Complex Formation Equilibria of Some Aliphatic α-Hydroxycarboxylic Acids. 1. The Determination of Protonation Constants and the Study of Calcium(II) and Magnesium(II) Complexes

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Complex formation equilibria of calcium(II) and magnesium(II) with five aliphatic α-hydroxycarboxylic acids, viz. glycolic (HL), lactic (HL), 2-hydroxyisobutyric (HL), L(+)-tartaric (H_2L) and citric (H_3L) acids, were studied by means of potentiometric (glass electrode) titrations at 25°C in an ionic medium of 0.5 M $NaClO_4$. In the case of the monocarboxylic acids only weak mononuclear CaL and MgL complexes were found to form. For the complexation between tartaric acid and Ca(II) the p,q,r analysis gave best results for the model consisting of CaL and CaH_2L_2 complexes. In the case of the corresponding Mg(II) system the computer analysis gave no evidence for the formation of protonated complexes. Ca(II) and Mg(II) were found to form ML and MHL complexes with citric acid. The stability constants for these complexes with their standard deviations are given and compared to the comparable literature values. The protonation constants were studied in separate titrations.

Hydroxycarboxylic acids are naturally occuring compounds which have a pronounced influence on the inorganic constituents of soil, water and sediment. Humic substances are described as polymers containing hydroxyl and carboxyl functional groups. An important property of humic and fulvic acids is their tendency to form complexes with metal ions. The investigation of the corresponding complexes of monomeric units can help us to understand the chemistry of natural waters. Citric and tartaric acids are very common in various plants. For example, plants take up trace metals by their roots as citrate complexes. Aliphatic hydroxycarboxylic acids have also been studied for use in detergents and fertilizers. Detergents contain builders to bind metals, which affect water hardness (mainly Ca and Mg). The use of polyphosphates, NTA (nitrilotriacetic acid) and EDTA as complexing agents has been reduced because of their environmental effects. Hydroxycarboxylic acids used in detergents are e.g. citric, tartaric and gluconic acids as well as glycolates.

Most alkaline-earth metals are widely distributed in minerals and seawater. Calcium and magnesium are both major components of the earth's crust, in which they occur in deposits such as dolomite ($CaCO_3 \cdot MgCO_3$) and

carnallite ($MgCl_2 \cdot KCl \cdot 6H_2O$). Carbonate rocks are rapidly eroded when exposed to water containing dissolved CO_2. This means the formation of free Ca^{2+} and Mg^{2+} ions in natural waters. Calcium and magnesium are classified as hard acids in Pearson's concept of soft and hard bases (SHAB).[1] This means that they form most stable complexes with ligands classified as hard bases. Hydroxycarboxylic acids are hard bases, because they have oxygen as a donor atom. The complexation between alkaline-earth metals and aliphatic hydroxycarboxylic acids has not been studied recently.[2–4]

The aim of this series of investigations is to study the complexing tendencies of five aliphatic α-hydroxycarboxylic acids [glycolic, lactic, 2-hydroxyisobutyric, L(+)-tartaric and citric acids] in comparable experimental conditions in order to evaluate their applicability for use in detergents and fertilizers. Also, the chemistry of natural waters is considered. In the first part of this series the complex formation of calcium(II) and magnesium(II) is reported.

Experimental

Chemicals and analysis. A stock solution of calcium(II) perchlorate was prepared by dissolving $Ca(NO_3)_2 \cdot 4H_2O$

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in $HClO_4$ and heating the solution twice to dryness. The calcium concentration was determined by titration with 0.1 M NaOH solution after passage through a cation exchanger. The calcium concentration was also determined by titration with EDTA. The acid concentration of the stock solution was determined by titration with NaOH. A stock solution of magnesium(II) perchlorate was prepared from $Mg(ClO_4)_2 \cdot 6H_2O$ and analyzed by the same methods as calcium.

The hydroxycarboxylic acids studied were commercially available and used without further purification [glycolic acid (2-hydroxyethanoic acid, $C_2H_4O_3$, HL, Fluka AG), lactic acid (2-hydroxypropanoic acid, $C_3H_6O_3$, HL, Merck), 2-hydroxyisobutyric acid (2-hydroxy-2-methylpropanoic acid, $C_4H_8O_3$, HL, Riedel-deHaen AG), L(+)-tartaric acid (L(+)-2,3-dihydroxybutanedioic acid, $C_4H_6O_6$, H_2L, Merck) and citric acid (2-hydroxypropane-1,2,3-tricarboxylic acid, $C_6H_8O_7$, H_3L, Merck)]. The concentrations of the aqueous solutions of the ligand acids were determined by potentiometric titration with a standard solution of NaOH.

NaOH solution was standardized by potassium hydrogen phthalate. A known amount of dry potassium hydrogen phthalate was dissolved in hot distilled water and titrated with NaOH solution using phenolphthalein as indicator. The buffer solution (E_0-solution) for the calibration of the electrode system was 0.01 and 0.49 M with respect to $HClO_4$ and $NaClO_4$, respectively.

Apparatus. The potentiometric measurements were performed with a locally constructed automatic titration system. The system consisted of a multichannel high-impedance amplifier, a Hewlett-Packard 3478A multimeter and a Metrohm 665 Dosimat piston. The equipment was controlled with an Amstrad PC 1640 SD computer using the program TIT3.[5] The electrode system consisted of an Orion 91-01SC glass electrode as an indicator electrode and an Orion 9002 Ag,AgCl(s) double-junction reference electrode which had 0.5 M $NaClO_4$ solution as an electrolyte. Although the free metal concentration can give valuable information, metal electrodes were not used in this work. This is because of the poor results obtained in our laboratory concerning the applicability of calcium electrodes to this kind of work.

During the titrations, a stream of argon was bubbled through the solution to maintain an inert atmosphere in the vessel and to stir the solution. The gas was first bubbled through solutions of 10% NaOH and 10% H_2SO_4 to remove acid and alkaline impurities. Before the gas came into contact with the equilibrium solution, it was passed through a pure ionic medium of 0.5 M $NaClO_4$.

Method. The investigation was carried out as a series of potentiometric titrations at $25 \pm 0.1°C$ in 0.5 M ($NaClO_4$) solution. The electrode system was calibrated by titration of 40 ml of the E_0-solution (composition as described above) with standard 0.1 M NaOH. The free H^+

concentration, h, was determined by measuring the EMF of the cell:

$$- RE \mid \text{equilibrium solution} \mid ME +$$
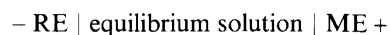
where ME is glass electrode and RE denotes the reference electrode. If we assume the activity coefficients to be constant, following expression [eqn. (1)] is valid:

$$E = E_0 + 59.16 \log h + E_j \tag{1}$$

where E_0 is determined at each titration and E_j is $- 100 h$ in 0.5 M $NaClO_4$.[6] The titrations concerning the protonation constants of the hydroxycarboxylic acids were performed in separate experiments ($B = 0$) within the concentration range 0.006–0.019 M for glycolic acid, 0.007–0.019 M for lactic acid, 0.010–0.017 M for 2-hydroxyisobutyric acid, 0.006–0.013 M for tartaric acid and 0.004–0.011 M for citric acid. In the titrations concerning the complex formation the total concentrations of ligand (C) and metal (B) were varied within the limits $0.007 < C < 0.023$ M and $0.001 < B < 0.008$ M for glycolic acid, $0.006 < C < 0.012$ M and $0.002 < B < 0.006$ M for lactic acid, $0.007 < C < 0.011$ M and $0.002 < B < 0.008$ M for 2-hydroxyisobutyric acid, $0.004 < C < 0.008$ M and $0.002 < B < 0.005$ M for tartaric acid, and $0.003 < C < 0.008$ M and $0.002 < B < 0.004$ M for citric acid. The experiments covered the pH range $2.5–2.8 < - \log h < 6.0–10.8$ and the C/B ratios 1–15.

Data treatment. The protonation constants of the ligand acids and the stability constants of the metal complexes were calculated from the potentiometric data with the program LETAGROP.[7,8] For visualizing the experimental results, the treatment of the three-component equilibria, H^+–ligand–metal, was started with a calculation of the experimental $Z_{A/C}$-value for each point of a titration. $Z_{A/C}$ is defined as the average number of protons bound to each ligand [eqn. (2)]:

$$Z_{A/C} = [H - (h - k_w h^{-1})]/C \tag{2}$$

where H denotes the total concentration of the protons. Also, curves representing the average number of ligands bound to metal ($\bar{n}$ vs. log [L]) were used. The equilibrium reactions in a three-component system can be described by the general relation (charges are omitted):

$$pH + qM + rL \rightleftharpoons H_pM_qL_r, \quad \beta_{p,q,r} \tag{3}$$
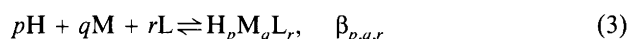
The equilibrium model was determined by searching the p,q,r triplets and the corresponding formation constants $\beta_{p,q,r}$ that best describe the experimental data. This was done with the computer program by minimizing the error squares sum $U = \Sigma(H_{calc} - H_{exp})^2$. The LETAGROP calculations also gave the standard deviations $3\sigma(\log \beta_{p,q,r})$. The program SOLGASWATER[9] was used to calculate distribution diagrams for the equilibrium systems.

Results and discussion

Protonation constants. The data used to determine the protonation constants of each individual hydroxycarboxylic acid comprise 3–8 titrations and 101–265 experimental points. The obtained protonation constants are listed with some literature values in Table 1. If possible, the results are compared to constants determined at the corresponding experimental conditions used in this work. In the case of the three monocarboxylic acids the magnitudes of the protonation constants are similar. The constant of 2-hydroxyisobutyric acid is slightly higher than those of glycolic and lactic acids, which was expected on the basis of earlier studies. The protonation constant obtained for lactic acid is slightly lower compared to that determined by Marklund *et al.*[11] Protonation constants of (+)-tartaric and citric acids determined in this work are in accord with constants obtained by other investigators.[12–16]

Calcium(II) and magnesium(II) complexes. The data for the determination of the stability constants of the calcium(II) and magnesium(II) complexes with hydroxycarboxylic acids consists of 3–6 titrations and 105–359 experimental points. The stability constants obtained in this work are compared to literature values in Tables 2 and 3.

In the case of glycolic, lactic and 2-hydroxyisobutyric acids the experimental results ($Z_{A/C}$ vs. $-\log h$ and $\bar{n}$ vs.

log [L]) clearly showed that only weak mononuclear CaL^+ and MgL^+ complexes were formed. The LETA-GROP calculations gave the following stability constants for calcium(II) complexes [for definitions see eqn. (3)]: $\log \beta_{0,1,1} = 0.92 \pm 0.03$ for glycolic acid, $\log \beta_{0,1,1} = 1.05 \pm 0.08$ for lactic acid and $\log \beta_{0,1,1} = 1.09 \pm 0.03$ for 2-hydroxyisobutyric acid [the errors given correspond to $3\sigma(\log \beta_{p,q,r})$]. Correspondingly, constants for magnesium(II) complexes are as follows: $\log \beta_{0,1,1} = 1.03 \pm 0.02$ for glycolic acid, $\log \beta_{0,1,1} = 0.93 \pm 0.08$ for lactic acid and $\log \beta_{0,1,1} = 0.98 \pm 0.05$ for 2-hydroxyisobutyric acid. These constants are in good agreement with those found in the literature.[2,4,17] Owing to the weakness of the complexes studied it is not possible to establish an exact stability order.

The experimental data for tartaric and citric acid complexes were visualized as $Z_{A/C}$ vs. $-\log h$ curves. Figure 1 shows some of the data with different concentrations for the Ca(II)–citric acid system. The curves are compared to that representing the protonation of the ligand ($B = 0$, $\bar{n}_H$). Values for $Z_{A/C} > 2$ ($-\log h < 3.5$) have been discarded because no complexation was found in this area. For searching the composition and stability of the tartaric and citric acid complexes a p,q,r analysis (systematic testing of p,q,r combinations) was performed using the LETAGROP program. The aim of the analysis was to find the complexes giving the lowest error squares sum $U = \Sigma(H_{calc} - H_{exp})^2$. Figure 2 shows the results of

Table 1. Protonation constants of aliphatic α-hydroxycarboxylic acids at 25°C.

Ligand	*I*(M)	Formula	log(β±3σ)	Reference
Glycolic acid	0.5	HL	3.586±0.003	This work
	0.5	HL	3.56±0.01	10
	0.5	HL	3.55±0.03	4
	0.5	HL	3.62±0.03	4
Lactic acid	0.5	HL	3.45±0.03	This work
	0.6	HL	3.572±0.001	11
	0.5	HL	3.61±0.01	4
2-Hydroxyisobutyric acid	0.5	HL	3.760±0.006	This work
	0.5	HL	3.75±0.00	4
	0.1	HL	3.79±0.01	4
(+)-Tartaric acid	0.5	HL^-	3.724±0.004	This work
	0.5	H_2L	6.471±0.004	This work
	0.5	HL^-	3.72±0.01	12
	0.5	H_2L	6.36±0.03	12
	1.0	HL^-	3.690±0.008	13
	1.0	H_2L	6.433±0.009	13
	0.6	HL^-	3.699±0.002	14
	0.6	H_2L	6.401±0.002	14
Citric acid	0.5	HL^{2-}	5.317±0.007	This work
	0.5	H_2L^-	9.464±0.007	This work
	0.5	H_3L	12.296±0.008	This work
	0.6	HL^{2-}	5.217±0.003	15
	0.6	H_2L^-	9.298±0.003	15
	0.6	H_3L	12.067±0.004	15
	0.5	HL^{2-}	5.30±0.04	4
	0.5	H_2L^-	9.41±0.04	4
	0.5	H_3L	12.18±0.03	4
	0.5	HL^{2-}	5.596±0.008	16
	0.5	H_2L^-	9.888±0.09	16
	0.5	H_3L	12.941±0.07	16

Table 2. Stability constants of calcium(II) complexes of aliphatic α-hydroxycarboxylic acids at 25°C.

Ligand	I(M)	Formula	$\log(\beta \pm 3\sigma)$	Reference
Glycolic acid	0.5	CaL^+	0.92 ± 0.03	This work
	0.1	CaL^+	1.11	2
Lactic acid	0.5	CaL^+	1.05 ± 0.08	This work
	0.5	CaL^+	0.92	4
	0.5	CaL_2	1.62	4
	1.0	CaL^+	0.90 ± 0.01	17
	1.0	CaL_2	1.24 ± 0.015	17
2-Hydroxyisobutyric acid	0.5	CaL^+	1.09 ± 0.03	This work
	1.0	CaL^+	0.92 ± 0.015	17
	1.0	CaL_2	1.42 ± 0.025	17
(+)-Tartaric acid	0.5	CaL	1.66 ± 0.05	This work
	0.5	CaH_2L_2	10.84 ± 0.08	This work
	0.25	CaL	2.10 ± 0.04	18
	0.25	$CaHL^+$	5.02 ± 0.05	18
	0.1	CaL	1.95 ± 0.1	4
	0.1	$CaHL^+$	1.16 ± 0.09 (log K)	4
Citric acid	0.5	CaL^-	2.71 ± 0.01	This work
	0.5	$CaHL$	6.70 ± 0.09	This work
	0.1	CaL^-	3.50 ± 0.06	19
	0.1	$CaHL$	8.02 ± 0.15	19
	0.1	CaL^-	3.45 ± 0.10	4
	0.1	$CaHL$	2.13 ± 0.10 (log K)	4
	0.1	CaH_2L^+	1.0 ± 0.0 (log K)	4
	0.15	CaL^-	1.78 ± 0.04	2
	0.1	CaL^-	2.17	2
	0.1	$CaHL$	1.46 (log K)	2
	0.1	CaH_2L^+	0.88 (log K)	2

this analysis for calcium(II) complexes of tartaric acid (Fig. 2a) and citric acid (Fig. 2b). The lowest value of U was obtained for the complexes CaL (log $\beta_{0,1,1}$ = 1.66 ± 0.05) and CaH_2L_2 (log $\beta_{2,1,2}$ = 10.84 ± 0.08) for L(+)-tartaric acid, and CaL (log $\beta_{0,1,1}$ = 2.71 ± 0.01) and

CaHL (log $\beta_{1,1,1}$ = 6.70 ± 0.09) for citric acid. The distribution diagram for the calcium–citric acid complexes shows the amount of different species present in the solution as a function of pH (Fig. 3). Correspondingly, the complexes found for magnesium(II) systems are as fol-

Table 3. Stability constants of magnesium(II) complexes of aliphatic α-hydroxycarboxylic acids at 25°C.

| Ligand	I(M)	Formula	$\log(\beta \pm 3\sigma)$	Reference
Glycolic acid	0.5	MgL^+	1.03 ± 0.02	This work
	0.1	MgL^+	0.92	2
Lactic acid	0.5	MgL^+	0.93 ± 0.08	This work
	0.1	MgL^+	0.93	2
	1.0	MgL^+	0.73 ± 0.03	17
	1.0	MgL_2	1.30 ± 0.06	17
2-Hydroxyisobutyric acid	0.5	MgL^+	0.98 ± 0.05	This work
	1.0	MgL^+	0.81 ± 0.02	17
	1.0	MgL_2	1.47 ± 0.04	17
(+)-Tartaric acid	0.5	MgL	1.11 ± 0.08	This work
	0.1	MgL	1.44	4
	0.1	$MgHL^+$	0.95 ± 0.01 (log K)	4
Citric acid	0.5	MgL^-	2.71 ± 0.01	This work
	0.5	$MgHL$	6.55 ± 0.12	This work
	0.1	MgL^-	3.45 ± 0.07	4
	0.1	$MgHL$	1.81 ± 0.04 (log K)	4
	0.1	MgH_2L^+	0.7 ± 0.1 (log K)	4
	0.1	MgL^-	3.38 ± 0.07	19
	0.1	$MgHL$	7.66 ± 0.19	19
	0.15	MgL^-	2.00	2
	0.1	MgL^-	2.06	2
	0.15	$MgHL$	0.91 (log K)	2
	0.1	$MgHL$	1.20 (log K)	2
	0.1	MgH_2L^+	0.77 (log K)	2
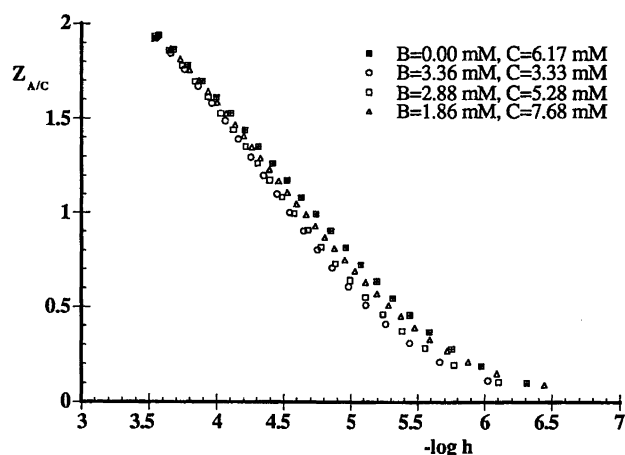
Fig. 1. Some experimental data for the calcium(II)–citric acid system plotted as $Z_{A/C}$ vs. $-\log h$. The concentrations of calcium (B) and citric acid (C) in separate titrations are given in the figure.

Fig. 3. Distribution diagram F_i [fraction of total calcium(II)] vs. $-\log h$ for the calcium(II)–citric acid system. The calculations have been made using the program SOLGASWATER with constants determined in this work (Tables 1 and 2). $B = 0.002$ M, $C = 0.008$ M.

lows: MgL ($\log \beta_{0,1,1} = 1.11 \pm 0.08$) for L(+)-tartaric acid, and MgL$^-$ ($\log \beta_{0,1,1,} = 2.71 \pm 0.01$) and MgHL ($\log \beta_{1,1,1} = 6.55 \pm 0.12$) for citric acid.

The equilibrium model for the system of calcium with L(+)-tartaric acid differs from that obtained by other investigators.[4,18] They have described the system by CaL and CaHL$^+$ complexes. The stability constant for the CaL species is slightly lower compared to the values found in the literature, which is probably due to the higher ionic strength used in this work. In the case of the complexation of magnesium with tartaric acid, protonated species were not detected with the experimental conditions used.
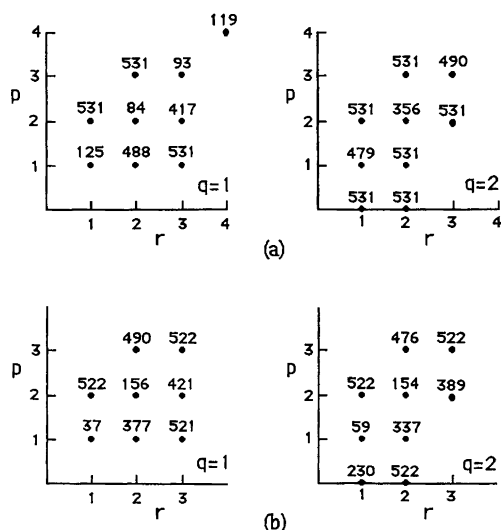
With respect to the citrate complexes, it is obvious that protonated species do occur with both metals discussed. In this work only MHL complexes were found. The two protonated species MH$_2$L$^+$, which have been proposed by some investigators,[2,4] was not found to form in the pH region used in this work. The stability constants found in the literature were determined at lower ionic strength than the 0.5 M used in this work. The published constants for calcium and magnesium complexes with citric acid does not show any agreement.[2,4,19] For these reasons the comparison is difficult.

According to this investigation the monocarboxylic acids studied do not differ significantly from each other in complexing calcium and magnesium. Tartaric and citric acids form more stable complexes, because they have more donor atoms to form metal chelates. In the case of glycolic, lactic, 2-hydroxyisobutyric and citric acids calcium and magnesium are equally strong complex formers, whereas tartrate systems differ both in the model determined and in the stability constants calculated. The CaL complex of L(+)-tartaric acid is more stable than the corresponding MgL complex.

Fig. 2. The LETAGROP search for $H_pCa_qL_r$ complexes of tartaric acid (a) and citric acid (b). The figures give error square sums $U(\text{pr})_q \times 10^4$ when one new complex is varied together with CaL.
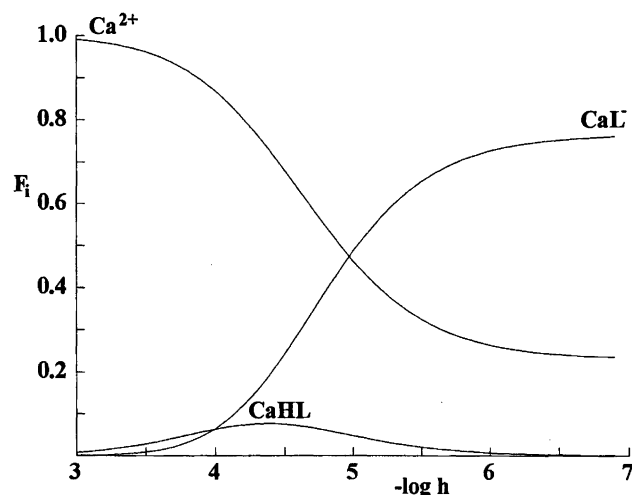
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