

THE REGULARITIES OF DISSOCIATION OF WEAK DIBASIC ORGANIC ACIDS WITH THE CLOSE Ka' AND Ka'' VALUES

E. Kvaratskhelia and R. Kvaratskhelia
Georgian Academy of Sciences
Institute of Inorganic Chemistry and Electrochemistry
Mindely str. 11
Tbilisi, 380086, Republic of Georgia

Weak dibasic carboxylic acids play an important part in many electroorganic and biochemical processes. Therefore the regularities of dissociation and formation of the hydrogen ions concentration in the solutions of these acids rouse great interest.

Here we consider case of dissociation of weak dibasic acid with the close Ka' and Ka'' values when dissociation on first step is not complete and the hydrogen ions concentration in dilute (for example, 0.001M) solution of this acid is caused by dissociation on both steps:



Analysis of this case shows that Ka' and Ka'' can be expressed by the following equations:

$$Ka' = \frac{[H^+]^{(x-y)}}{0.001-x} \quad (3) \quad Ka'' = \frac{[H^+]^y}{x-y} \quad (4)$$

where x is the part of the total concentration of hydrogen ions [H⁺] which is formed due to first dissociation step and y is the part of [H⁺], connected with second step. If we use a designation m=x/[H⁺] (the share of [H⁺] caused by first step) the equations (3) and (4) can be expressed by equations:

$$Ka' = \frac{[H^+]^{2(2m-1)}}{0.001-m[H^+]} \quad (5) \quad Ka'' = \frac{[H^+]^{(1-m)}}{2m-1} \quad (6)$$

Taking into account that x+y=[H⁺] we can express the equations (3) and (4) in the form without [H⁺]:

$$Ka' = \frac{x^2-y^2}{0.001-x} \quad (7) \quad Ka'' = \frac{y(x+y)}{x-y} \quad (8)$$

Analysis of case of dissociation of the weak dibasic acid with the close Ka' and Ka'' values with the aid of the equations (5) and (6) shows that the values m<0.6 are less probable because in this case the values of Ka'/Ka'' are less than one. The case of m=0.7 is also less probable because here the values of Ka'/Ka'' are insignificantly more than one even under the high [H⁺] values. The condition m>0.8 is the most probable because in this case the Ka'/Ka'' values reach the really existing quantities.

The equations (7) and (8) show that in the millimolar solution of the weak dibasic acid with the close Ka' and Ka'' values the most realistic values of the ratio y/x are: less than 0.2 (when the Ka' values are equal to 10⁻⁴–10⁻³), less than 0.1 (within the Ka' values interval 5.10⁻⁵–10⁻⁴) and less than 0.07 (when Ka'=10⁻⁵–5.10⁻⁵).

With the aid of the equations (5)-(8) we made the graphic dependences Ka', Ka'', Ka'/Ka'' vs [H⁺], m, x, y, y/x. These equations take also the possibility to calculate the "theoretical" Ka'' values with the aid of the reference Ka' values and the most probable values of m, x and y. Such calculation was carried out by us for 70 weak dibasic acids with the close Ka' and Ka'' values (the corresponding reference values of Ka' and Ka'' are taken from CRC Handbook of Chemistry and Physics, 81st Edition, 2001). Below the calculated by us Ka'' values

for some acids (together with the reference Ka'' values) are presented.

Acid	pKa'(ref.)	pKa''(ref.)	pKa''(cal.)
Adipic	4.41	5.41	5.10
Azelaic	4.53	5.33	5.04
DL-Tartaric	3.03	4.37	4.56
Glutaric	4.32	5.42	5.05
Itaconic	3.85	5.45	5.18
Malonic	2.85	5.70	5.26
Mesaconic	3.09	4.75	4.72
Methylsuccinic	4.13	5.64	5.11
Pimelic	4.71	5.58	5.12
Sebacic	4.59	5.59	5.17
Terephthalic	3.54	4.34	4.62
Phthalic	2.94	5.43	5.18
Fumaric	3.02	4.38	4.70
Malic	3.40	5.11	5.01
Succinic	4.21	5.64	5.33

The difference between the reference and calculated pKa'' values in all cases is not appreciable and is less than one order (the maximum difference is equal to 0.62). The Ka'' values calculated by us are "theoretical": the difference between these and experimentally determined reference Ka'' values is connected with the specific peculiarities of behaviour of acids with the various structure in solutions and can be a criterion of influence of the structural peculiarities of acids on monoanion acidity.

In case of the weak dibasic acids with the comparatively high Ka' values causing a complete dissociation on first step the Ka'' value for the millimolar solution of this acid can be expressed by the following equation:

$$Ka'' = \frac{[H^+]([H^+]-0.001)}{0.002-[H^+]} \quad (9)$$

Taking into account the complete dissociation on first step, we can write:

$$[H^+] = 0.001 + x \quad (10)$$

where x is the part of [H⁺] formed by second dissociation step. Therefore we obtain an equation connected Ka'' and x without [H⁺]:

$$Ka'' = \frac{x(0.001+x)}{0.001-x} \quad (11)$$

With the aid of this equation we made the graphic dependence Ka''-x which took the possibility to determine the share of second dissociation step in the total concentration of hydrogen ions with the aid of the Ka'' values. Such weak dibasic acids are, for example, oxalic, meta- and para-sulfobenzoic acids and also some acids with the higher basicity which have the comparatively high Ka' and Ka'' values and sufficiently low values of other dissociation constants (Ka'', Ka'^v etc.): mellitic, pyromellitic, etidronic, DL-cysteic, diaminopimelic acids, L-cystine.

