Polish J. Chem., **75**, 905–908 (2001) **COMMUNICATION**

Mixed and Concentration Equilibrium Constants of Protonation and Complexation Reactions at Low and High Ionic Strength. System: Carboxylic Acid – Co(II), Ni(II) and Cu(II) Ion

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(Received July 26th, 2000; revised manuscript January 26th, 2001)

The aim of this work it was to establish the influence of ionic strength on the dissociation constants of acids and to determine the stability constants of complex compounds as well as the determination of the relationship between the mixed and concentration constants. The complex-forming systems of 3d electron metal ion – carboxylic acid type were the subject of the studies. The dissociation constants for the acetic, propionic, butyric and valeric acids and their hydroxyl derivatives were determined, then the stability constants of complexes of these acids with Co(II), Ni(II) and Cu(II) ions were established. Measurements were carried out by the potentiometric method for two values of the ionic strength, equal 0.1 and 2.0, kept by sodium perchlorate. These so different ionic strengths were chosen because of:

- $\mu = 0.1$ M is characteristic for living cells, thus the obtained results could be used for specific model solutions, the more so as the studied acids and complexes have diverse biological significance [1].
- $\mu = 2.0$ M and higher give optimal conditions for the potentiometric measurements.

Proton activity was measured with the use of the ion-selective glass electrode, then knowing these activities and concentration of the analytical reagents, the mixed equilibrium constants were calculated using the programme developed by Martell and Motekaitis [2]. Simultaneously, after former determination of the proton activity coefficients $f_H = a_H/[H]$ for the standard solutions, the concentration equilibrium constants were determined by recalculation the proton activities for concentrations using the method described by Uitert [3].

The determined values of the equilibrium constants, presented in this work, are the collection of data earlier obtained by the author for the solutions of the ionic strength of 2.0 [4–7] and now enlarged for the solutions of 0.1 the ionic strength and other complex-forming systems.

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Table 1. Protonation constants of carboxylic and hydroxycarboxylic acids at ionic strength 0.1 and 2.0 ($NaClO_4$).

Acid	$\mu = 0.1$		$\mu = 2.0$
	BpKa	cpKa	BpKa = cpKa
Acetic	4.50	4.40	4.60
Hydroxyacetic (glycolic)	3.49	3.39	3.60
Propionic	4.70	4.60	4.82
2-Hydroxypropionic (lactic)	3.38	3.28	3.50
3-Hydroxypropionic	4.21	4.11	4.31
Butyric	4.94	4.84	5.05
2-Hydroxybutyric	3.58	3.48	3.70
3-Hydroxybutyric	4.24	4.13	4.34
Valeric	5.03	4.94	5.15
2-Hydroxyvaleric	3.69	3.58	3.80

BpKa – Brönsted (mixed) protonation constants.
cpKa – concentration protonation constants.

From the data presented in Table 1 and 2 it can be seen that relationship between the mixed and concentration equilibrium constants is different for the two ionic strengths used. In solutions of 0.1 ionic strength the mixed equilibrium constants are in each case higher than the concentration constants for both the protonization and complexation reactions. The difference between $BlogK_a$ and cpK_a and between Blogβ and clogβ is practically the same and equals 0.10 on the average for each acid and complex. On the other hand, in solutions of 2.0 ionic strength the determined values of both mixed and concentration equilibrium constants are the same (differences are smaller than the error of their determination). It is obvious that the differences between the mixed and concentration constants originate from the differences in the determined values of proton activity coefficients $\overline{f_H}$ in solutions of different ionic strength. For solutions of 0.1 ($NaClO_4$) ionic strength, the $\overline{f_H}$ values were determined as equal 0.84 ± 0.01 and for solutions of 2.0 ($NaClO_4$) ionic strength these values were 1.02 ± 0.005. The mean values of the activity coefficients $\overline{f_H}$ were calculated from a few hundreds characteristics of the glass electrode, taken in the same conditions before each series of the potentiometric measurements. It was optimistically assumed that the proton activity coefficient does not change during the whole potentiometric measurement, if the glass electrode is left in the solution after taking its characteristics. This assumption was quite reasonable, because E_0 of the glass electrode was maintained in general equal ± 0.2 mV between the successive series of measurements.

The protonization constants of the studied acids and the stability constants of complexes were determined in solutions of virtually different ionic strengths, equal 0.1 and 2.0 M ($NaClO_4$). Data presented in Table 1 show that the BpK_a value of each acid is higher in the solution of the ionic strength equal 2.0 than the value determined at $\mu = 0.1$ and this difference is on the average 0.11. The same diffrence for the cpK_a

values is equal 0.21. The obtained results prove that the ionic strength, which has a significant influence on activity coefficients, in case of proton activity has a relatively low effect.

Table 2. Stability constants of Co(II), Ni(II) and Cu(II) complexes with carboxylic and hydroxycarboxylic acids at ionic strength 0.1 and 2.0 ($NaClO_4$).

Ligand	Metal ion	$\mu = 0.1$		$\mu = 2.0$	$\mu = 0.1$		$\mu = 2.0$
		$B\log\beta_1$	$c\log\beta_1$	$B\log\beta_1 = c\log\beta_1$	$B\log\beta_2$	$c\log\beta_2$	$B\log\beta_2 = c\log\beta_2$
Acetate	Co	1.70	1.59	1.50	2.30	2.21	2.10
	Ni	1.80	1.71	1.60	2.59	2.49	2.40
	Cu	2.50	2.41	2.30	3.80	3.71	3.60
Hydroxyacetate (glycolate)	Co	2.25	2.16	2.05	3.39	3.29	3.20
	Ni	2.34	2.24	2.15	3.60	3.51	3.40
	Cu	3.05	2.94	2.85	4.69	4.59	4.50
Propionate	Co	1.52	1.41	1.31	2.00	1.90	1.81
	Ni	1.64	1.54	1.45	2.35	2.24	2.14
	Cu	2.44	2.34	2.23	3.77	3.67	3.58
2-Hydroxypropionate (lactate)	Co	2.02	1.92	1.82	3.08	2.97	2.87
	Ni	2.15	2.05	1.94	3.38	3.28	3.19
	Cu	2.85	2.74	2.64	5.00	4.90	4.79
3-Hydroxypropionate	Co	1.21	1.11	1.02	1.52	1.42	1.32
	Ni	1.36	1.25	1.15	1.81	1.70	1.60
	Cu	2.10	1.99	1.89	3.34	3.25	3.14
Butyrate	Co	2.36	2.25	1.16	1.78	1.67	1.57
	Ni	1.51	1.40	1.30	2.04	1.94	1.85
	Cu	2.30	2.19	2.09	3.41	3.30	3.20
2-Hydroxybutyrate	Co	1.82	1.72	1.62	2.67	2.57	2.48
	Ni	1.96	1.86	1.75	2.95	2.86	2.76
	Cu	2.62	2.53	2.43	3.92	3.82	3.73
3-Hydroxybutyrate	Co	0.99	0.89	0.80	1.24	1.14	1.05
	Ni	1.13	1.04	0.94	1.49	1.39	1.30
	Cu	1.92	1.82	1.72	3.11	3.01	2.90
Valerate	Co	1.26	1.15	1.05	1.54	1.44	1.35
	Ni	1.40	1.30	1.19	1.80	1.71	1.60
	Cu	2.13	2.04	1.92	3.11	3.00	2.90
2-Hydroxyvalerate	Co	1.71	1.61	1.52	2.43	2.33	2.24
	Ni	1.81	1.70	1.60	2.60	2.49	2.39
	Cu	2.56	2.45	2.35	2.72	2.63	2.53

$B\log\beta$ – Brönsted (mixed) stability constants.

$c\log\beta$ – concentration stability constants.

Despite of the fact that the acids studied differ in length of the carbon chain, in protonization constants and in presence of hydroxyl-group, for each the same identical pK_a increase at the change of the ionic strength from 0.1 to 2.0 was found and it was equal 0.11 on the average. A linear decrease of pK_a of single-proton acids with the increase of ionic strength occurs only in solutions of concentration lower than 0.1 M. Therefore, the determined stable increase of pK_a can be treated as an estimative correction at recalculation the protonization constants from the 0.1 ionic strength to 2.0 ionic strength and *vice versa*.

Comparison of the stability constants of Co(II), Ni(II) and Cu(II) complexes with the ten studied acids determined for two different ionic strengths (Table 2) show that in each of the system studied the stability constants of complexes forming in solutions of $\mu = 0.1$ are of 0.20 on the average higher than the constants determined at $\mu = 2.0$. This concerns both $\log\beta_1$ and $\log\beta_2$ values. Up to now the problem of influence of the ionic strength on stability of complexes described in this work was sporadic discussed. The literature data show only the values of the stability constants for Co(II), Ni(II) and Cu(II) complexes with acetic acid, Cu(II) complexes with propionic acid and Co(II) and Ni(II) with lactic acid determined for two different ionic strength [8, vol. 6]. For all these systems, similarly as is this work, values of the stability constants were higher at lower ionic strength.

Summarizing the obtained results, one can state that the influence of the ionic strength increase from 0.1 to 2.0 ($NaClO_4$) on direction and value of changes in the stability constants is as follows:

– the protonization constants ΔpK_a increase of 0.11,

– the stability constants $\Delta\log\beta_1$ and $\Delta\log\beta_2$ decrease of 0.20.

It should be pointed out that there exist no uniform and exhausting data on the relationship between complex stability and the ionic strength. There exist some regularities, but only for some groups of compounds [8]. However, for most complexes data, that could be used for a proper correction, do not exist. Determined in this work the same for all the complexes decrease of the $\Delta\log\beta$, equal 0.20, can be assumed as a correction for recalculating the stability constants from the 0.1 ionic strength to 2.0 and *vice versa* complexes of a similar composition to the studied ones.

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