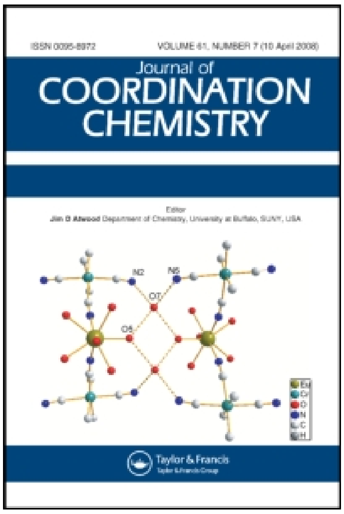

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A COMPARISON OF CARBOXYLATE COMPLEXES OF LANTHANUM (III): FORMATE, ACETATE AND PROPIONATE

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A COMPARISON OF CARBOXYLATE COMPLEXES OF LANTHANUM (III): FORMATE, ACETATE AND PROPIONATE

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The stability constants of La(III)-formate and La(III)-propionate complexes in aqueous medium were determined by a potentiometric method using a glass electrode. The temperature was kept at 25°C and an ionic strength of 1.00 M ($NaClO_4$) was used. Four mononuclear complexes were detected for both systems. The pK_a values for the carboxylic acids (formic and propionic) were determined at the same conditions. The final values of the overall stability constants determined by a matrix solution of weighted simultaneous equations were: $\beta_1 = (13.2 \pm 0.6)$ L mol^{-1}, $\beta_2 = (48 \pm 4)$ L^2 mol^{-2}, $\beta_3 = (118 \pm 15)$ L^3 mol^{-3}, $\beta_4 = (85 \pm 15)$ L^4 mol^4 for La(III)-formate system and $\beta_1 = (42 \pm 3)$ L mol^{-1}, $\beta_2 = (299 \pm 25)$ L^2 mol^{-2}, $\beta_3 = (1201 \pm 138)$ L^3 mol^{-3}, $\beta_4 = (2527 \pm 174)$ L^4 mol^{-4} for La(III)-propionate system. These data and those for La(III)/acetate from the literature were used to compare the tendency to complex.

Keywords: lanthanum; formate; acetate; propionate; stability; potentiometry

INTRODUCTION

Stability trends of the trivalent lanthanide ions were studied using solutions of hydroxy-carboxylate acids.[1-3] It was found that if these anions act as monodentate ligands with only the carboxylate involved in coordination, the anion of the stronger acid forms weaker complexes.

Stability of lanthanum-carboxylate complexes has been studied in our laboratory. In a recent publication, stability constants of the lanthanum(III)-acetate complexes were reported.[4] In order to obtain further data about the affinity of lanthanides for

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carboxylates, the present paper reports a competitive and indirect potentiometric study[5–7] of complexes between lanthanum(III) ions and formate and propionate anions in water, making use of a combination glass electrode and pH measurements. Potentiometry is a suitable method because carboxylic acid and its conjugate carboxylate anion form a buffer solution causing variation in pH when a metal ion is added. The equilibrium is altered and a new pH value is observed.

These equilibrium studies support the use of fatty acids in solvent extraction of some metal cations,[8–10] a study that is being extended to trivalent cations and uranyl. In fact carboxylic groups are hard bases and are able to interact with hard cations of rare earth metals.

EXPERIMENTAL

Apparatus

A Metrohm 654 pH meter adapted to a Metrohm combination glass electrode was used in all measurements. The volumes were taken with a Metrohm E274 (5 mL) micro burette. The supporting electrolyte was sodium perchlorate (1.00 M) and the temperature was kept constant at (25.0 ± 0.1)°C.

Sigma Plot (v. 5.0) computer software and programs in QUICK BASIC were used in an IBM-AT type computer in order to analyze data for the equilibria.[11]

Reagents and Solutions

Sodium perchlorate solution (Merck) was standardized gravimetrically.[12] Sodium hydroxide (Merck) and carboxylic acid solutions were standardized, respectively, with primary standard potassium hydrogen phthalate (Merck) and the standardized sodium hydroxide solution. All solutions were standardized potentiometrically utilizing a Metrohm 682 Titroprocessor - 665 Dosimat and a combination glass electrode.

The lanthanum(III) perchlorate solution was prepared as described previously.[4]

PROCEDURE

The experimental technique has already been described.[4] Buffer solutions containing formic acid and sodium formate were prepared by adding measured volumes of standard sodium hydroxide solution to known volumes of standard formic acid solution and the ionic strength was adjusted to 1.00 M ($NaClO_4$). The same procedure was utilized to prepare buffer solutions of propionic acid and sodium propionate.

An aliquot of the resulting buffer solution was transferred to a Metrohm thermostatic cell and the pH_1 value was measured. Then, a known volume of 0.4892 M lanthanum(III) solution was added to this buffer with a micro burette under stirring and the pH_2 value was measured. Successive additions of the cation solution were carried out.

With those pH values, considering the mass balances and all corrections for dilution by reagent addition, the average ligand number ($\bar{n}$) and free ligand concentration [L^-] data can be determined.[5]

RESULTS AND DISCUSSION

In these studies, different series with distinct buffers and different metallic ion concentrations were examined. Figures 1 and 2 show the experimental data of $\bar{n}$ *vs.* [L^-], for La(III)-formate and La(III)-propionate systems, respectively. The calculated curves were obtained from the final values of the stability constants. Since the same experimental curve was obtained for different La(III) concentrations in both cases, no evidence of polynuclear species was found in the metal concentration range employed (9.38 – 79.8 mM).

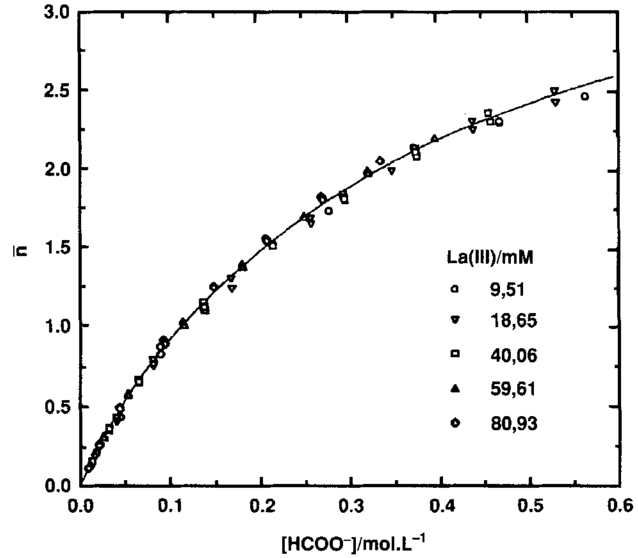

FIGURE 1 Experimental values of $\bar{n}$ *vs.* free concentration of formate and the calculated curve from the determined stability constants.

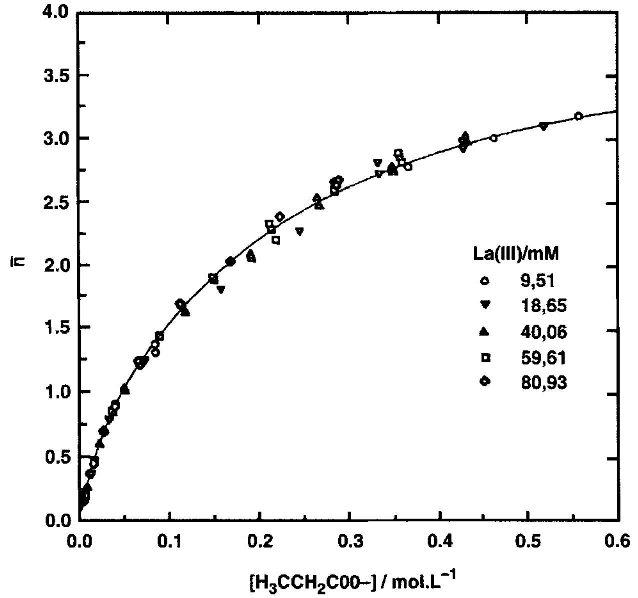

FIGURE 2 Experimental values of n̄ *vs.* free concentration of propionate and the calculated curve from the determined stability constants.

The formation curve of the La(III)-formate system reaches a constant n̄ value (near 3) indicating a system with at least three successive complexes while the La(III)-propionate system (n̄ near 3.5) indicates at least four successive complexes.

In order to obtain more accurate n̄ values, the treatment of data was carried out using the conditional pK_a of the weak acid (HL) for each particular working solution. The rationale for this procedure was previously reported.[5]

Usually initial resolution of stability constants is effected with the classical graphical approach due to Leden,[13] but in this study the stability constants were first determined using the average ligand number.[14] Formation curves shown in Figures 1 and 2 were adjusted directly using the average ligand number equation and the Sigma Plot (v.5.0) computer software. This software uses the least squares method, in an iterative process in order to minimize the deviation square sum between the experimental and calculated n̄ data.[15] The formation curve for both systems was adjusted assuming a system with three, four or five species. The best fit was obtained assuming four species in both systems. The graphical method was then performed and four different complexes were found for La(III)-formate and La(III)-propionate systems in the ligand concentration range (0 – 0.6 M).

Another way to evaluate the equilibrium constants is from a matrix program using properly weighted simultaneous equations, detailed previously.[16] This procedure is more reliable than the graphical method since values with large deviation (individual percent error > 3%) can be eliminated.

The average deviation between the calculated and experimental average ligand concentration was ± 1.19% for La(III)-formate and ± 0.95% for the La(III)-propionate system.

The values obtained for the stability constants of formate and propionate systems are listed in Table I. Both methods gave similar values for the formation constants. The 'direct adjust' method can be utilized as an alternative and rapid method to determine the stability constants.

The final values for the stability constants including the La(III)-acetate system[4] determined by the weighted simultaneous equation and the pK_a for the three carboxylic acids are in Table II. The standard deviation was found by comparison of experimental $\bar{n}$ and evaluated $\bar{n}$ using the set of constants.

The linear relationship between log β_1 and pK_a is confirmed as observed in some other examples.[17] But the same behavior was observed for log β_3 *vs.* pK_a and it was more evident because the comparison refers to the formation of the neutral species HL and LaL_3. This results means that the free energy change involved in the complex formation is proportional to the formation of the corresponding weak acid, HL. This behavior is consistent with formation of neutral species between hard cations, H^+ 10 and La^{3+}, with hard bases, carboxylate groups.

The stability constants obtained in the present study and for the La(III)-acetate systems can be compared with stabilities for the same systems from the literature. Table III shows that for the La(III)-formate system only two species were detected.The value of b_1 found by Smith *et al.*[18] is very close to the present study.

TABLE I Stability constants obtained for La(III)-formate and La(III)-propionate systems

Method	$\beta_1/L.mol^{-1}$	$\beta_2/L^2.mol^{-2}$	$\beta_3/L^3.mol^{-3}$	$\beta_4/L^4.mol^{-4}$
		La(III)-formate		
Simult. equations	13.2	48.2	118	84.8
'direct adjust'	12.6	48.1	112	88.0
		La(III)-propionate		
Simult. equations	41.6	299	1201	2527
'direct adjust'	40.0	321	954	2716

TABLE II Final stability constants obtained for La(III)-carboxylates systems and the pK_a for the carboxylic acids

Ligand	$\beta_1/L.mol^{-1}$	β_2/L^2mol^{-2}	β_3/L^3mol^{-3}	β_4/L^4mol^{-4}	pK_a
formate	(13.2 ± 0.6)	(48 ± 4)	(118 ± 15)	(85 ± 15)	3.64
acetate	(34 ± 2)	(274 ± 17)	(464 ± 88)	(1925 ± 111)	4.56
propionate	(42 ± 3)	(299 ± 25)	(1201 ± 138)	(2527±174)	4.92

In the case of the La(III)-acetate complexes, the stability constants for the first and the second species, $[La(Ac)^{2+}$ and $[La(Ac)_2]^+$, are in a good agreement with the ones obtained at higher ionic strength[1,20,21] but for the third species, $[La(Ac)_3]$, only the stability constant obtained by Bear *et al.*[1] is close to our β_3. The higher values found for β_2[22] and β_3[23] probably result from exclusion of the higher species.

For the La(III)-propionate system only two species were found in the other studies.[24–25] The values obtained by Choppin and Graffeo[24] are in very good agreement with the stability constants from the present paper.

The distribution diagrams of the mononuclear complexes for the La(III)-formate and La(III)-propionate obtained with the final β_n constants are shown in Figure 3.

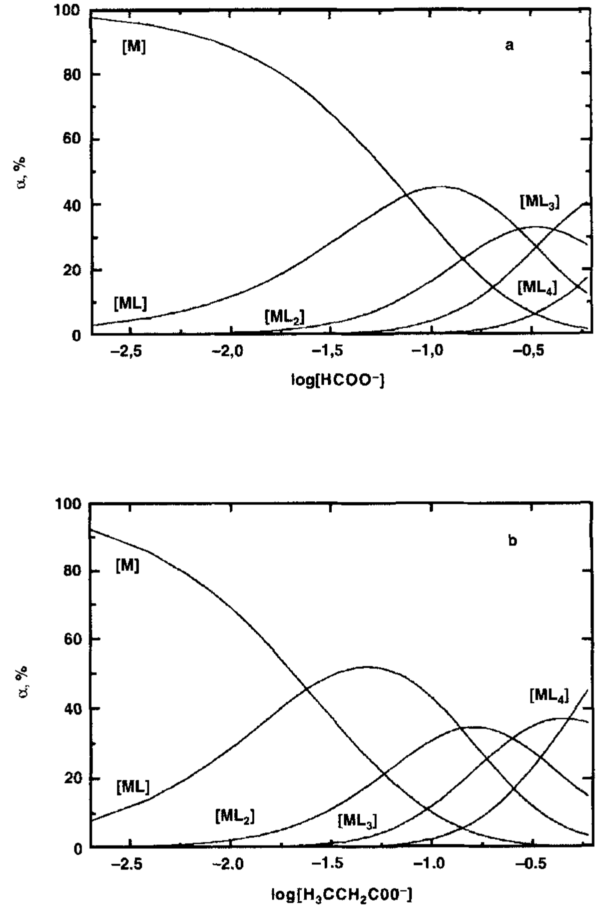

FIGURE 3 Distribution diagram for the species present in the (a) La(III)-formate and (b) La(III)-propionate systems. T = (25.0 ± 0.1) °C I = 1.00 M ($NaClO_4$).

TABLE III Stability constants for La(III)-carboxylates from the literature

Conditions	β_1/M^{-1}	β_2/M^{-2}	β_3/M^{-3}	β_4/M^{-4}	*Ref*
La(III)/formate					
I = 0,1 M ($NaClO_4$) 25°C	12,6	-	-	-	18
I = 1,0 M ($NaClO_4$) 25°C	13,2 ± 0,6	48 ± 4	118 ± 15	85 ± 15	*
La(III)/acetate					
I = 0,1 M (KCl) 25°C	150	$6{,}6 \times 10^3$	$1{,}6 \times 10^5$	$2{,}1 \times 10^6$	19
I = 0,1 M (KCl) 85°C	500	$3{,}8 \times 10^4$	$9{,}9 \times 10^5$	$7{,}9 \times 10^6$	19
I = 2,0 M ($NaClO_4$) 20°C	36 ± 1	300 ± 30	950 ± 200	~900	20
I = 2,0 M ($NaClO_4$) 25°C	34,5 ± 1,5	290 ± 40	1450 ± 150	-	21
I = 0,1 M ($NaClO_4$) 20°C	105	1810	-	-	22
I = 0,25 M ($NaNO_3$) 25°C	55	1778	6310	-	23
I = 2,0 M ($NaClO_4$) 25°C	28	196	392	-	1
I = 1,0 M ($NaClO_4$) 25°C	34 ± 2	274 ± 17	464 ± 88	1925 ± 111	4
La(III)/propionate					
I = 2,0 M ($NaClO_4$) 25°C	33,9	263	-	-	24
I = 0,1 M ($NaClO_4$) 20°C	78	1170	-	-	25
I = 1,0 M ($NaClO_4$) 25°C	42 ± 3	299 ± 25	1201 ± 138	2527 ± 174	*

Acknowledgments

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