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EFFECT OF CITRIC ACID CONCENTRATION ON ITS DISSOCIATED AND NON-DISSOCIATED FORMS

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Abstract. *The authors have studied the acid-base properties of citric acid by potentiometric titration at a temperature of 298 K and concentrations of $CH_3Cit(OH)$ of 0.01 and 0.02 mol/L. The results of potentiometric titration depend on the concentration of substances and the time of setting the equilibrium pH value of the titrated solution. The potentiometric method determined three carboxyl groups of citric acid corresponding to pK_a1, pK_a2, and pK_a3. The values of citric acid dissociation constants for 0.02 mol/L concentration are 2.75, 4.45, and 5.82. The authors constructed the distribution diagrams of dissociated forms for both studied concentrations of citric acid. According to the data obtained, the distribution curves shift to the right on the pH scale with increasing acid concentration.*

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Hydroxycarboxylic acids occur in nature and have high biological activity [1, 2]. For example, citric acid is a bifunctional, complex α-oxycarboxylic acid. It contains four functional groups: three carboxyl groups and one hydroxyl group increasing its acidic properties.

The most important characteristic of an acid is the value of its dissociation constant. It characterises the reactivity and is used for equilibrium calculations. Furthermore, the values of dissociation constants additionally complete the thermodynamic data base of the calculated quantities.

The study of hydroxycarboxylic acid equilibria in aqueous media is particularly important for physical and analytical chemistry. However, this aspect has not been widely researched. Only three values of the dissociation constants of citric acid are usually given in the literature:

pK_a1, pK_a2, and pK_a3. Therefore, it is common to write its formula as $H_3Cit(OH)$. Such data are given in [3, 4]: $pK_a1 = 3.13$, $pK_a2 = 4.71$, $pK_a3 = 6.21$ (using the spectrophotometric method); $pK_a1 = 3.02$, $pK_a2 = 4.68$ and $pK_a3 = 6.18$ (using the potentiometric method).

The purpose of this study is to investigate the acid-base properties of citric acid by potentiometric titration at T=298.15 K and a concentration of 0.02 mol/l and compare them with previously obtained data at a concentration of 0.01 mol/l. The results will be used in further study of complexation processes in the system Fe^{II}-Fe^{III}-$H_3Cit(OH)$-H_2O.

Crystalline citric acid of ‘CP’ grade was used for the experiments; no additional purification was performed. We prepared the KOH solution from fixanal. We kept the ionic strength of the solution constant by adding $NaNO_3$. We determined the concentration of this salt by weight method [5, 6]. All calculations were performed on a computer using *Excel* programme [7, 8].

We conducted potentiometric measurements using the ionometer ‘Econix-Expert-001’. We calibrated the instrument using buffer solutions under experimental conditions and the ionic strength of the working solution I=0.1 mol/l ($NaNO_3$). We performed the titration with KOH solution. The pH values of the citric acid solution are varied according to the volume of alkali added and given in Table 1.

Table 1. Dependence of pH values of citric acid solution on the volume of KOH at T=298.15 K; $C_{H3Cit(OH)}$=0.02 and I=0.1 mol/l.

№	V_{KOH}, ml	pH	C_{KOH}	$C_{H3Cit(OH)}$
1	0	2.323	0	0.02
2	0.4	2.411	0.0004	0.01984127
3	0.8	2.509	0.0008	0.019685039
4	1.4	2.660	0.0014	0.019455253
5	1.8	2.755	0.0018	0.019305019
6	2.0	2.807	0.0020	0.019230769
7	2.4	2.914	0.0024	0.019083969
8	3.0	3.074	0.0030	0.018867925
9	3.4	3.186	0.0034	0.018726592
10	4.4	3.487	0.0044	0.018382353
11	5.0	3.678	0.0050	0.018181818
12	5.4	3.797	0.0054	0.018050542
13	5.8	3.917	0.0058	0.017921147
14	6.4	4.097	0.0064	0.017730496
15	6.8	4.212	0.0068	0.017605634
16	7.2	4.323	0.0072	0.017482517
17	7.8	4.482	0.0078	0.017301038
18	8.0	4.536	0.0080	0.017241379
19	8.4	4.655	0.0084	0.017123288
20	8.8	4.761	0.0088	0.017006803
21	9.2	4.875	0.0092	0.016891892
22	9.6	4.991	0.0096	0.016778523
23	10.0	5.109	0.0100	0.016666667
24	10.4	5.228	0.0104	0.016556291
25	10.8	5.351	0.0108	0.016447368
26	11.2	5.470	0.0112	0.016339869
27	11.4	5.525	0.0114	0.016286645
28	11.6	5.582	0.0116	0.016233766
29	12.0	5.699	0.0120	0.016129032
30	12.4	5.825	0.0124	0.016025641
31	12.8	5.942	0.0128	0.015923567
32	13.2	6.074	0.0132	0.015822785
33	13.6	6.215	0.0136	0.01572327
34	14.0	6.392	0.0140	0.01562500
35	14.4	6.613	0.0144	0.01552795
36	14.6	6.760	0.0146	0.015479876
37	14.8	6.970	0.0148	0.015432099
38	15.0	7.297	0.0150	0.015384615
39	15.2	8.398	0.0152	0.015337423
40	15.3	9.360	0.0153	0.015313936
41	15.4	9.700	0.0154	0.015290520
42	15.5	9.973	0.0155	0.015267176
43	15.6	10.208	0.0156	0.015243902
44	15.7	10.407	0.0157	0.015220700
45	15.8	10.564	0.0158	0.015197568
46	16.0	10.849	0.0160	0.015151515
47	16.2	11.055	0.0162	0.015105740
48	16.4	11.206	0.0164	0.015060241
49	16.6	11.320	0.0166	0.015015015
50	16.8	11.402	0.0168	0.014970060
51	17.2	11.538	0.0172	0.014880952
52	16.8	11.402	0.0168	0.014970060
53	17.2	11.538	0.0172	0.014880952

We plotted the differential titration curve in dpH/dV-VT coordinates (Fig. 1). The equivalence point corresponds to the maximum of the curve; it is determined with high accuracy. The equivalence point and the maximum of the curve correspond to the ionisation constant with the highest value. The values of the consecutive dissociation constants of citric acid are quite similar. Therefore, the individual steps are not noticeable on the titration curve [9].

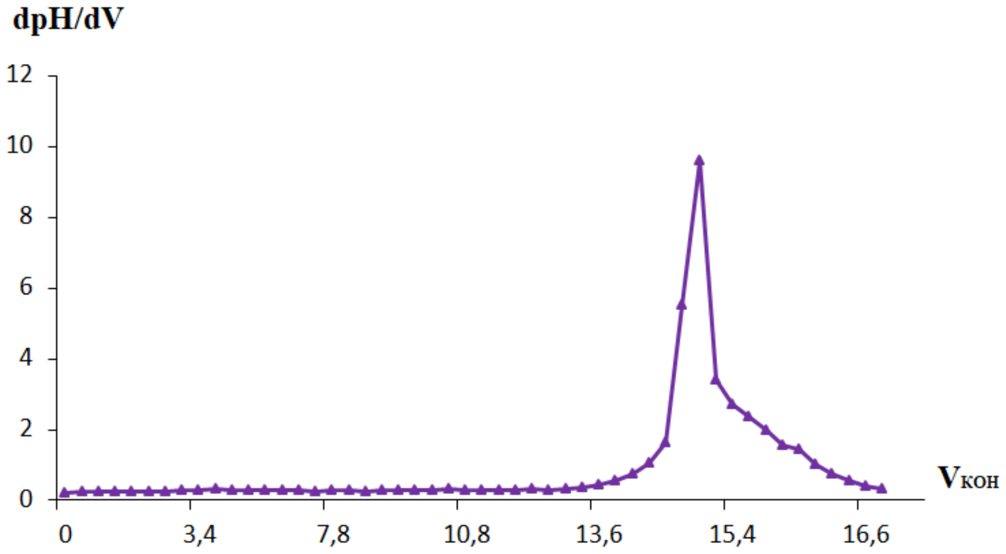

Fig. 1. Graphical differential titration curve of citric acid-$H_3Cit(OH)$, C_{KOH}=0.2 mol/l at 298.15 K and $C_{H3Cit(OH)}$=0.02 mol/l.

We describe the electrolytic dissociation of $H_{3Cit(OH)}$ (citric acid) in aqueous solution:

$$H_3Cit(OH) \leftrightarrow H_2Cit(OH)^- + H^+, K_{a1}$$
$$H_2Cit(OH)^- \leftrightarrow HCit(OH)^{2-} + H^+, K_{a2}$$
$$HCit(OH)^{2-} \leftrightarrow Cit(OH)^{3-} + H^+, K_{a3}$$

Using computer programmes, we calculated the values of pKa_1 (2.75±0.06), pKa_2 (4.45±0.05), and pKa_3 (5.82±0.08).

We next determined the mole fractions of the citric acid forms using the following equations:

$$\alpha_0 = \frac{[H^+]^3}{[H^+]^3 + [H^+]^2K_{a1} + [H^+]K_{a1,2} + K_{a1,2,3}}$$

$$\alpha_1 = \frac{[H^+]^3K_{a1}}{[H^+]^3 + [H^+]^2K_{a1} + [H^+]K_{a1,2} + K_{a1,2,3}}$$

$$\alpha_2 = \frac{[H^+]^3K_{a1,2}}{[H^+]^3 + [H^+]^2K_{a1} + [H^+]K_{a1,2} + K_{a1,2,3}}$$

$$\alpha_3 = \frac{[H^+]^3K_{a1,2,3}}{[H^+]^3 + [H^+]^2K_{a1} + [H^+]K_{a1,2} + K_{a1,2,3}}$$

The results are presented in Table 2.

Table 2. Values of mole fractions (%) of molecular and ionic forms of citric acid at $C_{H3Cit(OH)}$=0.02 mol/l.

pH	α_0	α_1	α_2	α_3	pH	α_0	α_1	α_2	α_3
1.0	9.83E-01	0.017472	6.2E-06	8.75673E-11	6.0	6.49E-06	0.0115473	0.409712	0.578733971
1.2	9.73E-01	0.0274109	1.54E-05	3.45082E-10	6.2	1.94E-06	0.0054607	0.307077	0.687460187
1.4	9.57E-01	0.0427568	3.81E-05	1.35209E-09	6.4	5.51E-07	0.0024609	0.219329	0.778209342
1.6	9.34E-01	0.0661079	9.34E-05	5.25114E-09	6.6	1.51E-07	0.0010677	0.150818	0.848113805
1.8	8.99E-01	0.1008598	0.000226	2.01242E-08	6.8	4.01E-08	0.0004504	0.100837	0.898712352
2.0	8.49E-01	0.1508987	0.000535	7.56285E-08	7.0	1.05E-08	0.0001863	0.066102	0.933711946
2.2	7.79E-01	0.2195988	0.001235	2.76459E-07	7.2	2.70E-09	7.603E-05	0.042755	0.957168807
2.4	6.89E-01	0.3079162	0.002744	9.73717E-07	7.4	6.89E-10	3.076E-05	0.027410	0.972558813
2.6	5.82E-01	0.4120872	0.005821	3.27332E-06	7.6	1.75E-10	1.237E-05	0.017472	0.982515755
2.8	4.66E-01	0.5225594	0.011699	1.04264E-05	7.8	4.42E-11	4.956E-06	0.011096	0.988899410
3.0	3.52E-01	0.6258321	0.022205	3.13659E-05	8.0	1.11E-11	1.981E-06	0.007030	0.992968341
3.2	2.51E-01	0.7086301	0.039849	8.92112E-05	8.2	2.81E-12	7.908E-07	0.004447	0.995552241
3.4	1.70E-01	0.7614329	0.067863	0.000240786	8.4	7.06E-13	3.153E-07	0.002810	0.997189224
3.6	1.10E-01	0.7792399	0.110071	0.000618972	8.6	1.78E-13	1.257E-07	0.001775	0.998224752
3.8	6.78E-02	0.7604606	0.170246	0.001517318	8.8	4.46E-14	5.006E-08	0.001121	0.998879189
4.0	3.97E-02	0.7061851	0.250564	0.003539309	9.0	1.2E-14	1.994E-08	0.000707	0.999292535
4.2	2.20E-02	0.6209591	0.349191	0.007817412	9.2	2.82E-15	7.94E-09	0.000446	0.999553508
4.4	1.15E-02	0.5140699	0.458165	0.016256316	9.4	7.08E-16	3.161E-09	0.000282	0.999718238
4.6	5.64E-03	0.3990271	0.563641	0.031695845	9.6	1.78E-16	1.259E-09	0.000178	0.999822202
4.8	2.59E-03	0.2900939	0.649439	0.057881340	9.8	4.47E-17	5.011E-10	0.000112	0.999887810
5.0	1.11E-03	0.1978261	0.701914	0.099147919	10.0	1.12E-17	1.995E-10	7.08E-05	0.999929210
5.2	4.50E-04	0.1268088	0.713098	0.159642846	10.2	2.82E-18	7.943E-11	4.47E-05	0.999955334
5.4	1.71E-04	0.07647	0.681539	0.241819334	10.4	7.08E-19	3.162E-11	2.82E-05	0.999971817
5.6	6.12E-05	0.0433462	0.612281	0.344311146	10.6	1.78E-19	1.259E-11	1.78E-05	0.999982218
5.8	2.06E-05	0.023073	0.51654	0.460366613					

The diagram of mole fraction distribution of different forms of citric acid dissociation at its concentration of 0.02 mol/l (Fig. 2) shows the formation of the anionic form $H_2Cit(OH)^-$ in the pH range of 1.0-6.0; its dissociation constant is 2.75±0.06. Its accumulation rate is 78%. Subsequently, $HCit(OH)^2$ is formed in the pH range of 3.0-7.6; its dissociation constant is 4.45±0.05. The percentage content of this form is 71.3%. The acid is in the form of $Cit(OH)^{3-}$ at pH 4.4-8.6. Its dissociation constant is 5.82±0.08. The maximum content of this form of acid is 100% (Table 3).

According to the figure, as the concentration of citric acid changes, the distribution curves shift towards higher pH values (Fig. 3). Furthermore, the maximum mole fractions of citric acid forms; their dominance areas were determined using the distribution diagrams (Table 3).

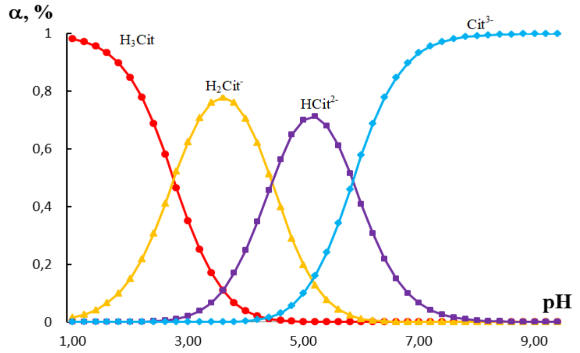

Fig. 2. Dependence of citric acid forms content on solution pH at C $_{H3Cit(OH)}$=0.02 mol/l.

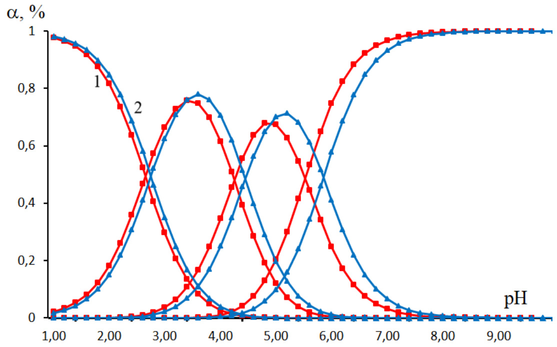

Fig. 3. Distribution diagram of citric acid form content on solution pH at T=298.15 K; C_{KOH}=0.2 and *I*=0.1 mol/l; curves refer, mol/l: 1 - $_{CH3Cit(OH)}$=0.01; 2 – $C_{H3Cit(OH)}$=0.02.

Table 3. Numerical values of the logarithms of the dissociation constants and the maximum degree of citric acid accumulation as a function of pH at $C_{H3Cit(OH)}$=0.02 mol/l.

№, item n/a	Dominance area on the pH scale	Ionic form	pH_{Max}	Value of lg dissociation constant	Max. accumulation rate, α, %
1	1.0-4.4	$H_3Cit(OH)$	-	-	-
2	1.2-6.0	$H_2Cit(OH)^-$	3.6	2.75	77.9
3	3.0-7.6	$HCit(OH)^{2-}$	5.2	4.45	71.3
4	4.4-9.6	$Cit(OH)^{3-}$	8.6	5.82	100

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