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THERMODYNAMICS OF LANTHANIDE ANTHRANILATE COMPLEX FORMATION IN AQUEOUS SOLUTION

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ABSTRACT

The thermodynamic parameters for the formation of the 1 : 1 lanthanide anthranilate complexes have been determined in the ionic medium of 0.1 M $NaClO_4$ at 25°C. Thermodynamic evidence that the amino group of the ligand is coordinated along with the carboxylate group is presented.

INTRODUCTION

Complexation of the various carboxylate acid derivatives with lanthanide cations has been extensively studied. It has been suggested [1–3] that the factors affecting the complexations are the relative affinity and basicity of the various donor atoms, and the geometry of the ligands. The thermodynamic properties of lanthanide complexes with glycine [4] and a variety of aminocarboxylates [5] showed that the glycine acts as a monodendate ligand, while the chelate involving the ring nitrogen and the carboxylate group forms α-picolinate.

We have reported [7] the thermodynamic parameters for Eu(III) complexation with anthranilate and discussed the role of the amino group of the ligand. As an extension of the study, we have investigated the anthranilate complexation with eight other elements in the lanthanide series. The thermodynamic parameters have been determined using the entropy titration method.

EXPERIMENTAL

Chemicals

Stock solutions of the lanthanide perchlorate were prepared by dissolving lanthanide oxide (American Potash and Chemical Corp.) in concentrated

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$HClO_4$. Standardization of the lanthanide perchlorate stock solution was accomplished by EDTA titration with xylenol orange indicator. The anthranilic acid (BDH AR grade) was recrystallized in absolute ethanol. The stock solution of anthranilate was prepared using the sodium salt of the anthranilic acid and standardized using the standard acid–base titration method. All the working solutions were adjusted to give a total ionic strength of 0.1 M using $NaClO_4$. 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 was used in conjunction with a Fisher standard combination electrode. The calorimetric titration was performed using the Tronac Model 450 calorimeter. The accuracy of the calorimeter was tested by measuring the heat of protonation of THAM (tris-hydroxymethylaminomethane). The entropy titration method [8] was employed to determine the thermodynamic parameters of the lanthanide complexation with anthranilate. The experimental procedure was described previously [7].

RESULTS AND DISCUSSION

Values of 4.84, 2.20 kJ mole^{-1} and 100 J K^{-1} mole^{-1} have been reported [7] for pK_a, ΔH_p and ΔS_p, respectively, for anthranilic acid. Table 1 gives typical entropy titration data for the Gd(III)–anthranilate system from which the thermodynamic parameters are calculated. Table 2 lists the thermodynamic parameters obtained for various lanthanide anthranilate complexes. The error limits indicate 1 S.D.

The thermodynamic parameters for the complexation of the lanthanide ions in aqueous solution can be explained with the net effect between the ionic combination and the disruption of the hydrate structure about the cation. It is noted from Table 2 that the entropies of the complexation for the heavier lanthanide ions are about 20 J K^{-1} mole^{-1} larger than those for the lighter lanthanide ions, while the enthalpies of the complexation for the heavier lanthanide ions are about 4.5 kJ mole^{-1} endothermic. This kind of difference in ΔH_1 and ΔS_1 of the complexation for the lighter and heavier lanthanide ions is usually explained in terms of hydration number change in the lanthanide series. Choppin et al. [6,9] have suggested that the hydration effects due to the lanthanide complexation in aqueous solution are included in ΔH_1 and ΔS_1, but not in ΔG_1, so called the compensation effects. The steady increase in ΔG_1 which would result from the compensation effect reflects the ionic nature of the complexes. The cation size of the lanthanide elements decreases with increase in atomic number in the lanthanide series, as the results show.

TABLE 1

Entropy titration data for the Gd(III)–anthranilate system (1 : 1) ($\mu = 0.1$ M $NaClO_4$, $T = 25°C$)

Vol. of titrant (ml)	Q(mJ)		$C_L \times 10^2$(M)
	Total	Corrected	
1.10	1755	1791	0.6388
1.20	1915	1951	0.6969
1.30	2075	2111	0.7550
1.40	2234	2270	0.813
1.50	2394	2430	0.8711
1.60	2553	2589	0.9292
1.70	2713	2749	0.9873
1.80	2873	2909	1.0454
1.90	3032	3068	1.1034
2.00	3192	3228	1.1615

Initial volume=50.00 ml; pH=5.412; $C_M = 2.0678 \times 10^{-2}$ M.

We have collected the thermodynamic parameters for Sm(III) complexation with some aminocarboxylates [10] and malonate [11]. All values were obtained in the ionic medium of 0.1 M. Figure 1 is a plot of the values of ΔS vs. the number of carboxylate groups of the ligands which indicates the linear relationship with the slope of 60 J K^{-1} $mole^{-1}$. Similar results [6] have been reported for the values of ΔS studied at 0.5 M ionic strength. Large deviations of DCTA (*trans*-1,2-diaminocyclohexane tetraacetate) from the line have been accounted for by an extra dehydration related to the rigidity

TABLE 2

Thermodynamic Parameters for the formation of lanthanide monoanthranilate ($\mu = 0.1$ M $NaClO_4$, $T = 25°C$)

Metal(III) ion	$\Delta G1$ (kJ $mole^{-1}$)	$\Delta H1$ (kJ $mole^{-1}$)	$\Delta S1$ (J K^{-1} mole)
La	22.97 ± 1.44	4.44 ± 0.01	91.96 ± 4.89
Sm	24.14 ± 1.27	4.14 ± 0.01	94.89 ± 4.30
Eu [a]	24.31 ± 1.04	4.60 ± 0.03	97.03 ± 3.57
Gd	24.81 ± 0.69	5.40 ± 0.02	101.38 ± 2.38
Dy	26.53 ± 1.04	8.83 ± 0.01	118.66 ± 3.52
Ho	23.51 ± 0.53	8.45 ± 0.02	107.28 ± 1.81
Er	25.73 ± 1.27	8.58 ± 0.02	115.14 ± 4.32
Yb	27.87 ± 1.38	8.54 ± 0.01	122.13 ± 4.72
Lu	26.65 ± 1.62	9.75 ± 0.01	122.13 ± 5.49

[a] From ref. 7.

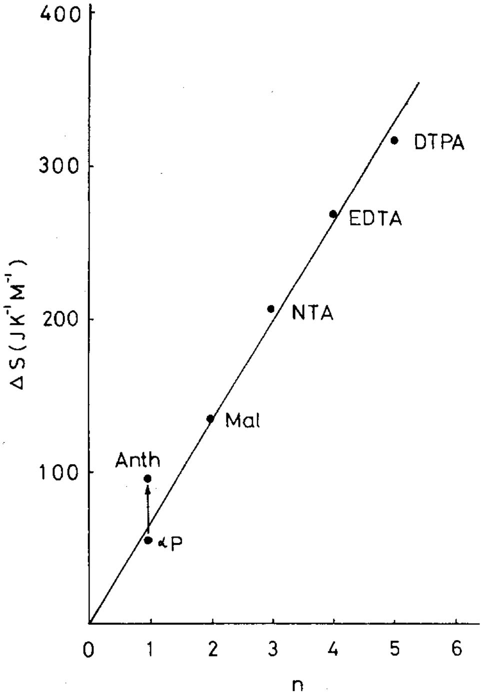

Fig. 1. A plot of the entropy of complexation vs. the number of carboxylate groups of the ligands (*n*). Ligands: diethylenetriaminepentaacetate (DTPA); ethylenediaminetetraacetate (EDTA); nitrilotriacetate (NTA); malonate (Mal); α-picolinate (α-p); anthranilate (Anth).

of the ligand [6]. Same arguments may be applied for the anthranilate complexes. The entropy effects of two carboxylate groups are in good agreement for malonate, the mono- and dithiodiacetate. The entropy effect can be estimated to be 66 J K^{-1} $mole^{-1}$ per –COOH (half ΔS of malonate) at 0.1 M ionic strength. The excess entropy for the anthranilate is approximately $95-66=29$ J K^{-1} $mole^{-1}$, which agrees well with the deviation of the anthranilate from the line of Fig. 1. The extra endothermic enthalpy of 8.64 kJ $mole^{-1}$ is obtained using $\Delta H_{excess} = T\Delta S_{excess}$. The corrected enthalpy for the anthranilate is comparable to the value of the enthalpy for the α-picolinate ($\Delta H_1 = -7.32$ kJ $mole^{-1}$ in the ionic medium of 0.5 M) [6]. Therefore, the excess enthalpy and entropy of the lanthanide anthranilate complexation arise from the chelate formation through the direct interaction between the amino group of the ligand and the central cation.

In conclusion, the amino group of the anthranilate ligand involves chelate formation with a carboxylate group and thus the lanthanide–monoanthranilate complex is stabilized by the excess entropy effect due to the extra dehydration forming the stable six-membered ring.

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