Complex Formation Equilibria Between Fumaric Acid and Lanthanides

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Abstract

Complexation in the lanthanide–fumaric acid (H_2L) system has been studied by potentiometric titration over the pH range of 3–4. The measurements were performed in 0.10 M $NaClO_4$ at 25 °C. The data indicate the formation of the species LnL^+ and $LnHL^{2+}$ but not of Ln_2L. The results are compared to comparable data for complexing by various carboxylic and dicarboxylic acids.

Introduction

The purpose of the present investigation was to interpret complexation in the Ln–fumaric acid system and to compare the results to the lanthanide complex formation by various mono- and dicarboxylic acids. In an earlier paper [1] the thermodynamic parameters for formation of the lanthanide–fumarate complexes (LnL^{2+}) in 0.10 M $NaClO_4$ at 25 °C were reported. The evaluation of the equilibria was, however, based on a very restricted number of experimental data, and the possible formation of protonated and polynuclear species was not considered. In these measurements wide concentration ranges of metal and ligand have been used in order to more fully study whether and under what conditions protonated and/or polynuclear complexes can form.

Experimental

Reagents and Apparatus

Stock solutions of lanthanide perchlorates were prepared and analyzed as described previously [2]. Stock solutions of fumaric acid (*trans*-butenedoic acid) were prepared from analytical grade reagent (Matheson–Colman and Bell Co.). These solutions were standardized by potentiometric titration with a standard solution of sodium hydroxide.

The EMF readings were obtained from a Corning pH meter 130 using a Thomas pH combination

electrode. The KCl filling solution of the electrode was replaced by a saturated solution of NaCl to eliminate problems due to $KClO_4$ precipitation in the electrode junction.

Method

The investigation was carried out as a series of potentiometric titrations at 25 °C in an ionic medium of constant $[Na^+] = 0.10$ M ($NaClO_4$). The glass electrode was calibrated using buffer solutions of pH = 7.00 ± 0.01 and pH = 4.00 ± 0.01. The measurements were performed at $3 < pH < 4$ and the $-\log[H^+]$ readings obtained from a plot of pH (measured) *versus* $-\log[H]$ (calculated) plot. The calibration plot was made by titration of a solution of sodium perchlorate of 0.10 M concentration with a standard perchloric acid solution.

The protonation constants of fumaric acid were determined in solutions without any metal present. In these measurements the total concentration of fumaric acid (C_L) was kept constant and the total hydrogen ion concentrations (C_H) was decreased by adding CO_2-free standard sodium hydroxide solution.
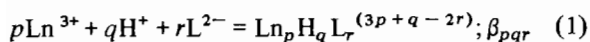
Two types of potentiometric titrations were performed to obtain the stability constants. In the first type buffered ligand solutions were titrated into lanthanide solutions. The total concentrations of metal, C_M, varied from 0.002 to 0.010 M while that of the ligand, C_L, was 0.03 M. The total hydrogen ion concentration in the titrant solutions was varied systematically between 0.015 and 0.03 M.

During the second type of titrations the ratio $C_L:C_M$ was kept constant while the C_H was decreased by addition of standard NaOH solution. The concentrations C_M and C_L were varied within the limits $0.002 < C_M < 0.0125$ M and $0.002 < C_L < 0.0125$ M to provide $C_L:C_M$ ratios of approximately 0.2, 0.3, 0.5, 0.7, 1, 2, 4 and 6. The readings were taken over the range $3 < pH < 4$.

Data Treatment

Calculations were performed on an IBM PC with a SIMPLEX algorythm program written by Dr. W. E. Cacheris. Hydrolysis of lanthanide ions was neglected since the pH was always less than 4. In the analysis it was assumed that pertinent equilibria were:

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$$pLn^{3+} + qH^+ + rL^{2-} = Ln_pH_qL_r^{(3p+q-2r)}; \beta_{pqr} \quad (1)$$

$$H^+ + L^{2-} = HL^-; \beta_{011} \quad (2)$$

$$2H^+ + L^{2-} = H_2L; \beta_{021} \quad (3)$$

Results and Discussion

For the protonation constants the values log $\beta_{011} = 4.08 \pm 0.02$ and log $\beta_{021} = 6.92 \pm 0.02$ were obtained. These values are in fair accord to those reported by Komar *et al.* [3].

The potentiometric data were analyzed in terms of $\bar{n}$ values, the average number of ligands bound per metal cation, defined by:

$$\bar{n} = \frac{C_L - [L^{2-}](1 + \beta_{011}[H^+] + \beta_{021}[H^+]^2)}{C_{Ln}} \quad (4)$$

C_{Ln} and C_L represent the total concentrations of Ln and fumarate, respectively while $[H^+]$ and $[L^{2-}]$ represent the concentrations of the free hydrogen and ligand ions. Figure 1 shows plots of $\bar{n}$ *vs.* $-\log[L^{2-}]$ for different C_M/C_L ratios and different pH values. From the experimental $\bar{n}$ values, the formation of 1:2 (Ln:L) complexes was unlikely under these experimental conditions. Moreover, the pH dependence indicates that protonated species (e.g. LnHL) were present.

The best fit in the computation of the potentiometric data was obtained with a model consisting of two complex species LnL^+ and $LnHL^{2+}$, as expected from the $\bar{n}$ analysis. The stability constants for the formation of LnL^+ and $LnHL^{2+}$ species are listed in Table I where β_{101} and β_{111} are defined by eqn. (1) and $\beta_{1(11)}$ represents the equilibrium
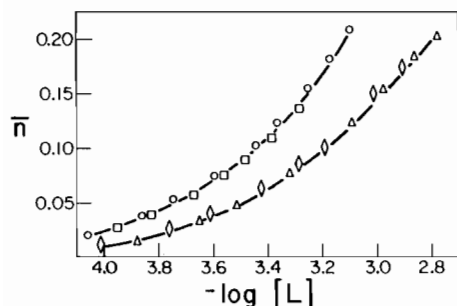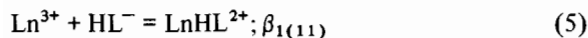
$$Ln^{3+} + HL^- = LnHL^{2+}; \beta_{1(11)} \quad (5)$$

Fig. 1. A part of experimental data plotted as curves $\bar{n}$ ($-\log[L]$) for the Gd(III)–fumaric acid system. Different symbols denote the following starting concentrations (mol/l). Cup solution: o, $C_M = 0.0215$ and $C_H = 2.7e - 05$; □, $C_M = 0.0430$ and $C_H = 5.4e - 05$; △, $C_M = 0.0215$ and $C_H = 2.7e - 05$; ◊, $C_M = 0.0430$ and $C_H = 54e - 05$. Titrant. o, $C_L = 0.0315$ and $C_H = 0.0303$; □, $C_L = 0.0315$ and $C_H = 0.0303$; △, $C_L = 0.0315$ and $C_H = 0.0203$; ◊, $C_L = 0.0315$ and $C_H = 0.0203$.

TABLE I. Stability Constants[a] for the Lanthanide–Fumaric Acid Complexes. $I = 0.10$ M (NaClO$_4$); $T = 25$ °C

Ln^{3+}	log β_{101} ± 0.02	log β_{111} ± 0.04	log $\beta_{1(11)}$
La	2.47	6.01	1.93
Pr	2.61	6.07	1.99
Nd	2.56	6.15	2.07
Sm	2.82	6.22	2.14
Eu	2.78	6.15	2.07
Gd	2.59	6.14	2.06
Tb	2.57	6.03	1.95
Dy	2.50	6.02	1.94
Ho	2.51	6.01	1.93
Er	2.46	5.95	1.87
Tm	2.44	5.99	1.91
Yb	2.37	5.91	1.83
Lu	2.47	5.98	1.90

[a]Errors derived from repetitive titrations.

The values of log β_{101} in Table I are 0.1–0.4 units smaller than the values reported in ref. 1. This is consistent with the results of calculations assuming different species as the formation of LnHL was not considered in ref. 1.

The values of log β_{101} are larger than to be expected from the correlation of log β_{101} of monocarboxylate complexes and the ligand acid pK_a using pK_{a2} (4.08) for fumarate (Fig. 2). However, it does fall on the monocarboxylate correlation line if pK_{a1} + pK_{a2} (6.92) is used. This is consistent with the proposal in ref. 1 that complexation induces transfer of electronic charge through the pi bonded system from the unbonded carboxylate group to the bonded one. Thus, the negative charge on the bonded group approximates the sum of the charges on the carboxylate groups of the fumarate anion. This polarization of charge may explain the absence of significant formation of dinuclear complexes, Ln$_2$L. The total charge would be distributed equally in Ln$_2$L leading to log $\beta \lesssim 1.5$ for addition of each Ln. This value must be further decreased to include the statistical effect of formation of dinuclear complexes. If we assume $\beta = (Ln_2L)/[LnL] \sim 10^3$, we can estimate that in our experiments at pH 4, [Ln$_2$L] < 1% of [LnL] whereas [LnHL] $\sim 25\%$ of [LnL].

The *cis* isomer, maleic acid, complexes via chelation with lanthanides [1, 4]. Formation of Ln$_2$L complexes by maleate would be expected to be minimized by the *cis* structure which favors chelation. No evidence for such Ln$_2$L formation was reported in either ref. 1 or 4. Moreover, the formation of LnHL is hindered; e.g. log $\beta_{1(11)}$ of SmH-Maleate is <0.3 compared to 2.14 for SmHFumarate.

The value of log $\beta_{1(11)}$ of Sm(III) and fumarate fall on the correlation line in Fig. 2 when a pK_a 4.1 is used. This reflects that Ln^{3+} polarizes more of
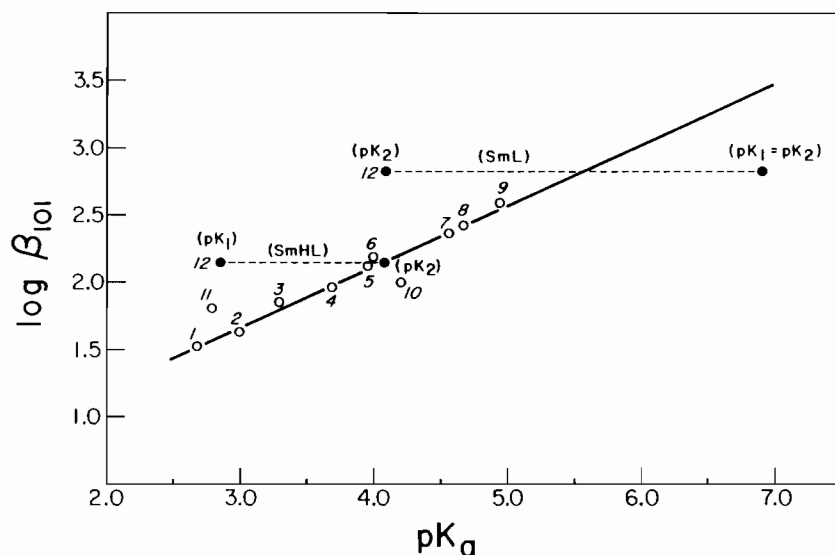
Fig. 2. Relationship between the stability constants, $\log \beta_{101}$ or $\log \beta_{1(11)}$, for the formation of SmL or SmHL and the acid constant, pK_a, of HL. Different numbers denote the following ligand acids: *1*, chloroacetic acid [7]; *2*, iodoacetic acid [7]; *3*, 3-nitrobenzoic acid [8]; *4*, 3-fluorobenzoic acid [8]; *5*, 4-fluorobenzoic acid [8]; *6*, benzoic acid [1]; *7*, acetic acid [7]; *8*, propanoic acid [7]; *9*, o-phthalic acid [6]; *10*, succinic acid [5]; *11*, malonic acid [5]; *12*, fumaric acid.

the total carboxylate charge than does H^+. The values of $\log \beta_{1(11)}$ in Table I are in the same range as analogous constants for lanthanide complexation by malonic [5], succinic [5], and o-phthalic [6] acids.

The enthalpy and entropy values of lanthanide fumarate and maleate complexation [1] are consistent with this discussion. These values were not corrected for the LnHL species formation but this would not effect them seriously.

Acknowledgements

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