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Note

THERMODYNAMIC PARAMETERS OF EUROPIUM ANTHRANILATE COMPLEX FORMATION IN AQUEOUS SOLUTION

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The thermodynamic parameters of the complexations in aqueous solution of trivalent lanthanide cations with various aminocarboxylate ligands have been reported [1]. In this study we have measured the thermodynamic parameters of Eu(III) anthranilate (1 : 1) complexation in aqueous solution to learn if the amino group of the ligand is involved in the chelate formation.

EXPERIMENTAL

Chemicals

The stock solution of europium perchlorate was prepared by dissolving europium oxide (Merck) in concentrated $HClO_4$. The anthranilic acid (B.D.H. AR grade) was recrystallized in absolute ethanol. The stock solution of anthranilate was prepared using the sodium salt of anthranilic acid. The standardization of the europium perchlorate stock solution was accomplished by EDTA titration with xylanol orange indicator. The anthranilate stock solution was standarized by the standard acid—base titration method. $NaClO_4$ was used to adjust the total ionic strength of the working solutions to 0.1 M. The sodium anthranilate buffer solutions were prepared by half neutralization of the anthranilate solutions with the standard $HClO_4$ solutions.

Apparatus

A Fisher 520 digital pH meter with a Fisher standard combination electrode was used for the acid constant determination. The titration vessel was jacked to allow a flow of water maintaining the temperature at 25 ± 1°C. The calorimetric titrations were performed using a Tronac Model 450 calorimeter. The accuracy of the calorimeter was tested by measuring the heat of protonation of THAM (trishydroxymethylaminomethane).

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TABLE 1

Entropy titration data for Eu(III) anthranilate (1 : 1) (μ = 0.1 M $NaClO_4$; T = 25°C)

Vol. of titer. (ml)	Q (mJ)		Q corrected	$C_L \times 10^2$ (M)
	Total		Corrected	
1.10	1488		1526	0.6501
1.20	1619		1663	0.7079
1.30	1758		1796	0.7653
1.40	1891		1931	0.8226
1.50	2025		2067	0.8797
1.60	2164		2202	0.9365
1.70	2297		2337	0.9931
1.80	2430		2473	1.0495
1.90	2570		2608	1.1057
2.00	2705		2743	1.1616

Initial volume = 50 ml; pH = 5.820; $C_M = 2.0678 \times 10^{-2}$ M.

Procedure

The acid constant (pK_a) and the enthalpy of protonation (ΔH_p) of the anthranilic acid were determined by pH and calorimetric titration using standard NaOH solution, respectively. The thermodynamic parameters of the europium complexation with anthranilate were obtained by the entropy titration method which has been described elsewhere [2,3]. The heat of formation for the anthranilate complex was determined by subtracting the heat of water formation and the heat of protonation of anthranilic acid from the total heat of titration of the europium solution with the anthranilate buffer solution in the calorimeter. The heat of dilution of the anthranilate buffer solution, which was measured by titration of the solution into a 0.1 M $NaClO_4$ solution, was found to be negligible. The entropy titration data for Eu(III) monoanthranilate are presented in Table 1.

RESULTS AND DISCUSSION

The pK_a value of anthranilic acid and the ΔG_p, ΔH_p, ΔS_p values for the protonation of the acid in a medium of 0.1 M $NaClO_4$ ionic strength at 25° C are listed in Table 2. The thermodynamic parameters of europium mono-

TABLE 2

Thermodynamic parameters of anthranilic acid (μ = 0.1 M $NaClO_4$; T = 25.0°C)

pK_a	$-\Delta G_p$ (kJ M^{-1})	ΔH_p (kJ M^{-1})	ΔS_p (J M^{-1} K^{-1})
4.84 ± 0.01	27.60 ± 0.03	2.20 ± 0.01	100.0 ± 0.1

TABLE 3

Thermodynamic parameters of the europium complexes

Ligands	$-\Delta G_1$ (kJ M^{-1})	ΔH_1 (kJ M^{-1})	ΔS_1 (J $M^{-1} K^{-1}$)	Ref.
Anthranilate	24.31 ± 1.04	4.60 ± 0.03	97.0 ± 3.6	This work
α-Picolionate	20.58	−6.36	47.7	1(a)
Malonate	25.9	13.8	133	4
Acetate(ML)	11.6	6.1	59	5
Acetate(ML_2)	18.8	12.1	103	5

anthranilate complexation are given in Table 3, along with those of the α-picolionate, malonate and acetate.

A number of thermodynamic studies on the lanthanide complexations with a variety of aminocarboxylate ligands have shown that the α-picolionate ligand [1a—c] forms the chelates involving the ring nitrogen and the carboxylate group, while the glycinate zwitterion [1d,e] forms the monodentate complexes. It is noted from Table 3 that the enthalpy of complexation is positive for the anthranilate and negative for the α-picolionate. However, the value of the entropy of complexation for the anthranilate is about twice as large as that for the α-picolionate. Furthermore, the magnitude of the complexation entropy of the anthranilate is comparable to those of the malonate and biacetate. Thus, we may conclude that the amino group of the anthranilate ligand involves chelate formation with a carboxylate group. Apparently, the europium monoanthranilate complex is stabilized by the excess entropy effect due to the extra dehydration forming the stable six-membered ring.

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