

UDC 547.541

## THE REGULARITIES OF ELECTROLYTIC DISSOCIATION OF WEAK MONOBASIC, DI-BASIC AND TRI-BASIC ORGANIC ACIDS CONTAINED IN HONEY

**E.Kvaratskhelia, R.Kvaratskhelia and R.Kurtanidze**

*R.Agladze Institute of Inorganic Chemistry and Electrochemistry,  
Iv. Javakhishvili Tbilisi State University  
11 Mindelyst., 0186 Tbilisi, Georgia  
E-mail: elicko@mail.ru, ekvarats@yahoo.com*

*The original method suggested by authors for an analysis of the processes of electrolytic dissociation of weak multibasic organic acids was used for the calculation of the dissociation parameters of some dibasic and tribasic weak organic acids contained in honey. These acids include malic, succinic, tartaric and citric acids. The dissociation parameters of some monobasic, weak honey acids (gluconic, lactic and butyric acids) are also determined. The concentration intervals of predominance of various charged and uncharged substances in the diluted solutions of all above mentioned acids are established. The simple empirical equations for fast approximate calculation of the dissociation parameters are also suggested.*

**Keywords:** Weak organic acids, Dissociation constant, Dissociation step, Hydrogen ions concentration, Equations

### 1. INTRODUCTION

A number of weak mono and multibasic organic acids are known to occur in honey. They include gluconic, butyric, lactic, formic, acetic, malic, succinic, tartaric, oxalic and citric acids. The content of these acids varies from 1 to 600 mg/kg (generally, in light honeys much lower values are found than in dark honeys, e. g. honeydew). The pH values of honeys vary in the interval: 3.5 – 5.5. Taking into account that the hydrogen ions determining the acidity and other important properties of honey originate from dissociation of above mentioned acids, the regularities of the processes of electrolytic dissociation of the honey acids are of vital importance. In case of dibasic and tribasic organic honey acids these processes are characterized by complex “overlapping” equilibriums because of the joint participation of the separate dissociation

steps in the formation of hydrogen ions concentration.

The original method suggested by us for an analysis of the dissociation processes of weak multibasic organic acids with the “overlapping” equilibriums effect [1-4] was used for the calculation of the dissociation parameters (the usual and “partial” degrees of dissociation, concentrations of all anions, hydrogen ions and undissociated acid molecules, the concentration intervals of predominance of various charged and uncharged substances) for the dilute solutions of dibasic and tribasic organic honey acids: malic, succinic, tartaric and citric acids. The dissociation parameters of some weak monobasic organic honey acids: gluconic (the major organic honey acid), lactic and butyric acids were also determined.

### 2. WEAK MULTIBASIC ORGANIC ACIDS

In case of weak dibasic organic acid  $H_2A$  the mass action equations for both dissociation steps may be written as follows [1-3]:

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

$$K_2 = \frac{c\alpha_2(\alpha_1 + \alpha_2)}{\alpha_1 - \alpha_2} F_2 = \frac{c\alpha_1\alpha'_2(1 + \alpha'_2)}{1 - \alpha'_2} F_2 \quad (2)$$

where  $K_1$  and  $K_2$  are the thermodynamic dissociation constants of first and second steps,  $\alpha_1$  and  $\alpha_2$  are the usual degrees of dissociation of the corresponding steps,  $\alpha'_2$  is

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

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

The degrees of dissociation  $\alpha_1$ ,  $\alpha_2$  and  $\alpha'_2$  may be evaluated successively by iterative solution of the following quadratic equations:

$$\alpha_1 = \frac{1}{2} \left[ -\frac{K_1}{cF_1} + \sqrt{\left( \frac{K_1}{cF_1} \right)^2 + 4 \left( \alpha'_2 + \frac{K_1}{cF_1} \right)} \right] \quad (5)$$

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

$$\alpha'_2 = \frac{1}{2} \left[ -\left( 1 + \frac{K_2}{\alpha_1 cF_2} \right) + \sqrt{\left( 1 + \frac{K_2}{\alpha_1 cF_2} \right)^2 + \frac{4K_2}{\alpha_1 cF_2}} \right] \quad (7)$$

In case of weak tribasic organic acid  $H_3A$  the mass action equations have the following forms [1-3]:

$$K_1 = \frac{(\alpha_1 + \alpha_2 + \alpha_3)(\alpha_1 - \alpha_2)c}{1 - \alpha_1} F_1 = \frac{c\alpha_1^2(1 + \alpha'_2 + \alpha'_2\alpha'_3)(1 - \alpha'_2)}{1 - \alpha_1} F_1 \quad (8)$$

$$K_2 = \frac{(\alpha_1 + \alpha_2 + \alpha_3)(\alpha_2 - \alpha_3)c}{\alpha_1 - \alpha_2} F_2 = \frac{c\alpha_1\alpha'_2(1 + \alpha'_2 + \alpha'_2\alpha'_3)(1 - \alpha'_3)}{1 - \alpha'_2} F_2 \quad (9)$$

$$K_3 = \frac{(\alpha_1 + \alpha_2 + \alpha_3)\alpha_3 c}{\alpha_2 - \alpha_3} F_3 = \frac{c\alpha_1\alpha_3(1 + \alpha_2' + \alpha_2'\alpha_3')}{1 - \alpha_3'} F_3 \quad (10)$$

The values of the usual degrees of successively evaluated by an iterative solution dissociation, according to Eqs. (8)-(10), can be of three quadratic equations [1, 3]:

$$\alpha_1 = \frac{1}{2} \left[ -\left( \frac{K_1}{cF_1} + \alpha_3 \right) + \sqrt{\left( \frac{K_1}{cF_1} + \alpha_3 \right)^2 + 4 \left( \alpha_2^2 + \alpha_2\alpha_3 + \frac{K_1}{cF_1} \right)} \right] \quad (11)$$

$$\alpha_2 = \frac{1}{2} \left[ -\left( \frac{K_2}{cF_2} + \alpha_1 \right) + \sqrt{\left( \frac{K_2}{cF_2} + \alpha_1 \right)^2 + 4 \left( \alpha_3^2 + \alpha_1\alpha_3 + \frac{K_2\alpha_1}{cF_2} \right)} \right] \quad (12)$$

$$\alpha_3 = \frac{1}{2} \left[ -\left( \frac{K_3}{cF_3} + \alpha_1 + \alpha_2 \right) + \sqrt{\left( \frac{K_3}{cF_3} + \alpha_1 + \alpha_2 \right)^2 + \frac{4K_3\alpha_2}{cF_3}} \right] \quad (13)$$

The values of “partial” degrees of dissociation may be calculated with the aid of following equations:

$$\alpha_2' = \alpha_2 / \alpha_1 \quad (14)$$

$$\alpha_3' = \alpha_3 / \alpha_2 \quad (15)$$

or with the aid of the more complex equation presented in [3].

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

$$\lg f_i = -\frac{z_i^2 A \sqrt{I}}{1 + a_i B \sqrt{I}} \quad (16)$$

where  $a_i$  is the cation-anion distance of closest approach,  $A$  and  $B$  are constants depending on constants of multibasic honey acids at 25°C the properties of water at given temperature,  $z_i$  necessary for calculations were taken from [6]: is the charge of ion. The ionic strength  $I = c(\alpha_1 + 2\alpha_2) = c\alpha_1(1 + 2\alpha_2')$  for dibasic acids and  $I = c(\alpha_1 + 2\alpha_2 + 3\alpha_3) = c\alpha_1(1 + 2\alpha_2' + 3\alpha_2'\alpha_3')$  for tribasic acids. The values of  $A$  and  $B$  at 25°C and  $a_i$  for honey acids were estimated according to the data presented in [5]. The activity coefficient of undissociated acids is assumed to be unity. The values of the dissociation constant of malic acid:  $K_1=3.981\times10^{-4}$ ;  $K_2=7.762\times10^{-6}$ , succinic acid:  $K_1=6.166\times10^{-5}$ ;  $K_2=2.291\times10^{-6}$ , L-tartaric acid:  $K_1=1.047\times10^{-3}$ ;  $K_2=4.57\times10^{-5}$ , citric acid:  $K_1=7.413\times10^{-4}$ ;  $K_2=1.738\times10^{-5}$ ;  $K_3=3.981\times10^{-7}$ .

The concentrations of all charged and uncharged products of dissociation for dibasic acids can be expressed by following equations:

$$[HA^-] = c(\alpha_1 - \alpha_2) = c\alpha_1(1 - \alpha_2') \quad (17)$$

$$[H^+] = c(\alpha_1 + \alpha_2) = c\alpha_1(1 + \alpha_2') \quad (19)$$

For tribasic acids we may write the following equations:

$$[H_2A^-] = c(\alpha_1 - \alpha_2) = c\alpha_1(1 - \alpha_2') \quad (21)$$

$$[HA^{2-}] = c(\alpha_2 - \alpha_3) = c\alpha_1\alpha_2'(1 - \alpha_3') \quad (22)$$

$$[A^{3-}] = c\alpha_3 = c\alpha_1\alpha_2'\alpha_3' \quad (23)$$

$$[H^+] = c(\alpha_1 + \alpha_2 + \alpha_3) = c\alpha_1(1 + \alpha_2' + \alpha_2'\alpha_3') \quad (24)$$

$$[H_3A] = c(1 - \alpha_1) \quad (25)$$

With the aid of the Eqs. (17)-(25) we can determine the intervals of the acid concentration in which the various charged or uncharged substances dominate. This is possible according to the following equations expressed the conditions of equality of the various products of dissociation:

$$[H^+] = [H_2A] : \alpha_1 = \frac{1 - \alpha_2}{2} = \frac{1}{\alpha_2' + 2} \quad (26)$$

$$[HA^-] = [H_2A] : \alpha_1 = \frac{1 + \alpha_2}{2} = \frac{1}{2 - \alpha_2'} \quad (27)$$

$$[A^{2-}] = [H_2A] : \alpha_1 = 1 - \alpha_2 = \frac{1}{\alpha_2' + 1} \quad (28)$$

$$[A^{2-}] = [HA^-] : \alpha_1 = 2\alpha_2 \quad (29)$$

$$\alpha_2' = 0.5 \quad (30)$$

$$[H^+] = [H_3A] : \alpha_1 = \frac{1 - \alpha_2 - \alpha_3}{2} = \frac{1}{2 + \alpha_2' + \alpha_2'\alpha_3'} \quad (31)$$

$$[H_2A^-] = [H_3A] : \alpha_1 = \frac{1 + \alpha_2}{2} = \frac{1}{2 - \alpha_2'} \quad (32)$$

$$[HA^{2-}] = [H_3A] : \alpha_1 = 1 - \alpha_2 + \alpha_3 = \frac{1}{1 + \alpha_2'(1 - \alpha_3')} \quad (33)$$

$$[A^{3-}] = [H_3A] : \alpha_1 = 1 - \alpha_3 = \frac{1}{1 + \alpha_2'\alpha_3'} \quad (34)$$

$$[H_2A^-] = [HA^{2-}] : \alpha_1 = 2\alpha_2 - \alpha_3 = \frac{1}{2 - \alpha_3'} \quad (35)$$

In Tables 1-4 the values of the dissociation parameters of malic, succinic, tartaric and citric acids in their dilute (0.0001 –

0.01M) solutions at 25°C calculated with the aid of the above mentioned equations are presented.

**Table 1.** The values of the dissociation parameters of malic acid in its diluted solutions at 25°C.

Concentration, mol · dm <sup>-3</sup>	$\alpha_1$	$\alpha_2$	$\alpha'_2$	pH
0.0001	0.831	0.0688	0.0828	4.051
0.0002	0.736	0.0372	0.0505	3.817
0.0003	0.672	0.0256	0.0382	3.687
0.0004	0.624	0.0196	0.0314	3.597
0.0005	0.586	0.0159	0.0272	3.530
0.0006	0.555	0.0134	0.0242	3.476
0.0007	0.529	0.0116	0.0219	3.431
0.0008	0.507	0.0102	0.0202	3.393
0.0009	0.488	0.00914	0.0187	3.360
0.001	0.471	0.00827	0.0176	3.330
0.002	0.366	0.00428	0.0117	3.143
0.004	0.278	0.00221	0.00794	2.966
0.006	0.235	0.00150	0.00640	2.866
0.008	0.208	0.00114	0.00550	2.796
0.01	0.188	0.00093	0.00491	2.743

**Table 2.** The values of the dissociation parameters of succinic acid in its diluted solutions at 25°C.

Concentration, mol · dm <sup>-3</sup>	$\alpha_1$	$\alpha_2$	$\alpha'_2$	pH
0.0001	0.539	0.0219	0.0406	4.255
0.0002	0.426	0.0113	0.0266	4.063
0.0003	0.366	0.00769	0.0210	3.956
0.0004	0.327	0.00583	0.0179	3.882
0.0005	0.298	0.00470	0.0157	3.826
0.0006	0.277	0.00394	0.0142	3.780
0.0007	0.259	0.00339	0.0131	3.742
0.0008	0.245	0.00298	0.0122	3.709
0.0009	0.233	0.00266	0.0114	3.680
0.001	0.219	0.00240	0.0109	3.661
0.002	0.164	0.00123	0.00748	3.490
0.004	0.119	0.000625	0.00524	3.329
0.006	0.0989	0.000422	0.00426	3.236
0.008	0.0864	0.000319	0.00369	3.171
0.01	0.0778	0.000257	0.00331	3.121

**Table 3.** The values of the dissociation parameters of L-tartaric acid in its dilute solutions at 25°C.

Concentration, mol · dm <sup>-3</sup>	$\alpha_1$	$\alpha_2$	$\alpha'_2$	pH
0.0001	0.928	0.274	0.295	3.926
0.0002	0.866	0.166	0.192	3.693
0.0003	0.819	0.122	0.149	3.558
0.0004	0.780	0.0972	0.125	3.464
0.0005	0.748	0.0809	0.108	3.393
0.0006	0.720	0.0695	0.0965	3.335
0.0007	0.695	0.0609	0.0876	3.288
0.0008	0.674	0.0543	0.0806	3.246
0.0009	0.654	0.0490	0.0749	3.211
0.001	0.637	0.0447	0.0702	3.179
0.002	0.520	0.0241	0.0463	2.978
0.004	0.411	0.0140	0.0341	2.788
0.006	0.353	0.00884	0.0250	2.684
0.008	0.316	0.00678	0.0215	2.611
0.01	0.289	0.00552	0.0191	2.554

**Table 4 .** The values of the dissociation parameters of citric acid in its diluted solutions at 25°C.

Concentration, $\alpha_1$ mol · dm <sup>-3</sup>	$\alpha_2$	$\alpha_3 \alpha'_2$	$\alpha'_3$	pH
0.0001	0.897	0.126	$5.24 \times 10^{-4}$	0.140 0.00418 3.996
0.0002	0.824	0.0769	$1.87 \times 10^{-4}$	0.0934 0.00242 3.751
0.0003	0.770	0.0542	$9.73 \times 10^{-5}$	0.0704 0.00179 3.615
0.0004	0.727	0.0420	$6.13 \times 10^{-5}$	0.0578 0.00146 3.521
0.0005	0.692	0.0344	$4.29 \times 10^{-5}$	0.0497 0.00125 3.449
0.0006	0.662	0.0292	$3.21 \times 10^{-5}$	0.0440 0.00110 3.392
0.0007	0.636	0.0253	$2.52 \times 10^{-5}$	0.0398 $9.94 \times 10^{-4}$ 3.345
0.0008	0.614	0.0224	$2.03 \times 10^{-5}$	0.0365 $9.04 \times 10^{-4}$ 3.304
0.0009	0.594	0.0201	$1.69 \times 10^{-5}$	0.0338 $8.43 \times 10^{-4}$ 3.269
0.001	0.576	0.0182	$1.44 \times 10^{-5}$	0.0316 $7.89 \times 10^{-4}$ 3.237
0.002	0.462	0.00956	$4.94 \times 10^{-6}$	0.0207 $5.17 \times 10^{-4}$ 3.040
0.004	0.359	0.00499	$1.77 \times 10^{-6}$	0.0139 $3.54 \times 10^{-4}$ 2.854
0.006	0.307	0.00341	$1.00 \times 10^{-6}$	0.0111 $2.94 \times 10^{-4}$ 2.750
0.008	0.273	0.00260	$6.65 \times 10^{-7}$	0.00954 $2.56 \times 10^{-4}$ 2.678
0.01	0.249	0.00211	$4.86 \times 10^{-7}$	0.00849 $2.30 \times 10^{-4}$ 2.622

The Eqs. (26)-(35) may be used for a determination the concentration intervals of prevailing of various dissociation products of the honey acids. For all acids monoanion remains the predominant anion in all studied

interval of acids concentration (the inequalities  $\alpha_1 > 2\alpha_2$  for dibasic acids and  $\alpha_1 > 2\alpha_2 - \alpha_3$  for citric acid are fulfilled). The  $[HA^-]$  value exceeds the  $[H_2A]$  value when  $c \leq 0.0008$  mol · dm<sup>-3</sup> (malic acid),  $c \leq 0.0001$  mol · dm<sup>-3</sup>

(succinic acid) and  $c \leq 0.002 \text{ mol} \cdot \text{dm}^{-3}$  (L-tartaric acid) (the inequality  $\alpha_1 > \frac{1+\alpha_2}{2}$  is fulfilled). In case of citric acid the  $[\text{H}_2\text{A}^-]$  value exceeds the  $[\text{H}_3\text{A}]$  value up to  $c = 0.001 \text{ mol} \cdot \text{dm}^{-3}$ . The dianion concentration exceeds the concentration of undissociated acid only in the cases of tartaric and citric acids when  $c \leq 0.0002 \text{ mol} \cdot \text{dm}^{-3}$  (L-tartaric acid) and  $c \leq 0.0001 \text{ mol} \cdot \text{dm}^{-3}$  (citric acid) (the inequalities  $\alpha_1 > 1 - \alpha_2$  and  $\alpha_1 > 1 - \alpha_2 + \alpha_3$  are fulfilled respectively). The hydrogen ion concentration exceeds the concentration of undissociated acid when  $c \leq 0.0008 \text{ mol} \cdot \text{dm}^{-3}$  (malic acid),  $c \leq 0.0001 \text{ mol} \cdot \text{dm}^{-3}$  (succinic acid),  $c \leq 0.003 \text{ mol} \cdot \text{dm}^{-3}$  (L-tartaric acid) and

$$\alpha_n = ac^{-b} \quad (36)$$

The pH values were approximated by following empirical equation:

$$pH = a - b \lg c \quad (37)$$

In Table 5 the values of the  $a$  and  $b$  coefficients for the calculation of  $\alpha_1, \alpha_2, \alpha'_2$  and  $pH$  values are presented.

**Table 5.** The values of the coefficients of the Eqs. (36) and (37).

<b>a</b>	<b>b</b>								
	<b>Acid</b>	<b><math>\alpha_1</math></b>	<b><math>\alpha_2</math></b>	<b><math>\alpha'_2</math></b>	<b>pH</b>	<b><math>\alpha_1</math></b>	<b><math>\alpha_2</math></b>	<b><math>\alpha'_2</math></b>	<b>pH</b>
Malic	0.08612	$1.466 \times 10^{-5}$	$1.7022 \times 10^{-4}$	1.188	0.25	0.92	0.67	0.713	
Succinic	0.0171	$3.133 \times 10^{-6}$	$1.8323 \times 10^{-4}$	1.89	0.375	0.962	0.587	0.589	
Tartaric	0.195	$1.8967 \times 10^{-4}$	$9.7275 \times 10^{-4}$	0.962	0.173	0.793	0.62	0.738	
Citric	0.15632	$5.70164 \times 10^{-5}$	$2.9376 \times 10^{-4}$	1.0000	0.193	0.84	0.677	0.744	

The  $\alpha_3$  and  $\alpha'_3$  values for citric acid can be approximated by following empirical equations:

$$\alpha_3 = 2.799 \times 10^{-10} c^{-1.568} \quad (38)$$

$$\alpha'_3 = 5.0298 \times 10^{-6} c^{-0.728} \quad (39)$$

Eq. (37) may be used for the approximate calculation of the pH values of all studied honey acids in a broad interval of the  $c$  values: 0.0001-

$0.001 \text{ mol} \cdot \text{dm}^{-3}$  (citric acid) (the inequalities  $\alpha_1 > \frac{1-\alpha_2}{2}$  for dibasic acids and  $\alpha_1 > \frac{1-\alpha_2-\alpha_3}{2}$  for citric acid are fulfilled).

Taking into account the comparative complexity of calculations by the Eqs. (5)-(7) and (11)-(13), we suggest the simple empirical equations for fast approximate determination of the dissociation parameters of studied honey acids.

The values of the usual and "partial" degrees of dissociation may be approximated by the following general empirical equation:

acids and  $c = 0.0001\text{-}0.002 \text{ mol} \cdot \text{dm}^{-3}$  for succinic acid. For an approximation of the  $\alpha_2$  values Eq.(36) can be used in intervals:  $c = 0.0001\text{-}0.001 \text{ mol} \cdot \text{dm}^{-3}$  (tartaric and citric acids),  $c = 0.0001\text{-}0.008 \text{ mol} \cdot \text{dm}^{-3}$  (malic acid) and  $c = 0.0001\text{-}0.01 \text{ mol} \cdot \text{dm}^{-3}$  (succinic acid). For all studied acids the  $\alpha_2$  values may be approximated in the interval:  $c = 0.0001\text{-}$

$0.002 \text{ mol} \cdot \text{dm}^{-3}$ . The Eqs. (38) and (39) can be used in the intervals:  $c = 0.0001\text{-}0.002 \text{ mol} \cdot \text{dm}^{-3}$  and  $c = 0.0001\text{-}0.001 \text{ mol} \cdot \text{dm}^{-3}$ , respectively. The values of the relative error for all above mentioned empirical equations in the indicated concentration intervals do not exceed 5-6%.

### 3. WEAK MONOBASIC ORGANIC HONEY ACIDS

It is known that the law of dilution for weak monobasic acid is expressed by following equation:

$$K = \frac{c\alpha^2}{1-\alpha} F \quad (40)$$

$$\text{where } F = \frac{f_H f_{A^-}}{f_{HA}}$$

The values of the degree of dissociation can be successively evaluated by an iterative solution of following quadratic equation:

$$\alpha = \frac{1}{2} \left[ -\frac{K}{cF} + \sqrt{\left( \frac{K}{cF} \right)^2 + \frac{4K}{cF}} \right] \quad (41)$$

The values of the activity coefficients for  $H^+$  and  $A^-$  ions were approximated with the aid of Eq. (16). The values of the dissociation constants for studied in this work weak monobasic organic honey acids at 25°C necessary for calculations are: gluconic acid:  $K=1.38\times10^{-4}$  (7), lactic acid:  $K=1.38\times10^{-4}$  and butyric acid:  $K=1.479\times10^{-5}$  (6).

In Table 6 the values of the dissociation parameters of weak monobasic organic honey acids in their dilute ( $0.0001\text{-}0.01 \text{ mol} \cdot \text{dm}^{-3}$ ) solutions at 25°C calculated by Eq. (41) are presented. Because of an equality of the dissociation constant values of gluconic and lactic acids their dissociation parameters are identical.

**Table 6.** The values of the dissociation parameters of weak monobasic organic honey acids in their diluted solutions at 25°C.

Glutaric and Lactic acids Butyric acid						
Concentration, $\alpha$ pH	Concentration, $\alpha$ pH	mol $\cdot$ dm $^{-3}$	mol $\cdot$ dm $^{-3}$			
0.0001	0.6755	4.174	0.0001	0.3194	4.498	
0.0002	0.5586	3.957	0.0002	0.2391	4.327	
0.0004	0.4445	3.757	0.0004	0.1762	4.156	
0.0006	0.3832	3.646	0.0006	0.1466	4.060	
0.0008	0.3430	3.570	0.0008		0.1284	3.993
0.001	0.3139	3.512	0.001		0.1158	3.942
0.002	0.2353	3.338	0.002		0.0835	3.783
0.004	0.1738	3.170	0.004	0.0600	3.627	
0.006	0.1448	3.075	0.006	0.0493	3.537	
0.008	0.1270	3.008	0.008	0.0429	3.473	
0.01	0.1146	2.956	0.01	0.0385	3.423	

The anion concentration in case of gluconic and lactic acids exceeds the  $[HA]$  value when  $c \leq 0.0002 \text{ mol} \cdot \text{dm}^{-3}$  (in this interval  $\alpha > 0.5$ ). In case of butyric acid the

$[HA]$  value exceeds the  $[A^-]$  value in all studied interval of acid concentration ( $\alpha < 0.5$ ).

We suggest also the simple empirical equations for fast approximate calculation of the  $\alpha$  and  $pH$  values:

### Glutaric and Lactic acids

$$\alpha = 0.03124c^{-0.336} \quad (42)$$

(for  $c = 0.0001\text{-}0.002\text{mol} \cdot \text{dm}^{-3}$ )

$$pH = 1.537 - 0.658 \lg c \quad (43)$$

(for  $c = 0.0001\text{-}0.01\text{mol} \cdot \text{dm}^{-3}$ )

### Butyric acid

$$\alpha = 5.6159 \times 10^{-3} c^{-0.439} \quad (44)$$

(for  $c = 0.0001\text{-}0.004\text{mol} \cdot \text{dm}^{-3}$ )

$$pH = 2.286 - 0.552 \lg c \quad (45)$$

(for  $c = 0.0001\text{-}0.01\text{mol} \cdot \text{dm}^{-3}$ )

## 4. CONCLUSION

The suggested by authors new original equations for accurate and approximate calculation of the parameters of electrolytic dissociation of weak multibasic organic acids were used for analysis of the regularities of dissociation behaviour of some dibasic and tribasic weak organic acids contained in honey: : malic, succinic, tartaric and citric acids in their dilute solutions. The dissociation parameters of some monobasic weak honey acids (gluconic, lactic and butyric acids) were also determined. The values of the

usual and "partial" degrees of dissociation and concentration of various ionized and non-ionized forms were calculated. The equations for determination the regions of the acid concentration where the concentrations of monodi and trianions and hydrogen ions prevail in comparison with the undissociated acid concentration were also described. The simple empirical equations for fast approximate calculation of the dissociation parameters are also suggested.

## REFERENCES

1. Kvaratskhelia E. and Kvaratskhelia R. The Degrees of Dissociation of Weak Multibasic Organic Acids". *J. Solution Chem*, 2007, vol. 36, no. 6. pp. 787-792.
2. Kvaratskhelia E and Kvaratskhelia R. The Forms of the Law of Dilution for Weak Multibasic Organic Acids in Case of Overlapping Equilibria. *ECS Transaction*, 2009, vol. 16, no. 38. pp. 49-54.
3. Kvaratskhelia E. and Kvaratskhelia R. The "Partial" Degrees of Dissociation of Weak Multibasic Organic Acids. *J. Solution Chem*. 2009, vol. 38, no. 3, pp. 345-349.
4. Kvaratskhelia E. and Kvaratskhelia R. "The Determination of Acidity of the Dilute Solutions of Weak Multibasic Organic Acids". *J. Biomedical Science and Engineering*. 2010, vol. 3, no. 5. pp. 484-487.
5. J. Koryta, J. Dvorak, L. Kavan. Principles of Electrochemistry. 2<sup>nd</sup> Edition. L. Wiley and Sons, Chichester, New York, Brisbane, Toronto, Singapore, 1993.
6. CRC Handbook of Chemistry and Physics. 81<sup>st</sup> Edition. Boca Raton, Ann Arbor, London, Tokyo. 2001.
7. J. Bjerrum et al. Stability Constants. London: Chemical Society, 1958.

## ЗАКОНОМЕРНОСТИ ЭЛЕКТРОЛИТИЧЕСКОЙ ДИССОЦИАЦИИ СЛАБЫХ ОДНО-, ДВУХ- И ТРЕХОСНОВНЫХ ОРГАНИЧЕСКИХ КИСЛОТ, СОДЕРЖАЩИХСЯ В МЕДЕ

**E.P.Кварацхелия, Р.К.Кварацхелия и Р.Р.Куртанидзе**

*Институт неорганической химии и электрохимии им. Р.И. Агладзе  
Тбилисского Государственного Университета им. Ив. Джавахишвили  
0186 Тбилиси ул. Миндели 11, E-mail: [elicko@mail.ru](mailto:elicko@mail.ru), [ekvarats@yahoo.com](mailto:ekvarats@yahoo.com)*

*Оригинальный метод, предложенный авторами для анализа процессов электролитической диссоциации слабых многоосновных органических кислот, был использован для расчета параметров диссоциации некоторых двух- и трехосновных слабых органических кислот, содержащихся в меди. Этими кислотами являются яблочная, янтарная, винная и лимонная кислоты. Параметры диссоциации некоторых одноосновных слабых органических кислот, содержащихся в меди (глюконовая, молочная и масляная), были также определены. Рассчитаны концентрационные интервалы преобладания различных заряженных и незаряженных частиц в разбавленных растворах указанных кислот. Предложены также простые эмпирические уравнения для быстрого приближённого расчёта значений параметров диссоциации.*

**Ключевые слова:** слабые органические кислоты, константа диссоциации, степень диссоциации, глюконовая кислота, молочная кислота, масляная кислота

## **BALIN TƏRKİBİNDƏKİ BİR-, İKİ- VƏ ÜÇƏSASLI ZƏİF ÜZVİ TURŞULARIN ELEKTROLİTİK DİSSOSİASIYASININ QANUNAUYĞUNLUQLARI**

**E.P.Kvaratsxeliya, P.K. Kvaratsxeliya, P.P.Kurtanidze**

*İv.Cavaxışvili ad. Tbilisi Dövlət Universitetinin  
R.Aqladze adına Qeyri-üzvi və Elektrokimya İnstitutu  
0186 Tbilisi, Mindeli küç., 11  
e-mail: [elicko@mail.ru](mailto:elicko@mail.ru), [ekvarats@yahoo.com](mailto:ekvarats@yahoo.com)*

*Müəlliflər tərəfindən çoxəsaslı zəif üzvi turşuların elektrolojik dissosiasiyyası üçün təklif etdikləri orijinal metoddan istifadə edərək balin tərkibindəki iki- və üçəsaslı zəif üzvi turşuların elektrolitik dissosiasiyyasının parametrləri hesablanmışdır. Bunlar alma, kəhraba, şərab və limon turşularıdır. Balin tərkibindəki bəzi birəsaslı zəif turşuların (qlükon, süd və yağ) dissosiasiyya parametrləri də təyin olunmuşdur. Dissosiasiyya parametrlərinin təxminini və tez təyini üçün sadə empirik tənliklər təklif olunub.*

**Açar sözlər:** zəif üzvi turşular, dissosiasiyya sabiti, dissosiasiyya dərəcəsi, qlükon turşusu, süd turşusu, yağ turşusu.

*Redaksiyaya daxil olub 28.09.2015.*