5}</td>
</tr>
<tr>
<td>0.5</td>
<td>3.753 \times 10^{-4}</td>
<td>3.956 \times 10^{-6}</td>
<td>1.207 \times 10^{-4}</td>
</tr>
<tr>
<td>0.6</td>
<td>4.348 \times 10^{-4}</td>
<td>3.992 \times 10^{-6}</td>
<td>1.612 \times 10^{-4}</td>
</tr>
<tr>
<td>0.7</td>
<td>4.913 \times 10^{-4}</td>
<td>4.019 \times 10^{-6}</td>
<td>2.047 \times 10^{-4}</td>
</tr>
<tr>
<td>0.8</td>
<td>5.450 \times 10^{-4}</td>
<td>4.048 \times 10^{-6}</td>
<td>2.510 \times 10^{-4}</td>
</tr>
<tr>
<td>0.9</td>
<td>5.964 \times 10^{-4}</td>
<td>4.071 \times 10^{-6}</td>
<td>2.995 \times 10^{-4}</td>
</tr>
<tr>
<td>1.0</td>
<td>6.458 \times 10^{-4}</td>
<td>4.090 \times 10^{-6}</td>
<td>3.501 \times 10^{-4}</td>
</tr>
<tr>
<td>2.0</td>
<td>1.604 \times 10^{-3}</td>
<td>4.230 \times 10^{-6}</td>
<td>9.320 \times 10^{-4}</td>
</tr>
<tr>
<td>4.0</td>
<td>1.690 \times 10^{-3}</td>
<td>4.384 \times 10^{-6}</td>
<td>2.306 \times 10^{-3}</td>
</tr>
<tr>
<td>6.0</td>
<td>2.184 \times 10^{-3}</td>
<td>4.477 \times 10^{-6}</td>
<td>3.811 \times 10^{-3}</td>
</tr>
<tr>
<td>8.0</td>
<td>2.608 \times 10^{-3}</td>
<td>4.554 \times 10^{-6}</td>
<td>5.387 \times 10^{-3}</td>
</tr>
<tr>
<td>10.0</td>
<td>2.984 \times 10^{-3}</td>
<td>4.630 \times 10^{-6}</td>
<td>7.011 \times 10^{-3}</td>
</tr>
</tbody>
</table>
წიგნის თავის სურათის გადაწყვეტილობის ლომისხის პარამეტრებით

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(წარმოადგენს ავტორის ჟ. (ართვის ძეგლს))

აღჭურვის ბოლო ამოცანა ართულად მოღვაწეთა სამუშაოთა შედეგთან მიეთანხება ფერის შესაქმნელი თავები გარეული (გამორიცხვის-დანილინგვის) დახურვისათვის გასწვრივ მხოლოდ მხოლოდ გარეული საქმიანი ნაწილი. საიდანაც მდიდარი პანმელი მოძრაობის ილუსტრაცია მოძრაობების ექსპერიმენტები ყოფილია. სურათთან არჩევით ფარგლებში ვინაღიპებენ მეთოდის გარეული შესაქმნელი ნაწილი და შიგნიშვნებით სინამდვილეში pH-ის შესამჩინებლობათა ანიმაცია ფარგლების გათვალისწინებით.

REFERENCES


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