

INORGANIC SYNTHESIS  
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Complex Formation of Calcium Ions and Monosubstituted Succinic Acid Derivatives in Aqueous Solutions

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**Abstract**—Complex formation of calcium ions with succinic acid monoamide and methyl hydrogen succinate at 25°C and ionic strength  $I = 0.3$  (KCl) was studied by pH-potentiometric titration. The stability constants of the complexes were determined.

Fatty acid collecting agents used for dressing of phosphorus-containing ores are obtained from vegetable raw materials. They are insufficiently effective for flotation of ores with complicated mineralogical composition, especially under conditions of water recycling. One of promising ways for the development of effective collecting agents that are less sensitive to the salt composition of the pulp liquid phase is the use of compounds containing two different functional groups.

Nitrogen- or oxygen-containing monosubstituted succinic acid derivatives are of interest in this respect [1–3]. They are readily available owing to high reactivity of the anhydride ring in reactions of the anhydride with methanol or ammonia.

The pulp liquid phase formed during dressing of apatite (a calcium-containing mineral) contains a significant amount of calcium ions, which strongly affect the flotation process. Therefore, it was important to estimate stability of calcium compounds in aqueous solutions of succinic acid monoamide and monoester. The complex formation of unsubstituted succinic acid with calcium ions was studied in [4], and the stability constants of the resulting compounds were determined.

The aims of this work were to estimate the effect of amidation or esterification of one of carboxy groups in succinic acid on the stability of calcium salts and to determine the constants of Ca(II) complex formation with succinic acid monoamide and monomethyl ester.

EXPERIMENTAL

Methyl hydrogen succinate [5] and succinic acid monoamide were prepared by the reactions of succinic

anhydride with methanol and ammonia, respectively. Succinic acid monoamide was recrystallized three times from ethanol and dried under reduced pressure. Methyl hydrogen succinate was used without additional purification. The compounds synthesized were identified by melting points and neutralization equivalents (see table).

The Ca(II) complex formation with monosubstituted derivatives of succinic acid was studied by pH-potentiometric titration. The experimental conditions were the same as in the earlier study of Ca(II) complex formation with unsubstituted succinic acid [4]: 25°C and ionic strength  $I = 0.3$  supported by KCl. The ionization constants  $B$  of the compounds HL under consideration, which are required to calculate the complex formation constants, were determined previously under the same conditions [6].

The pH was measured with glass and silver chloride electrodes on an I-120.1 pH meter with an accuracy of  $\pm 0.01$  pH unit.

The concentration of monosubstituted succinic acid derivatives was 0.10–0.15 M, and the concentration of the added  $\text{Ca}(\text{NO}_3)_2$  solution, 0.1 M. The concentration ratios  $\text{Ca}(\text{II}) : \text{HL}$  were 1 : 5 and 1 : 3.

Characteristics of monosubstituted succinic acid derivatives

Compound	mp, °C		Neutralization, mol-equiv	
	found	[5]	found	calculated
Methyl hydrogen succinate	57	58	131.3	132.1
Succinic acid monoamide	156	157	116.2	117.0

The concentrations of succinic acid monosubstituted derivatives HL in solution were calculated from the precise weights of their portions and refined by pH-potentiometric titration. Chemically pure grade calcium nitrate and potassium chloride were used. The content of Ca(II) in solutions were determined by complexometric titration. The concentration of KOH solution prepared by dilution of its saturated solution [6] was refined by potentiometric titration. All the solutions were prepared in freshly boiled distilled water.

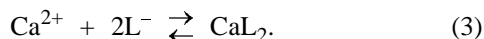
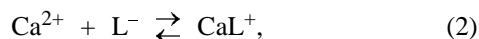
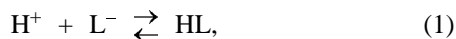
Solutions of a succinic acid monosubstituted derivative,  $\text{Ca}(\text{NO}_3)_2$ , and KCl were placed in a temperature-controlled cell. After adding each portion (0.1 ml) of the titrant (0.3 M KOH), the pH values were measured. The equilibrium was considered as attained if pH remained constant for 2–3 min. The glass electrode was calibrated by buffer solutions before each measurement. The calibration straight line was determined by the least-squares procedure and then used to refine the pH values obtained during titration. The pH meter readings were checked by a buffer solution with pH 4.01 after each titration. If the measured pH differed from this value by more than 0.02, the results were discarded. Points of the titration curve in the range pH 3.0–6.0 were used in the calculations.

The protonation constants of succinic acid monoamide and methyl succinate anions,

$$B = \frac{[\text{HL}]}{[\text{L}^-][\text{H}^+]}$$

were determined by the potentiometric titration at 25°C and ionic strength  $I = 0.3$  (KCl). Three to five replicate determinations were performed for each acid. In each determination, the protonation constant was calculated as the average of the calculated values for each point of the titration curve. The error in  $\log B$  was taken as the probable deviation of the arithmetic mean at a confidence level of 0.95. The calculated  $\log B$  values for succinic acid monoamide and methyl hydrogen succinate were  $4.51 \pm 0.01$  and  $4.42 \pm 0.01$ , respectively ( $I = 0.3$ ,  $T = 25^\circ\text{C}$ ).

The following equilibria were taken into account when calculating the stability constants of calcium complexes with succinic acid derivatives:



Hydrolysis of  $\text{Ca}^{2+}$  ions was not taken into account, as being negligible at  $\text{pH} < 6$  [7].

The equilibrium concentrations of species in solution were calculated from the following equations of material balance and mass action law:

$$c_L = [\text{HL}] + [\text{L}^-] + [\text{CaL}^+] + [\text{CaL}_2],$$

$$c_H = [\text{HL}] + [\text{H}^+],$$

$$c_M = [\text{Ca}^{2+}] + [\text{CaL}^+] + [\text{CaL}_2],$$

$$B = \frac{[\text{HL}]}{[\text{L}^-][\text{H}^+]}, \quad \beta_{\text{CaL}^+} = \frac{[\text{CaL}^+]}{[\text{Ca}^{2+}][\text{L}^-]},$$

$$\beta_{\text{CaL}_2} = \frac{[\text{CaL}_2]}{[\text{Ca}^{2+}][\text{L}^-]^2},$$

where  $c_L$ ,  $c_H$ , and  $c_M$  are total concentrations of the ligand, hydrogen ions, and metal ions, respectively;  $B$ , protonation constant of a monosubstituted succinic acid derivative; and  $\beta_{\text{CaL}_2}$  and  $\beta_{\text{CaL}^+}$ , stability constants of the corresponding calcium compounds.

The formation function  $\bar{n}$  for the system under study has the following form:

$$\bar{n} = \frac{\beta_{\text{CaL}^+}[\text{L}^-] + 2\beta_{\text{CaL}_2}[\text{L}^-]^2}{1 + \beta_{\text{CaL}^+}[\text{L}^-] + 2\beta_{\text{CaL}_2}[\text{L}^-]^2}.$$

This equation can be transformed to

$$\bar{n} + (\bar{n} - 1)[\text{L}^-]\beta_{\text{CaL}^+} + (\bar{n} - 1)[\text{L}^-]^2\beta_{\text{CaL}_2} = 0.$$

The experimental data were treated by the least-squares procedure. The number of independent determinations of complex formation constants for each compound was 8–10. The obtained  $\beta_{\text{CaL}^+}$  and  $\beta_{\text{CaL}_2}$  values for Ca(II) complexes with succinic acid monoamide and methyl hydrogen succinate at  $I = 0.3$  (KCl) and  $T = 25^\circ\text{C}$  were recalculated to zero ionic strength by the Davies equation. The experimental data were approximated by  $y = a + bx$  functions with at confidence level of 0.95 and with the confidence interval no greater than 2. The logarithms of the complex formation constants are presented below together with the previous data [4] on the stability of calcium succinates, given for comparison.

Compound	$\log \beta_{\text{CaL}^+}^0$	$\log \beta_{\text{CaL}_2}^0$
Succinic acid	$2.08 \pm 0.02$	$3.41 \pm 0.06$
Methyl hydrogen succinate	$1.91 \pm 0.02$	$3.56 \pm 0.03$
Succinic acid monoamide	$1.86 \pm 0.05$	$3.58 \pm 0.06$

These data show that the stability of calcium complexes with succinic acid monoamide and methyl hydrogen succinate is virtually independent of the nature of substituted carboxy group. Comparison of the  $\log\beta^0$  values for the compounds under study and calcium succinates shows that replacement of one carboxy group by an amide or ester group decreases the stability of the 1 : 1 Ca(II) complexes. Since succinic acid has two carboxy groups, it was suggested [8] that the probable structure of its Ca(II) chelate contains a seven-membered ring. In contrast to the acid, the monosubstituted derivatives under consideration contain one anion and one nonionic (amide or ester) group showing no tendency to form a coordination bond. The composition of the monosubstituted derivatives under study and the stability constants found in this work suggest that succinic acid monoamide and methyl hydrogen succinate behave as monodentate ligands. In the case of 1 : 2 calcium complexes with the monosubstituted derivatives, the  $\log\beta_{\text{CaL}_2}^0$  values are greater than in the case of the Ca(II) complex with succinic acid.

#### CONCLUSIONS

(1) The complex formation of Ca(II) with methyl hydrogen succinate and succinic acid monoamide was studied. The stability constants of the 1 : 1 and 1 : 2 Ca(II) complexes were determined by potentiometric titration.

(2) The stability of the 1 : 1 Ca(II) complexes decreases on replacement of one of carboxy groups in the succinic acid molecule by a nonionic ester or amide group.

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