

Copper(II) and nickel(II) complexes with oxalamide-*N,N'*-di- β -propionic acid

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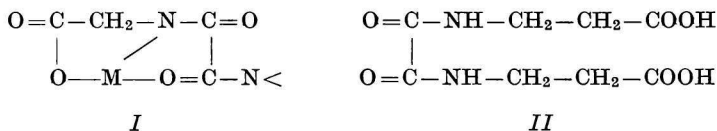
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Dedicated to Professor J. Majer, Corresponding Member of the Slovak Academy of Sciences, on his 50th birthday

Formation of oxalamide-*N,N'*-di- β -propionic acid complexes with Cu(II) in weakly acid and with Ni(II) in alkaline aqueous solutions has been studied using the method of potentiometric acid-base titration. The equilibrium constants of complexes have been computed. The complex-forming ability of homologous reagents OADA and OADP is discussed.

Образование комплексов оксаламид-*N,N'*-ди- β -пропионовой кислоты с Cu(II) в слабо кислых растворах и с Ni(II) в щелочных водных растворах изучается методом потенциометрического титрования со стеклянным электродом. Равновесные константы комплексов разчитаны компьютером. Дискуссии подвергается способность гомологических реактивов ОАДА и ОАДП образовать комплексы.

Formation of complexes CuLH_{-1} and $\text{Cu}_2\text{LH}_{-2}$ in weakly acid and $\text{Cu}(\text{LH}_{-1})_2^{4-}$, NiLH_{-1} , and $\text{Ni}(\text{LH}_{-1})_2^{4-}$ in alkaline solutions of oxalamide-*N,N'*-diacetic acid (OADA; H_2L) has been studied recently [1]. The interaction of OADA with Cu(II) and Ni(II), in which the stable chelate configuration *I* is formed, is a reaction of the biuret type [2]; a proton from the amide group splits off in formation of these complexes. In the present paper complexes of oxalamide-*N,N'*-di- β -propionic acid (OADP; H_2L ; formula *II*), a homologous reagent of OADA, are studied



Experimental

Automatic registration assembly ABU-12, PHM-26, TTT-11 and SBR (Radiometer, Denmark) was used for titration with 0.1 M-NaOH at $t = 20 \pm 1^\circ\text{C}$ and $I = 0.1$ (KNO_3). The pH-meter with a glass electrode G-202B and SCE was adjusted with the phosphate buffer to pH 6.50 (electrodes and buffer made by Radiometer). The value of the functions

\bar{z} and ${}_L\bar{z}$ was calculated from the titration curves, as described in [3]. The \bar{z} and ${}_L\bar{z}$ values indicate the average number of H^+ moles split off per one mole of metal and ligand, respectively.

The calculations were carried out in the Computer Centre of the Technical University, Brno, using a Tesla 200 computer and POT-3 program [4]. The input for the POT-3 program contained the characteristics of the studied chemical reactions, the estimated equilibrium constants values, the acidity constants of the reagent, the total concentrations of the metal ion and the ligand (c_M and c_L) and the experimentally determined pH and ${}_L\bar{z}$ values. The POT-3 program started with calculation of ${}_L\bar{z}$ for given pH values using the approximate equilibrium constants; it compared the experimental and the calculated ${}_L\bar{z}$ values (${}_L\bar{z}_{\text{exp}}$ and ${}_L\bar{z}_{\text{calc}}$) and it searched for the "best" equilibrium constants, characterized by a minimum $\Sigma({}_L\bar{z}_{\text{exp}} - {}_L\bar{z}_{\text{calc}})^2$ value.

Preparation of OADP

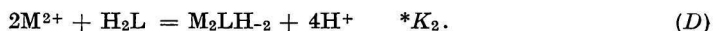
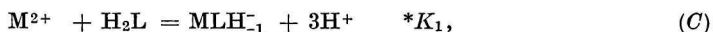
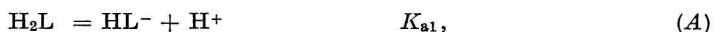
0.2 mole β -alanine in about 50 ml water was neutralized with equivalent NaOH and 0.1 mole diethyl oxalate was added to the solution. The ester phase disappeared after about 5 minutes shaking. Excess HCl was added 4 hrs later for precipitation of white crystals of free OADP. After recrystallization from hot water the product (yield about 30%) was titrated with 0.1 M-NaOH on phenolphthaleine. The titration gives $M_r = 230.0$ for the dibasic acid while from the formula $C_8H_{12}O_6N_2$ $M_r = 232.2$ was calculated.

Results and discussion

OADP splits off 2 protons in the region of pH 2–7. The values $pK_{a1} = 3.92$ and $pK_{a2} = 4.68$ were determined by an analysis of titration curves of solutions with c_L 1.25 and 1.87 mM.

Formation of blue colour and an increased volume of base which is necessary to attain pH 6–7 are observed in titration of OADP in the presence of Cu^{2+} . The increased consumption of base indicates that 1 proton is split off per 1 Cu in solutions with $c_M < c_L$. Blue precipitate formed at pH > 4.5 and $c_M > 2c_L$ interferes seriously with the pH measurement and titration curves, which can be measured only approximately in solutions containing precipitate, indicate that 4 protons are split off from the reagent H_2L . 31.8% Cu was determined by an analysis of the precipitate and 35.8% Cu was calculated from the formula Cu_2LH_{-2} . The difference between the calculated and the experimental value can be explained by coprecipitation of OADP and by hydration of the species.

Neutralization of OADP and OADA, both in absence and in presence of Cu^{2+} , is similar. Therefore equilibria (A–D) established in acid solutions of OADA [1], are supposed to take place also in solutions containing OADP and Cu(II) at pH < 7 .



Acid OADP solutions with Cu^{2+} (for c_M and c_L see Fig. 1) were titrated with 0.1 M-NaOH and the dependence of ${}_L\bar{z}$ on pH was determined. The ${}_L\bar{z}$ value indicates

the average number of protons split off from H_2L (compare eqn (1)); the charges of ions are omitted for the sake of simplicity).

$$\bar{z} = \frac{[HL] + 2[L] + 3[MLH_{-1}] + 4[M_2LH_{-2}]}{[H_2L] + [HL] + [L] + [MLH_{-1}] + [M_2LH_{-2}]} \quad (1)$$

The manual calculation of $*K_1$ and $*K_2$ from the potentiometric titration data [1] is extremely laborious. The application of the POT-3 program is more effective, however, it requires a knowledge of the estimated values of $*K_1$ and $*K_2$. In this estimate, it seems reasonable to assume, that the reaction (C) takes place in a more acid medium than (D). We have to find such a c_M , for which $\bar{z} = 2.0$ in a solution with $c_M > c_L$ at $pH = (pK_{a1} + pK_{a2})/2$. Then it holds $[H_2L] \ll [HL] \gg [L]$. For these special conditions approximations (2–4) can be accepted

$$0.5 c_L \approx [MLH_{-1}] \approx [HL], \quad (2)$$

$$[M] \approx c_M - 0.5 c_L, \quad (3)$$

$$*K_1 \approx K_{a1}(K_{a1} + K_{a2})^2/4(c_M - 0.5 c_L). \quad (4)$$

When the reaction (D) takes place in a more alkaline medium than (C), approximations (5–6) describe sufficiently well the concentrations in solutions with a pH corresponding to $\bar{z} = 3.5$.

$$[MLH_{-1}] \approx [M_2LH_{-2}] \approx 0.5 c_L, \quad (5)$$

$$[M] \approx c_M - 1.5 c_L, \quad (6)$$

$$*K_2 \approx *K_1[H]/(c_M - 1.5 c_L). \quad (7)$$

The values of $*K_1$ and $*K_2$ were calculated from the approximations (4) and (7) and they were precised by means of the program. Small differences between the estimated and calculated values of equilibrium constants in Table 1 demonstrate, that the approximations (2–7) describe quite well the concentrations in the studied solutions. A good coincidence of \bar{z}_{calc} and \bar{z}_{exp} may be seen in Fig. 1.

Precipitate of the Cu(II) salt is formed in neutral and alkaline solutions even in the presence of an excess of OADP (c_M 1.5 and c_L 30 mM). Ni(II) forms soluble brown complexes in these media. The titration of Ni(II) solution with c_M 1.67 and

Table 1

Constants of reactions (A–D) calculated from titration curves in the region of pH 3.4–4.7 and \bar{z} 0.24–2.44

pK	Value	
	Input	Calculated by POT-3
pK_{a1}	3.92 ^a	3.79 ± 0.02 ^c
pK_{a2}	4.68 ^a	4.92 ± 0.03
$p*K_1$	9.5 ^b	9.65 ± 0.03
$p*K_2$	10.8 ^b	10.64 ± 0.01

a) Determined graphically at $c_M = 0$.

b) Approximation (4) and (7).

c) ± Standard deviation.

c_L 5.9, 11.8, 17.7, and 29.5 mM was performed at pH 7–11. In this region the function \bar{z} , indicating the average number of moles of hydrogen ions split off per 1 mole Ni(II), increases from $\bar{z} = 0$ to $\bar{z} = 1.8$ with increasing pH. The formation

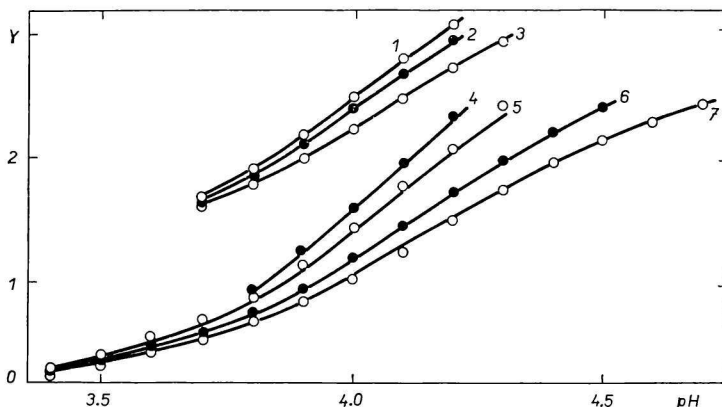


Fig. 1. The \bar{z} (pH) plot for the system Cu(II)—OADP.

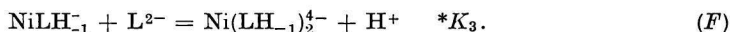
The points represent experimental values; the curves were calculated using the "best" values of constants given in Table 1.

$\bar{z} = Y - 1$ for curves 1–3 and $\bar{z} = Y$ for curves 4–7.

c_M (mM): 1.87 (1–3) and 1.25 (4–7).

c_L (mM): 2.50 (1 and 4); 2.25 (2); 1.87 (3); 2.00 (5); 1.50 (6); 1.25 (7).

curve \bar{z} (pH) consists of 2 steps. At pH 8.5–9.5 the value of \bar{z} is close to one and the value of $\Delta\bar{z}/\Delta\text{pH}$ in this acidity region is smaller than at pH > 9.5 and pH < 8.5. Regarding the mentioned parameters, the system Ni(II)—OADA, for which reactions (E) and (F) proved true [1], is identical with the system Ni(II)—OADP.



The plateau at the formation curves in the region of $\bar{z} = 1$ and pH ≈ 9 indicates, that (E) and (F) are the main equilibria taking place in solutions at pH < 9 and pH > 9, respectively. Using reagent OADA, the function \bar{z} (pH) was proved to be independent on c_L for the reaction (E). For OADP, the formation curve \bar{z} (pH) shifts to lower pH values with increasing c_L . The plot $[\text{H}]_{\bar{z}=0.5} = f(c_L)$ is linear, only the point for the lowest c_L deviates from the line, probably because of hydrolysis in the solution with a very small excess of reagent. The dependence of $[\text{H}]_{\bar{z}=0.5}$ on c_L may be explained in two different ways which seem to be of an equal probability.

First, it may be assumed, that the equilibrium (E) is accompanied by (G). The function \bar{z} is defined by eqn (8), which can be transformed into (9)



$$\bar{z} = \frac{[\text{NiLH}_{-1}] + [\text{NiL}_2\text{H}_{-1}]}{[\text{NiL}] + [\text{NiLH}_{-1}] + [\text{NiL}_2\text{H}_{-1}]}, \quad (8)$$

$$\bar{z}[\text{H}]/(1 - \bar{z}) = *K_4 + *K_5[\text{L}]. \quad (9)$$

When $[H] = [H]_{\bar{z}=0.5}$ then $\bar{z}/(1 - \bar{z}) = 1$ and for $c_L \gg c_M$ is $[L] \approx c_L$ at $pH > 7$. The graphical transformation $[H]_{\bar{z}=0.5} = f(c_L)$ based on eqn (9) is linear and gives the values p^*K_4 8.1 and p^*K_5 6.3.

The other possible explanation is based on the assumption that reaction (E) is accompanied by some unknown hydrolytic process. The smaller c_L is, the more the hydrolysis proceeds which results in a shifts of the formation curve. The "best" value $p^*K_4 = 7.7$, corresponds to $[H]_{\bar{z}=0.5}$ determined in a solution with the largest c_L , in which the hydrolysis is most suppressed.

The values of p^*K_4 determined in both ways were of the same order of magnitude (8.1 and 7.7) which confirms the existence of the equilibrium (E) in studied solutions. The greenish colloid which precipitates after several hours from Ni(II) solutions containing OADP at $pH > 10$ indicates a slow hydrolysis of the Ni(II) complex. No further study of the system Ni(II)—OADP was carried on because of the complicated interpretation of thermodynamic and mainly kinetic parameters of this hydrolysis, in which most probably the formation of oligonuclear species is involved.

Conclusion

The reagents OADP and OADA give analogous reactions with Cu(II) and Ni(II). The higher homologue OADP is a weaker acid than OADA (see Table 2). Since only 2 protons dissociate from both reagents in aqueous solution, neither the values K_{a3} , K_{a4} nor the stability constants of complexes can be determined. The equilibrium constants $*K_1$ and K'_1 for the complex $CuLH_{-2}$ with OADP and OADA differ only by one order of magnitude and the corresponding constants for Cu_2LH_{-2} are of the same order of magnitude. This indicates that an increase in the number of atoms in the chelate cycle from 5 (OADA) to 6 (OADP) does not affect markedly the stability of these Cu(II) complexes. Chaberek and Martell [5] reported a significant decrease in stability of Cu(II) chelates when 5-membered chelate rings were replaced by the 6-membered ones. The insignificant stability difference between the Cu(II) chelates with OADA and OADP indicates, that the chelate cycle with a coordinated carbonyl group

Table 2

Acidity constants of reagents OADA and OADP and equilibrium constants of their complexes

K	-log K			
	OADA		OADP	
	Cu	Ni	Cu	Ni
$K_{a1} = [HL^-][H^+] / [H_2L]$	3.1		3.9	
$K_{a2} = [L^{2-}][H^+] / [HL^-]$	3.6		4.7	
$*K_1 = [CuLH_{-1}][H^+]^3 / [Cu^{2+}][H_2L]$	8.6	—	9.7	—
$K'_1 = [CuLH_{-1}][H^+] / [Cu^{2+}][L^{2-}]$	1.9	—	0.9	—
$*K_2 = [Cu_2LH_{-2}][H^+]^4 / [Cu^{2+}]^2[H_2L]$	10.2	—	10.6	—
$K'_2 = [Cu_2LH_{-2}][H^+] / [CuLH_{-1}][Cu^{2+}]$	1.6	—	1.8	—
$*K_3 = [M(LH_{-1})_2^-][H^+] / [MLH_{-1}][L^{2-}]$	6.6	7.6	—	—
$*K_4 = [NiLH_{-1}][H^+] / [NiL]$	—	7.8	—	≈ 8

(compare I), which is identical in chelates of both reagents, contributes substantially to the complex stability. Also the Ni(II) complexes of OADP and OADA show a very small difference in stability.

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