Aqueous complexation and interactions of selected trivalent lanthanides with citric acid at varying ionic strengths

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Abstract

Formation constants of La^{3+} and Sm^{3+} with anions of citric acid have been determined experimentally by potentiometric titrations at 25°C and as a function of $NaClO_4$ molality. Four species were identified: $LnCit$, $LnHCit^+$, $LnCit^{3-}$ and $LnHCit^{2-}$. The data was used to build a SIT model in conjunction with the tabulated SIT parameters which gave accurate representation of the decrease in stability of the complexes with increasing ionic strength. The model was extrapolated to $I = 0\ m$; values of β^0 are reported.

Introduction

The Fuel Cycle Research and Development programme (FCRD) is focused on developing effective and economical means to reducing the volume, toxicity and lifetime of irradiated nuclear fuel (INF). As part of the FCRD, partitioning and transmutation (P&T) would recycle long-lived actinides (An) into commercial reactors to be transmutated into lighter, shorter-lived nuclides. Therefore, the separation of minor trivalent actinides (An^{3+}) from trivalent lanthanides (Ln^{3+}) at an industrial scale remains a significant technical challenge in advanced liquid-liquid reprocessing and closing the nuclear fuel cycle in the United States.

Carboxylic acids have played an important role in the field of An and Ln separations [1-3]. Studies have now shown that negligent control of the oxalate concentration in high-level waste reprocessing can jeopardise the solubility of Ln and An [4]. Recent bench-scale experiments have demonstrated that the more soluble 3-carboxy-3-hydroxypentanedioic acid (citric acid) is a promising aqueous complexant that can effectively aid in the separation of transition metals from f-elements mixtures [5]. Furthermore, citric acid was found to be a suitable buffer for the nitrogen donor ligand diethylenetriamine-N,N,N',N'',N''-pentaacetic acid (DTPA) which has a higher affinity for An over Ln as a result of An^{3+} binding to softer Lewis bases, more so than Ln^{3+}, which allows for practical separation of Ln and An by liquid-liquid extraction [1,3,5].

The complexation of Ln with anions of citric acid has been previously studied with conflicting results regarding the co-ordination of metal ions between carboxylic groups, the feasibility of protonated metal complexes, and the formation constants themselves. A detailed compilation of reported Ln-citrate complexes was given in Ref. [6]. Studies concerning Ln complexes are also generally limited to low ionic strengths [7]. Using potentiometric techniques and specific ion interaction modelling (SIT), we report protonation equilibria of citric acid and its complexes of La^{3+} and Sm^{3+} as a function of ionic strength at ambient room temperature.

Experimental

The salts $LaCl_3$ and $SmCl_3$ were prepared by dissolving the rare earth oxides (99.99% Sigma Aldrich) in concentrated hydrochloric acid and evaporating the solution to near dryness. The slurry was dissolved in de-ionised water (18.0 mΩ) and the metal concentration was determined by EDTA complexation with xylenol orange indicator. The free acid concentration of the metal stock solutions was measured with a calibrated pH electrode. $NaClO_4$ (99% VWR) was used as a background electrolyte without further purification. NaOH was prepared by dilution of 50% w/w stock with boiled DI water. The alkali concentration was determined by titration of potassium hydrogen phthalate which had been dried and stored in a desiccator. The protolytic impurity of the alkali was measured by titration of standardised HCl in conjunction with the Gran method and was determined to be less than 1% [8]. Citric acid (99.5% Sigma Aldrich) was used without further purification.

A semi-micro glass combination electrode (Metrohm) was filled with concentrated NaCl solution and calibrated with NIST standardised buffers (pH 2-7). The electrode readings were converted to p[H] (where [H] is the molar hydrogen ion concentration) by determining the standard potential and nernstian slope of the electrode at each ionic strength. Potentiometric titrations were carried out with a Metrohm automated titrator. The solutions were bubbled with N_2 gas and maintained at 25.0°C ± 0.1 using a circulating water bath and a NIST traceable thermocouple.

Results and discussion

Formation constants for citric acid, La^{3+} and Sm^{3+} citrate complexes at various ionic strengths are reported in Table 1. The constants were calculated using the least-squares fitting program Hyperquad [9]. The dissociation constants of water (pK_w) as a function of ionic strength were also supplied by the program. Typical titration curves for citric acid and Sm^{3+} at 0.1 m (molal) ionic strength are shown in Figure 1. Titrations of citric acid were carried out between $2 \leq p[H] \leq 11$ and

gave an excellent fit for three acidic protons. Ln^{3+} titrations were limited to $2 \leq p[H] \leq 5$ to diminish the possibility of metal hydrolysis. The general equilibrium for Ln^{3+} complexation was considered:

$$iLn^{3+} + jH^+ + kCit^{3-} \rightleftharpoons Ln_iH_jCit_k^{3i+j-3k} \qquad (1)$$

The four complexes reported here, LnCit, $LnHCit^+$, $LnHCit^{2-}$ and $LnCit_2^{3-}$, provided the best fit to the experimental data. Only the LnCit complex has been reported in the stability constant database for 0.1 M ionic strength; our values agree within ± 0.1 log units [7]. The calculated formation constants for Ln^{3+} with citric acid are considerably larger than those reported for other organic ligands containing one or two carboxylic groups [6]. Luminescence studies of Eu^{3+} citrate complexes concluded that the ligand prefers to bind multiple metal centres in a bidentate bonding manner [10]. NMR relaxation rates of Gd^{3+} with citrate salts suggest that the α-OH group also bonds with the metal ion once the citrate ligand is fully dissociated and forming a 1:1 complex, although no dissociation constants have been reported for the α-OH group. Additional relaxation studies have also conclude that the ligand co-ordinates to Gd^{3+} in a tridentate manner [11].

Figure 1: Titration curves for solutions of citric acid and Sm^{3+} citrate at 0.1 *m* (NaClO$_4$) ionic strength and 25°C; the data were fit using the modelling software Hyperquad
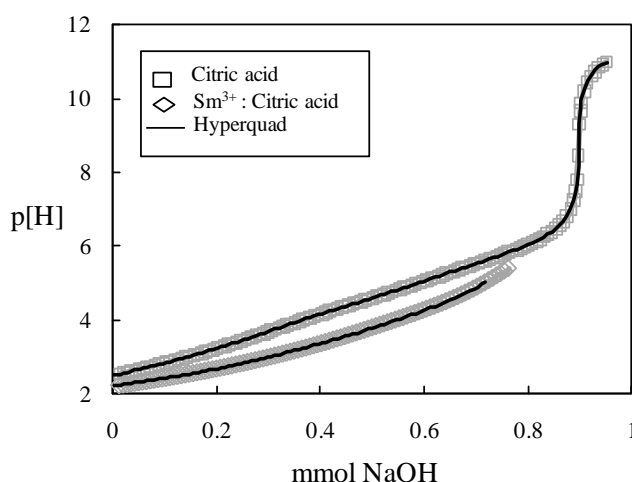

Table 1: The logarithm of formation constants (β) of citric acid, La^{3+}, and Sm^{3+} citrate complexes at various ionic strengths (NaClO$_4$) and 25°C

Equilibrium	i	j	k	0.1 *m*	0.5 *m*	1.0 *m*	2.5 *m*
$jH^+ + kCit^{3-} \rightleftharpoons H_jCit_k^{(i-3k)}$	−	1	1	5.697±0.002	5.242±0.008	5.206±0.008	5.206±0.008
	−	2	1	10.063±0.002	9.342±0.008	9.284±0.008	9.354±0.007
	−	3	1	12.984±0.003	12.069±0.009	11.954±0.009	12.071±0.009
$iLa^{3+} + jH^+ + kCit^{3-} \rightleftharpoons La_iH_jCit_k^{(3k+i-3k)}$	1	0	1	6.962±0.006	5.71±0.01	5.20±0.02	4.8±0.1
	1	1	1	10.292±0.005	9.257±0.007	8.790±0.009	8.95±0.01
	1	0	2	10.825±0.007	9.285±0.009	8.788±0.009	8.75±0.02
	1	1	2	15.10±0.01	13.59±0.01	12.92±0.02	13.19±0.03
$iSm^{3+} + jH^+ + kCit^{3-} \rightleftharpoons Sm_iH_jCit_k^{(3k+i-3k)}$	1	0	1	7.949±0.006	6.765±0.009	6.22±0.01	6.09±0.03
	1	1	1	10.834±0.009	9.970±0.006	9.591±0.009	9.68±0.01
	1	0	2	12.340±0.009	10.533±0.009	10.16±0.01	10.10±0.01
	1	1	2	16.47±0.01	14.80±0.01	14.28±0.01	14.36±0.02

Figure 2: The logarithm of formation constants of La^{3+} citrate complexes as a function of ionic strength (NaClO$_4$) at 25°C

The solid lines represent the SIT model
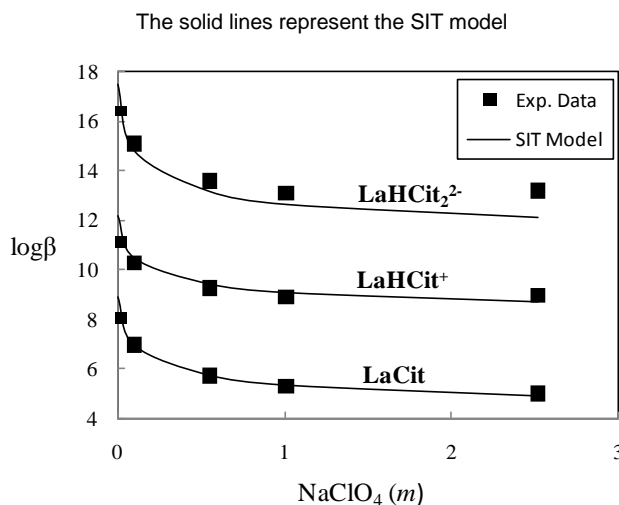
The formation constant for the complex LnHCit$^+$ shows a three-order magnitude increase in formation equilibrium from LnCit. One possible explanation for the lower stability of LnCit may be related to the added strain of the carbon-backbone once citrate is fully dissociated and binding to a metal through multiple carboxylic sites. Additionally, our hypothesis suggests that when one carboxylic group is protonated, the other is able to more freely bind to a metal ion (and possibly the α-OH) in a bidentate approach. The second formation constant, K_2 (where $\beta_2 = \beta_1 K_2$), of the complex LnCit$_2^{3-}$ also shows a decrease in stability from the first formation constant (LnCit).

The constants determined in this work were used to build an activity coefficient model. The activity coefficient of species i interacting with ion j at a certain ionic strength can be modelled using specific ion interaction (SIT) theory.

$$\log_{10}\gamma_i = -\frac{Z_i^2 0.5091\sqrt{I}}{1+1.5\sqrt{I}} + \sum_j \varepsilon(i,j)m_j \qquad (2)$$

A more detailed description can be found elsewhere [12-13]. All data points were weighed equally. Linear regression analysis and modelling was done using the program MATHCAD.

The formation constants of each species decreases with increasing ionic strength at which a minimum occurs at 1 m. Similar behaviour was reported for Ni^{2+} and Co^{2+} citrate complexes in NaCl media [14]. The SIT parameters for anions of citric acid in NaClO$_4$ media have been studied in the past and were used in the present model [15]. The parameters for sodium and hydrogen cations with perchlorate anions have also been documented [13]. Corrections for the activity of water were ignored [13]. The four complexes of La^{3+} and Sm^{3+} reported in this work were considered for ion interaction modelling. The experimental data for the species LnCit, LnHCit$^+$, and LnHCit^{2-} converged with the model and allowed us to calculate the parameters Δε, ε_{Ln}^{3+}, ε_{LnHCit}^{+}, and $\varepsilon_{LnHCit2}^{2-}$ for each species' formation interactions within the ionic climate; the parameter ε_{LnCit} was set to zero because of the species' neutral charge. Each model was extrapolated to $I = 0$ m; the values of β^0 for each species are reported in Table 1. The models fit exceptionally well for both complexes in the dilute and high ionic regions. The data for the complex LnCit$_2^{3-}$ did not converge and warrants further investigations. Estimating the formation constants of Ln-citrate complexes at higher electrolyte concentrations ($I > 5$ m) would likely require more rigorous models such as Pitzer modelling [16].

Table 1: SIT parameters for anions *i* and cations *j* that were used to build the reported model

Extrapolated formation constants ($I = 0$ m) are listed for each complex. Errors of $\varepsilon_{(i,j)}$ are ±0.01; p.w. – present work

i	*j*	$\varepsilon_{(i,j)}$	$\log\beta^0$	Ref.
H^+	ClO_4^-	0.14	–	13
Na^+	Cit^{3-}	-0.20	–	15
La^{3+}	ClO_4^-	0.33	–	p.w.
Sm^{3+}	ClO_4^-	0.40	–	p.w.
$LaCit$	–	0	8.86 ± 0.04	p.w.
$SmCit$	–	0	9.85 ± 0.05	p.w.
$LaHCit^+$	ClO_4^-	-0.13	12.21 ± 0.04	p.w.
$SmHCit^+$	ClO_4^-	-0.12	12.82 ± 0.07	p.w.
Na^+	$LaHCit_2^{2-}$	-0.44	17.5 ± 0.1	p.w.
Na^+	$SmHCit_2^{2-}$	-0.30	18.8 ± 0.1	p.w.

Acknowledgements

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