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THE ELECTROLYTIC DISSOCIATION OF MALEIC AND CITRACONIC ACIDS

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The parameters of electrolytic dissociation of the widely used in industry unsaturated dicarboxylic acids: maleic and citraconic (methylmaleic) acids: the values of usual and "partial" degrees of dissociation, the concentrations of all charged and non-charged dissociation products, the activity coefficients of all anions and hydrogen ions for their dilute (0.0001-1M) solutions have been determined with the help original accurate and empirical equations suggested by authors.

Keywords: Maleic acid; Citraconic acid; Degrees of Dissociation; Dissociation constants; Hydrogen Ions; Anions; Equations.

1. Introduction

Maleic and citraconic (methylmaleic) acids are widely used in industry. Maleic acid is mainly used to manufacture unsaturated polyesters resin, pesticide, tartaric acid, fumaric acid, succinic acid, DL-malic acid, dyeing auxiliary and preservative grease. This acid has also become a new acidulant in food and beverage industry. It may intensify special fruit aroma and improve food and beverage taste. At present this acid is mainly used in syrup, orange juice, sport beverage and other fortified syrup and food. Maleic acid is also an industrial material for the production of glyoxylic acid by ozonolysis. Citraconic acid is used as a fire

retardant; recent studies revealed that this acid is a competitive inhibitor of fumarate reduction. It should be noted that the useful properties of maleic and citraconic acids are directly connected with the peculiarities of electrolytic dissociation of these acids.

In this communication the regularities of dissociation of maleic and citraconic acids are determined with the aid of suggested by authors original method for analysis the complex equilibrium in the processes of dissociation of weak multibasic organic acids with the close values of the stepwise dissociation constants (the "overlapping" equilibrium effect) [1-12].

2. The equations

It was shown by us [1-3, 11, 12] that the mass action equations for the m dissociation step

of weak multibasic organic acid H_nA may be written as follows:

$$K_m = \frac{c(\alpha_m - \alpha_{m+1}) \sum_{m=1}^n \alpha_m}{\alpha_{m-1} - \alpha_m} F_m = \frac{c\alpha'_m (1 - \alpha'_{m+1}) \sum_{m=1}^n \alpha'_m \alpha_{m-1}}{1 - \alpha'_m} F_m \quad (1)$$

where K_m is the thermodynamic dissociation constant of m step, c is a total (analytical)

concentration of acid, α_m , α_{m+1} and α_{m-1} are the usual degrees of dissociation of corresponding

steps, α'_m , α'_{m+1} and α'_{m-1} are the “partial” degrees of dissociation (this term was first suggested by authors [3]), F_m is the quotient of the activity coefficients for m step:

$$F_m = \frac{f_{H^+} f_{H_{n-m}A^{m-}}}{f_{H_{n-(m-1)}A^{(m-1)-}}} \quad (2)$$

In case of dibasic maleic and citraconic acids the equations for the law of dilution for both dissociation steps may be presented as follows (according to equation (1)):

$$K_1 = \frac{c(\alpha_1^2 - \alpha_2^2)}{1 - \alpha_1} F_1 = \frac{c\alpha_1^2 [1 - (\alpha'_2)^2]}{1 - \alpha_1} F_1 \quad (3)$$

$$K_2 = \frac{c\alpha_2(\alpha_1 + \alpha_2)}{\alpha_1 - \alpha_2} F_2 = \frac{c\alpha_1\alpha'_2(1 + \alpha'_2)}{1 - \alpha'_2} F_2 \quad (4)$$

According to equations (3) and (4) the degrees of dissociation, α_1 , α_2 and α'_2 can be evaluated successively by iterative solution of following quadratic equations:

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

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

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

The values of the “partial” degree of dissociation α'_2 may be also determined with the aid of α_1 and α_2 values:

$$\alpha'_2 = \frac{\alpha_2}{\alpha_1} \quad (8)$$

The values of the activity coefficient of hydrogen ions and mono and dianions may be approximated with the aid of the Debye-Huckel equation:

$$\lg f_i = -\frac{z_i^2 A \sqrt{I}}{1 + a_i B \sqrt{I}} \quad (9)$$

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 $I = c(\alpha_1 + 2\alpha_2) = c\alpha_1(1 + 2\alpha_2')$. The activity coefficient of undissociated acid is assumed to be unity.

With the aid of the dissociation degree values we may also calculate the values of concentration of all dissociated and undissociated forms of both acids:

$$[H^+] = c(\alpha_1 + \alpha_2) = c\alpha_1(1 + \alpha_2') \quad (10)$$

$$[HA^-] = c(\alpha_1 - \alpha_2) = c\alpha_1(1 - \alpha_2') \quad (11)$$

$$[A^{2-}] = c\alpha_2 = c\alpha_1\alpha_2' \quad (12)$$

$$[H_2A] = c(1 - \alpha_1) \quad (13)$$

3. The results and discussion

The equations (5)-(8) were used for the calculation of the values of usual and "partial" degrees of dissociation for maleic and citraconic acids in their dilute (0.0001-1M) solutions. The K_1 and K_2 values for maleic acid were taken from [13]: $K_1=1.202 \times 10^{-2}$; $K_2=5.888 \times 10^{-7}$ (25°C). The corresponding values for citraconic

acid were taken from [14]: $K_1=5.129 \times 10^{-3}$; $K_2=7.079 \times 10^{-7}$ (25°C). The values of the constants of the equations (9) were taken from [15]. The calculated values of α_1 , α_2 , α_2' and pH at 25°C are presented in Tables 1 (maleic acid) and 2 (citraconic acid).

Table 1. Parameters of dissociation of maleic acid in its dilute solutions at 25°C

Acid concentration, M	α_1	α_2	α_2'	pH
0.0001	0.9920	6.09×10^{-3}	6.14×10^{-3}	4.006
0.0002	0.9844	3.12×10^{-3}	3.17×10^{-3}	3.711
0.0004	0.9701	1.60×10^{-3}	1.65×10^{-3}	3.420
0.0006	0.9567	1.09×10^{-3}	1.14×10^{-3}	3.252
0.0008	0.9442	8.30×10^{-4}	8.79×10^{-4}	3.134
0.001	0.9324	6.72×10^{-4}	7.21×10^{-4}	3.044
0.002	0.8818	3.54×10^{-4}	4.02×10^{-4}	2.773
0.004	0.8074	1.86×10^{-4}	2.31×10^{-4}	2.515
0.006	0.7533	1.29×10^{-4}	1.71×10^{-4}	2.373
0.008	0.7110	9.95×10^{-5}	1.40×10^{-4}	2.276
0.01	0.6766	8.23×10^{-5}	1.22×10^{-4}	2.203
0.02	0.5653	4.39×10^{-5}	7.76×10^{-5}	1.987
0.04	0.4563	2.38×10^{-5}	5.21×10^{-5}	1.787

0.06	0.3973	1.67×10^{-5}	4.19×10^{-5}	1.675
0.08	0.3584	1.29×10^{-5}	3.61×10^{-5}	1.598
0.1	0.3300	1.07×10^{-5}	3.23×10^{-5}	1.540
0.2	0.2503	5.61×10^{-6}	2.24×10^{-5}	1.362
0.4	0.1880	3.03×10^{-6}	1.61×10^{-5}	1.191
0.6	0.1582	2.11×10^{-6}	1.33×10^{-5}	1.093
0.8	0.1396	1.63×10^{-6}	1.16×10^{-5}	1.025
1.0	0.1266	1.33×10^{-6}	1.05×10^{-5}	0.972

Table 2. Parameters of dissociation of citraconic acid in its dilute solutions at 25°C

Acid concentration, M	α_1	α_2	α_2'	pH
0.0001	0.9816	7.30×10^{-3}	7.44×10^{-3}	4.010
0.0002	0.9648	3.74×10^{-3}	3.88×10^{-3}	3.720
0.0004	0.9348	1.92×10^{-3}	2.06×10^{-3}	3.436
0.0006	0.9084	1.31×10^{-3}	1.44×10^{-3}	3.274
0.0008	0.8849	9.94×10^{-4}	1.12×10^{-3}	3.162
0.001	0.8637	4.19×10^{-4}	9.32×10^{-4}	3.077
0.002	0.7814	8.05×10^{-4}	5.37×10^{-4}	2.824
0.004	0.6784	2.20×10^{-4}	3.24×10^{-4}	2.589
0.006	0.6126	1.51×10^{-4}	2.47×10^{-4}	2.460
0.008	0.5653	1.16×10^{-4}	2.06×10^{-4}	2.373
0.01	0.5289	9.48×10^{-5}	1.79×10^{-4}	2.307
0.02	0.4211	5.04×10^{-5}	1.20×10^{-4}	2.111
0.04	0.3267	2.69×10^{-5}	8.24×10^{-5}	1.926
0.06	0.2790	1.87×10^{-5}	6.71×10^{-5}	1.822
0.08	0.2486	1.45×10^{-5}	5.82×10^{-5}	1.750
0.1	0.2270	1.19×10^{-5}	5.23×10^{-5}	1.695
0.2	0.1698	6.43×10^{-6}	3.78×10^{-5}	1.527
0.4	0.1260	3.50×10^{-6}	2.78×10^{-5}	1.363
0.6	0.1055	2.46×10^{-6}	2.33×10^{-5}	1.269
0.8	0.09294	1.91×10^{-6}	2.06×10^{-5}	1.202
1.0	0.08420	1.58×10^{-6}	1.87×10^{-5}	1.150

In Table 3 the values of the activity coefficients of hydrogen ions and mono and dianions in the dilute solutions of maleic and citraconic acids at 25°C are presented (the activity coefficient of undissociated acid is assumed to be unity).

The equations (10)-(13) give the possibility of determination of the intervals of the acid concentration in which various charged and uncharged forms of acids prevail. The conditions of equality of these concentrations are:

$$[HA^-] = [H_2A] : \alpha_1 = \frac{1 + \alpha_2}{2} = \frac{1}{2 - \alpha_2} \quad (14)$$

$$[A^{2-}] = [H_2A]: \alpha_1 = 1 - \alpha_2 = \frac{1}{\alpha_2' + 1} \quad (15)$$

$$[H^+] = [H_2A]: \alpha_1 = \frac{1 - \alpha_2}{2} = \frac{1}{\alpha_2' + 2} \quad (16)$$

$$[HA^-] = [A^{2-}]: \alpha_1 = 2\alpha_2 \quad (17)$$

$$\alpha_2' = 0.5 \quad (18)$$

Table 3. Values of the activity coefficients of hydrogen ions and mono and dianions in the dilute solutions of maleic and citraconic acids at 25°C

Acid concentration, M	Maleic acid			Citraconic acid		
	f_{H^+}	f_{HA^-}	$f_{A^{2-}}$	f_{H^+}	f_{HA^-}	$f_{A^{2-}}$
0.0001	0.9886	0.9884	0.9546	0.9886	0.9885	0.9548
0.0002	0.9842	0.9838	0.9373	0.9844	0.9840	0.9378
0.0004	0.9783	0.9776	0.9140	0.9787	0.9780	0.9155
0.0006	0.9740	0.9729	0.8971	0.9746	0.9736	0.8996
0.0008	0.9705	0.9691	0.8836	0.9714	0.9701	0.8871
0.001	0.9676	0.9659	0.8722	0.9687	0.9672	0.8766
0.002	0.9571	0.9541	0.8317	0.9594	0.9567	0.8406
0.004	0.9448	0.9397	0.7845	0.9488	0.9444	0.8000
0.006	0.9368	0.9300	0.7546	0.9421	0.9365	0.7745
0.008	0.9309	0.9227	0.7324	0.9372	0.9304	0.7558
0.01	0.9262	0.9168	0.7152	0.9332	0.9256	0.7411
0.02	0.9112	0.8972	0.6603	0.9205	0.9095	0.6942
0.04	0.8957	0.8758	0.6051	0.9072	0.8918	0.6459
0.06	0.8865	0.8626	0.5731	0.8992	0.8807	0.6173
0.08	0.8800	0.8529	0.5508	0.8934	0.8725	0.5969
0.1	0.8749	0.8453	0.5336	0.8888	0.8659	0.5810
0.2	0.8679	0.8287	0.5012	0.8744	0.8445	0.5318
0.4	0.8561	0.8061	0.4579	0.8598	0.8214	0.4833
0.6	0.8500	0.7929	0.4347	0.8511	0.8071	0.4555
0.8	0.8461	0.7837	0.4193	0.8450	0.7967	0.4361
1.0	0.8434	0.7766	0.4081	0.8402	0.7884	0.4213

In case of maleic acid $[HA^-]$ value exceeds the $[H_2A]$ value when $c \leq 0.03M$ (the inequality $\alpha_1 > \frac{1 + \alpha_2}{2}$ is fulfilled). The concentration of undissociated acid exceeds the dianion concentration in all studied interval of the c

values (the inequality $\alpha_1 < 1 - \alpha_2$ is fulfilled). The $[H^+]$ value exceeds the $[H_2A]$ value when $c \leq 0.03M$ (the inequality $\alpha_1 > \frac{1 - \alpha_2}{2}$ is fulfilled). In all studied region of the maleic acid concentration monoanion remains the

predominant anion (the inequalities $\alpha_1 > 2\alpha_2$ and $\alpha_2' > 0.5$ are fulfilled).

In case of citraconic acid the monoanion concentration exceeds the concentration of undissociated acid when $c \leq 0.015\text{M}$ (the inequality $\alpha_1 > \frac{1+\alpha_2}{2}$ is fulfilled). The $[\text{A}^{2-}]$ value in all studied interval of the c values is lower than the $[\text{H}_2\text{A}]$ value (the inequality $\alpha_1 < 1 - \alpha_2$ is fulfilled). The $[\text{H}^+]$ value exceeds the $[\text{H}_2\text{A}]$ value when $c \leq 0.015\text{M}$ (the

inequality $\alpha_1 > \frac{1-\alpha_2}{2}$ is fulfilled). The $[\text{HA}^-]$ value always exceeds the $[\text{A}^{2-}]$ value (the inequalities $\alpha_1 > 2\alpha_2$ and $\alpha_2' > 0.5$ are fulfilled).

Taking into account the comparative complexity of calculations pursuant to the equations (5)-(7), we suggest also the simple empirical equations for fast approximate calculation of the α_1 , α_2 , α_2' and pH values in the dilute solutions of maleic and citraconic acids.

Maleic acid

$$\alpha_1 = 0.075338c^{-0.031} \quad (19)$$

(for $c = 0.0001-0.002\text{M}$)

$$\alpha_2 = 8.9125 \times 10^{-7} c^{-0.959} \quad (20)$$

(for $c = 0.0001-0.006\text{M}$)

$$\alpha_2' = 1.183 \times 10^{-6} c^{-0.928} \quad (21)$$

(for $c = 0.0001-0.002\text{M}$)

$$\text{pH} = 0.167 - 0.959 \lg c \quad (22)$$

(for $c = 0.0001-0.01\text{M}$)

Citraconic acid

$$\alpha_1 = 0.9914 - 128.778c \quad (23)$$

(for $c = 0.0001-0.002\text{M}$)

$$\alpha_2 = 1.07646 \times 10^{-6} c^{-0.958} \quad (24)$$

(for $c = 0.0001-0.01\text{M}$)

$$\alpha_2' = 1.66725 \times 10^{-6} c^{-0.912} \quad (25)$$

(for $c = 0.0001-0.001\text{M}$)

$$\text{pH} = 0.26 - 0.935 \lg c \quad (26)$$

(for $c = 0.0001-0.01\text{M}$)

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ЭЛЕКТРОЛИТИЧЕСКАЯ ДИССОЦИАЦИЯ МАЛЕИНОВОЙ И ЦИТРАКОНОВОЙ КИСЛОТ

Е.Р.Кварацхелия, Р.К.Кварацхелия, Р.Р.Куртанидзе

Параметры электролитической диссоциации широко используемых в промышленности ненасыщенных дикарбоновых кислот (малеиновой и цитраконовой (метилмалеиновой)): значения обычных и «парциальных» степеней диссоциации, концентрации всех заряженных и незаряженных продуктов диссоциации, коэффициентов активности всех анионов и ионов водорода в их разбавленных (0.0001-1M) растворах были определены с помощью предложенных авторами оригинальных точных и эмпирических уравнений.

Ключевые слова: *малеиновая кислота, цитраконовая кислота, степени диссоциации, константы диссоциации, ионы водорода, анионы, уравнения.*

MALEİN VƏ SİTRAKON TURŞULARININ ELEKTROLİTİK DISSOSİASİYASI**E.R.Kvaratsxeliya, R.K.Kvaratcxeliya, R.R.Kurtanidze**

Sənayedə geniş istifadə olunan malein və sitrakon (metilmalein) doymamış dikarbon turşularının parsial dissosiasiya dərəcələrinin qiymətləri, dissosiasiya məhsullarının konsentrasiyaları, turşuların duru məhlullarında (0.0001-1 M) bütün anionların və hidrogen ionlarının aktivlik koeffisiyentləri müəlliflər tərəfindən təklif olunan orilinal dəqiq və empirik tənliklər vasitəsi ilə təyin edilib.

Açar sözlər: *malein turşusu, sitrakon turşusu, dissosiasiya dərəcəsi, hidrogen ionları, anionlar, tənlik.*

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