

Equations for Approximate Calculation of the Dissociation Parameters of Weak Dibasic Organic Acids

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ABSTRACT. Simple empirical equations for fast approximate calculation of first and second dissociation degrees and pH for dilute solutions of weak dibasic organic acids are suggested. © 2011 Bull. Georg. Natl. Acad. Sci.

Key words: empirical equations, degrees of dissociation, pH, dibasic organic acids.

The special properties of many weak dibasic organic acids result in their wide use in medicine, pharmacology, food, cosmetic and chemical industries, and some of these acids participate in a series of important biological processes occurring in living organisms. Therefore, knowledge of the regularities of electrolytic dissociation of these acids, and the properties of their dilute solutions, are of great interest.

In our recent publications [1, 2] we suggested equations for accurate calculation of the degrees of dissociation of weak dibasic (and tribasic with low K_3 values) organic acids:

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

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

where K_1 and K_2 are the thermodynamic dissociation constants of the first and second dissociation steps, α_1 and α_2 are the “usual” degrees of dissociation of these steps, c is the total (analytical) concentration of acid, F_1 and F_2

are the quotients of the activity coefficients. The accurate values of α_1 and α_2 can be calculated successively by iterative solution of these quadratic equations.

The value of the “partial” degree of dissociation of the second step (this term was first suggested by us [1, 2]) may be calculated with the aid of the following equation:

$$\alpha'_2 = \frac{1}{2} \left[-\left(\frac{K_2}{\alpha_1 c F_2} + 1\right) + \sqrt{\left(\frac{K_2}{\alpha_1 c F_2} + 1\right)^2 + \frac{4K_2}{\alpha_1 c F_2}} \right] \quad (3)$$

or with the aid of α_1 and α_2 values:

$$\alpha'_2 = \alpha_2 / \alpha_1. \quad (4)$$

Taking into account the comparative complexity of calculations with the aid of equations (1)-(3), we tried to obtain also simple empirical equations for fast approximate calculation of the α_1 , α_2 and α'_2 values for the dilute solutions of weak dibasic (and tribasic with low K_3 values) organic acids with “overlapping” equilibria. Our investigations with the aid of the function linearization method showed that the dependence of the α_1 , α_2 and α'_2 values on acid concentration in the range $c=0.0001-0.001M$ can be approximated by the following general

equation:

$$\alpha = bc^{-a} \quad (5)$$

In Table 1 the values of the a and b parameters of equation (5) (a_1 and b_1 for α_1 , α_2 and b_2 for a_2, a_3 and b_3 for α_2') for a series of weak dibasic (and tribasic with low K_3 values) organic acids are presented.

The reliability of equation (5) for all three degrees of dissociation is confirmed by the values of its relative errors which do not exceed 5% in the range of acid concentration 0.0001-0.001M (the relative error is the ratio of the difference between the approximate a value and corresponding accurate value, divided by the approximate a value and converted to percent). In the higher concentration range (up to 0.01M) the values of relative errors rise to 10-15%.

It was also shown that the dependence of the pH values of the dilute solutions of the above considered acids on their concentration may be approximated by the following equation:

$$pH = b - a \lg c. \quad (6)$$

The values of the a and b parameters for a series of weak dibasic and tribasic organic acids are presented in Table 2.

The values of the relative errors for equation (6) in

The parameters of equation (5) for weak dibasic and tribasic organic acids at 25°C

Acid	a_1	b_1	a_2	b_2	a_3	b_3
Malonic	0.143	0.25881	0.953	$3.083 \cdot 10^{-6}$	0.810	$1.191 \cdot 10^{-5}$
Succinic	0.375	0.0171	0.962	$3.133 \cdot 10^{-6}$	0.587	$1.832 \cdot 10^{-4}$
Glutaric	0.394	0.013274	0.943	$5.834 \cdot 10^{-6}$	0.549	$4.395 \cdot 10^{-4}$
Adipic	0.408	0.010889	0.940	$6.053 \cdot 10^{-6}$	0.532	$5.559 \cdot 10^{-4}$
Pimelic	0.432	0.00673	0.948	$3.837 \cdot 10^{-6}$	0.516	$5.702 \cdot 10^{-4}$
Suberic	0.420	0.008912	0.943	$5.794 \cdot 10^{-6}$	0.523	$6.501 \cdot 10^{-4}$
Azelaic	0.415	0.009162	0.930	$7.656 \cdot 10^{-6}$	0.515	$8.356 \cdot 10^{-4}$
Sebacic	0.425	0.008109	0.954	$3.664 \cdot 10^{-6}$	0.529	$4.519 \cdot 10^{-4}$
Maleic	0.031	0.75338	0.959	$8.913 \cdot 10^{-7}$	0.928	$1.183 \cdot 10^{-6}$
Fumaric	0.167	0.20046	0.788	$1.824 \cdot 10^{-4}$	0.621	$9.099 \cdot 10^{-4}$
Mesaconic	0.190	0.16254	0.875	$4.487 \cdot 10^{-5}$	0.685	$2.761 \cdot 10^{-4}$
Itaconic	0.336	0.03148	0.955	$5.129 \cdot 10^{-6}$	0.619	$1.629 \cdot 10^{-4}$
Acetylenedicarboxylic	0.012	0.87905	0.775	$2.028 \cdot 10^{-4}$	0.763	$2.307 \cdot 10^{-4}$
L-Tartaric	0.173	0.19498	0.793	$1.897 \cdot 10^{-4}$	0.620	$9.727 \cdot 10^{-4}$
DL-Tartaric	0.177	0.18536	0.785	$1.910 \cdot 10^{-4}$	0.608	$1.030 \cdot 10^{-3}$
meso-Tartaric	0.200	0.14321	0.896	$2.710 \cdot 10^{-5}$	0.696	$1.892 \cdot 10^{-4}$
Malic	0.250	0.086124	0.920	$1.466 \cdot 10^{-5}$	0.670	$1.702 \cdot 10^{-4}$
Tartronic	0.070	0.5188	0.816	$1.122 \cdot 10^{-4}$	0.746	$2.163 \cdot 10^{-4}$
Citric	0.193	0.15632	0.870	$4.592 \cdot 10^{-5}$	0.677	$2.938 \cdot 10^{-4}$
Isocitric	0.229	0.10789	0.866	$5.164 \cdot 10^{-5}$	0.637	$4.786 \cdot 10^{-4}$
Oxaloacetic	0.094	0.42361	0.781	$2.051 \cdot 10^{-4}$	0.687	$4.842 \cdot 10^{-4}$
trans-Aconitic	0.132	0.28615	0.812	$1.314 \cdot 10^{-4}$	0.680	$4.592 \cdot 10^{-4}$
Phthalic	0.151	0.23552	0.949	$5.808 \cdot 10^{-6}$	0.798	$2.466 \cdot 10^{-5}$
Methylmalonic	0.176	0.1835	0.956	$2.622 \cdot 10^{-6}$	0.780	$1.429 \cdot 10^{-5}$
Methylsuccinic	0.375	0.018156	0.960	$3.177 \cdot 10^{-6}$	0.585	$1.750 \cdot 10^{-4}$
β -Methylglutaric	0.391	0.014454	0.949	$5.728 \cdot 10^{-6}$	0.558	$3.963 \cdot 10^{-4}$
β -Ethylglutaric	0.394	0.01374	0.937	$7.499 \cdot 10^{-6}$	0.543	$5.458 \cdot 10^{-4}$
β -Propylglutaric	0.402	0.012446	0.945	$6.138 \cdot 10^{-6}$	0.543	$4.932 \cdot 10^{-4}$
β -Isopropylglutaric	0.388	0.014158	0.949	$4.571 \cdot 10^{-6}$	0.561	$3.228 \cdot 10^{-4}$
2-Oxoglutaric	0.075	0.49882	0.849	$6.576 \cdot 10^{-5}$	0.774	$1.318 \cdot 10^{-4}$
Phenylmalonic	0.092	0.42169	0.910	$1.950 \cdot 10^{-5}$	0.818	$4.624 \cdot 10^{-5}$
Phenylsuccinic	0.322	0.036817	0.955	$4.093 \cdot 10^{-6}$	0.633	$1.112 \cdot 10^{-4}$
Benzylsuccinic	0.367	0.019588	0.959	$3.221 \cdot 10^{-6}$	0.592	$1.644 \cdot 10^{-4}$
Thiodiacetic	0.228	0.10665	0.817	$1.122 \cdot 10^{-4}$	0.589	$1.052 \cdot 10^{-3}$
Dithiodiacetic	0.182	0.17418	0.743	$3.556 \cdot 10^{-4}$	0.561	$2.042 \cdot 10^{-3}$
1,1-Cyclopropanedicarboxylic	0.030	0.76032	0.939	$6.383 \cdot 10^{-6}$	0.909	$8.395 \cdot 10^{-6}$
1,1-Cyclobutanedicarboxylic	0.181	0.17139	0.965	$1.828 \cdot 10^{-6}$	0.784	$1.067 \cdot 10^{-5}$
1,1-Cyclopentanedicarboxylic	0.235	0.10888	0.729	$4.742 \cdot 10^{-4}$	0.494	$4.355 \cdot 10^{-3}$
1,1-Cyclohexanedicarboxylic	0.269	0.07261	0.727	$4.426 \cdot 10^{-4}$	0.458	$6.095 \cdot 10^{-3}$

Table 2.

The parameters of equation (6) for weak dibasic and tribasic organic acids at 25°C

Acid	<i>a</i>	<i>b</i>	Acid	<i>a</i>	<i>b</i>
Malonic	0.842	0.641	Phthalic	0.827	0.706
Succinic	0.589	1.890	Methylmalonic	0.804	0.815
Glutaric	0.579	1.957	Methylsuccinic	0.606	1.795
Adipic	0.569	2.025	β-Methylglutaric	0.584	1.912
Pimelic	0.541	2.254	β-Ethylglutaric	0.582	1.929
Suberic	0.554	2.122	β-Propylglutaric	0.576	1.964
Azelaic	0.551	2.132	β-Isopropylglutaric	0.589	1.919
Sebacic	0.555	2.154	2-Oxoglutaric	0.857	0.516
Maleic	0.959	0.167	Phenylmalonic	0.886	0.447
Fumaric	0.742	0.959	Phenylsuccinic	0.654	1.515
Mesaconic	0.766	0.919	Benzylsuccinic	0.610	1.778
Itaconic	0.643	1.566	Thiodiacetic	0.699	1.171
Acetylenedicarboxylic	0.894	0.335	Dithiodiacetic	0.717	1.035
L-Tartaric	0.738	0.962	1,1-Cyclopropane-dicarboxylic	0.952	0.179
DL-Tartaric	0.736	0.983	1,1-Cyclobutane-dicarboxylic	0.795	0.854
meso-Tartaric	0.755	0.979	1,1-Cyclopentane-dicarboxylic	0.677	1.188
Malic	0.713	1.188	1,1-Cyclohexane-dicarboxylic	0.640	1.367
Tartronic	0.850	0.527			
Citric	0.744	1.000			
Isocitric	0.713	1.138			
Oxaloacetic	0.823	0.618			
trans-Aconitic	0.787	0.776			

the range of acid concentration 0.0001-0.001M do not exceed 2-3%.

We also considered the possibility of obtaining general equations for the α_1 , α_2 and pH values in which these parameters were connected with the dissociation constants and acid concentration only. Such equations were obtained as a result of the investigation dependences of the *a* and *b* parameters of equations (5) and (6) on the dissociation constant values of considered acids.

For α_1 value we suggest two general equations. The first equation corresponds to the pK_1 range 2.5-3.75:

$$\alpha_1 = 2.696 - 0.957 pK_1 - 0.5058 \cdot 10^{-8.257 \sqrt{K_1}} \lg c \quad (7)$$

For the pK_1 range 3.8-4.7 we suggest the following equation:

$$\alpha_1 = 2.122 + 0.338 pK_1 - (1.025 - 0.17 pK_1) \lg c \quad (8)$$

The values of the relative errors for these equations in the acid concentration range 0.0001-0.001M do not exceed 10-13%.

For α_2 values we suggest the following equation:

$$\alpha_2 = 337 K_2^{1.426 + m \lg c} \quad (9)$$

where $m=0.17-0.18$. The values of the relative error for this equation in the acid concentration range 0.0001-0.001M do not exceed 8%.

For the pH values of the dilute solutions of weak di- and tribasic organic acids we suggest the following equation:

$$pH = -1.489 + 0.8 pK_1 - (1.185 - 0.14 pK_1) \lg c \quad (10)$$

This equation can be used in the more extended acid concentration range: 0.0001-0.01M. The values of the relative error for this equation do not exceed 8%.

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შემოთავაზებულია მარტივი ემპირიული განტოლებები სუსტი ორფუძიანი ორგანული მჟავების განზავებულ ხსნარებში დისოციაციის ხარისხებისა და pH-ის მნიშვნელობათა სწრაფი მიახლოებითი გათვლისათვის. აღნიშნული განტოლებების გამოყენება შესაძლებელია აგრეთვე სუსტი სამფუძიანი ორგანული მჟავებისათვის, რომლებსაც დაბალი K_3 -ის სიდიდეები გააჩნია.

REFERENCES

1. E. Kvaratskhelia, R. Kvaratskhelia (2007), J. Solution Chem., **36**, 6: 787-792.
2. E. Kvaratskhelia, R. Kvaratskhelia (2009), J. Solution Chem., **38**, 3: 345-349.

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