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THERMODYNAMICS OF THIOCYANATE COMPLEXES OF TRIVALENT ACTINIDES AND LANTHANIDES

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ABSTRACT

The thermodynamic parameters ΔF, ΔH and ΔS of the complexes of Cm(III), Cf(III) and Tm(III) with the SCN^- ion have been determined at 30°C in ammonium ion medium of unit ionic strength by the temperature variation method. It has been concluded that both the thiocyanate complexes of trivalent actinides and lanthanides are predominantly inner-sphere type. The higher stability of the second complexes of trivalent actinides is reflected either in the enthalpy or the entropy change depending on the degree of hydration of the trivalent actinide ions. The implications of the greater free energy change for $PuSCN^{2+}$ as compared with other trivalent actinide or lanthanide first thiocyanate complexes are discussed.

INTRODUCTION

Complexing behaviour of trivalent actinides and lanthanides with various inorganic and organic ligands has been studied by several workers primarily to get more information which can be of use for inter- and intra-group separation of these metal ions [1—4]. From various studies, conclusions have been drawn regarding the inner- and outer-sphere character of the complexes of trivalent actinides and lanthanides with chloride, nitrate and thiocyanate ions. The rate of non-radiative transfer of energy between rare earth ions in solution in the presence of thiocyanate ions (<3.0 M) indicate the presence of outer-sphere complexes [5]. The nuclear magnetic resonance and relaxation study [6] of the binding of thiocyanate (0.05—3 M) to trivalent lanthanide ions gives N—Gd $\simeq$ 2.5 Å for $Gd(SCN)^{2+}$, $Gd(SCN)_2^+$ and $Gd(SCN)_3$ showing that SCN^- is in the first coordination sphere of the metal ion. A recent study [7] on fluorescence spectra and lifetime measurements of aqueous solutions of europium(III) nitrate and perchlorate show that, even at very low nitrate concentrations, inner-sphere complexes are formed whereas in the ClO_4^- medium up to a chlorate concentration of 1.0 M and at a $[ClO_4^-]/[Eu^{3+}]$ ratio of 28, outer-sphere interactions have been shown to occur. In our earlier work [2] on the thermodynamic parameters of the Eu(III)—SCN^- system, it was suggested that both $Eu(SCN)^{2+}$ and $Eu(SCN)_2^+$ are of the outer-sphere type. To get a better understanding of the controversial inner- or outer-sphere complexes of trivalent actinides and lanthanides with the SCN^- ion, the present work has been undertaken to determine the thermodynamic parameters of Cm(III), Cf(III) and Tm(III) thiocyanate complexes at 30°C in an ammonium ion medium of unit ionic strength by a solvent extraction method using ammonium dinonylnaphthalene sulphonate as the extractant.

EXPERIMENTAL

Materials

^{244}Cm and tracer Cf (mainly ^{252}Cf) were obtained from Oak Ridge National Laboratory (U.S.A.) and were purified as described in refs. 2 and 4, respectively. ^{147}Pm was obtained from the Radiochemical Research Centre, Amersham (U.K.) and ^{170}Tm from the Isotope Group, B.A.R.C. Ammonium dinonylnaphthalene sulphonate (NH_4D) was from the same stock used in the previous work [2,4]. All the other reagents used were of Analar quality.

Radioassay of the tracers

^{244}Cm was assayed by alpha liquid scintillation counting using the procedure given by Ihle et al. [8]. Cf was assayed by counting the prompt fission gammas (>3 MeV) in a well-type NaI(Tl) scintillation counter [9] with an estimated efficiency of ^{252}Cf fission counting of ~70%. The radioassay of ^{147}Pm in organic and aqueous phases was done by liquid scintillation counting of soft betas (~0.2 MeV) whereas ^{170}Tm was assayed by γ-scintillation counting using a well-type NaI(Tl) crystal.

Determination of the stability constants

One ml of NH_4D in *n*-hexane (~0.01 M) was equilibrated with 1 ml of aqueous solution containing various concentrations of NH_4SCN ($\mu = 1$ with NH_4ClO_4, pH ~ 2.5) and spiked with the desired tracers. The equilibrations were effected by slow rotation of the glass-stoppered tubes containing the two phases for 1 h in a thermostated bath maintained at 15, 20, 30, 37 and 45°C, the variation of temperature being ±0.1°C. After settling for 30 min in the same bath, aliquots of both phases were removed for radioassay.

Uptake of trivalent metal ions by NH_4D can be represented by

$$M^{3+}_{aq} + (NH_4D)_{m_{org}} \rightleftharpoons M[NH_{4_{m-3}}D_m]_{org} + 3\ NH^+_{4_{aq}} \tag{1}$$

In the presence of SCN^- in the aqueous phase, competing reactions exist.

$$M^{3+} + SCN^- \rightleftharpoons MSCN^{2+} \tag{2a}$$

$$M^{3+} + 2\ SCN^- \rightleftharpoons M(SCN)_2^+ \tag{2b}$$

The distribution coefficient, K_d, of the trivalent metal ion M(III) between NH_4D in the *n*-hexane and aqueous phases is defined as

$$K_d = \frac{\sum[M]_{org}}{\sum[M]_{aq}} \tag{3}$$

and can be expressed as a polynomial in $[\mathrm{SCN}^-]$.

$$\frac{1}{K_d} = \frac{1}{K_{d_0}} + \frac{\beta_1}{K_{d_0}} [\mathrm{SCN}^-] + \frac{\beta_2}{K_{d_0}} [\mathrm{SCN}^-]^2 + \ldots \tag{4}$$

where K_{d_0} is the value of K_d in the absence of SCN^- and β_1, β_2, etc. are the overall stability constants of the species MSCN^{2+} and $\mathrm{M(SCN)}_2^+$ etc. K_2, the stability constant for the formation of the species $\mathrm{M(SCN)}_2^+$ from MSCN^{2+} and SCN^-, is given by β_2/β_1. The criteria for determining the number of complexes present in a particular trivalent actinide or lanthanide thiocyanate system depended both on the "fit" of a particular model (β_1, $\beta_1\beta_2$, $\beta_1\beta_2\beta_3$, $\beta_1\beta_3$) as shown by the average Δ value (Δ being the difference irrespective of sign between the experimental and calculated $1/K_d$ values) and on the precision of the experimental data represented by the average standard deviation ($\pm\sigma$) in the experimental $1/K_d$ values [2,4,10]. Table 1 shows typical examples of these calculations for the M(III)—thiocyanate systems in which the average Δ values for various models have been listed along with average σ values. Δ values for the β_1 model were consistently very high for all the systems and have not been listed in the table. Data of $1/K_d$ vs. $[\mathrm{SCN}^-]$ for Cf(III), Pm(III) and Tm(III) are presented in Fig. 1 where the curves are constructed from the computer-calculated values. Equation (4) was used to calculate the stability constants of the thiocyanate complexes with their probable errors by a least square treatment of the $1/K_d$ vs. $[\mathrm{SCN}^-]$ data using a computer program LSQFIT.

Calculations of the thermodynamic parameters

Values of ΔF for the complexes have been calculated from the values of stability constants at 30°C. Plots of log β_1 and log β_2 vs. $1/T$ for the Cf(III), Cm(III)—thiocyanate systems are presented in Fig. 2. Values of ΔH with

TABLE 1

Average deviation for the curve fitting calculations (temp 30°C)

Metal ion (III)	Δ			Average experimental error in $1/K_d$ values ($\pm\sigma$)
	$\beta_1\beta_2$ model	$\beta_1\beta_2\beta_3$ model	$\beta_1\beta_3$ model	
Pu	0.0156	0.0075	0.0151	0.0179
Am	0.0201	0.0189	0.0295	0.0169
Cm	0.0130	β_3 negative	0.0247	0.0195
Cf	0.0141	0.0152	0.0194	0.0129
La	0.0060	0.0034		0.0080
Pm	0.0096	0.0102	0.0108	0.0059
Eu	0.0003	β_3 negative	0.0111	0.0074
Tb	0.0086	0.0034		0.0063
Tm	0.0231	β_3 negative	0.0134	0.0179
Lu	0.0209	0.0210		0.0161

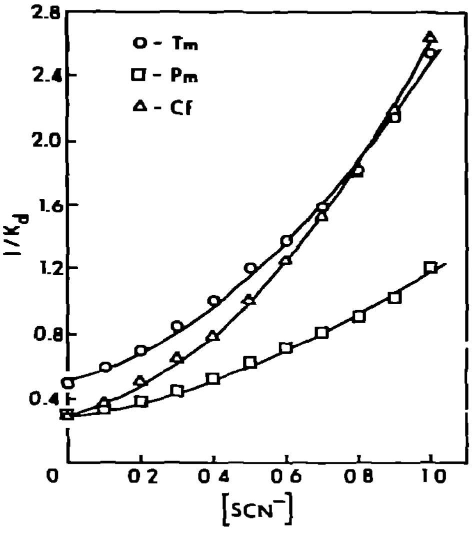

Fig. 1. Distribution data for Pm(III), Tm(III) and Cf(III) between 0.01 M NH_4D in *n*-hexane and aqueous thiocyanate solutions at 30 ± 0.1°C. $\mu = 1.0$ (NH_4ClO_4—NH_4SCN). The curve represents the fit of eqn. (4) to the experimental data ($\beta_1\beta_2$ model).

their standard deviations were calculated by a least squares fit of log(stability constant) vs. $1/T$ data using the van't Hoff equation. Values of ΔS were calculated from the ΔF and ΔH values using the Gibbs—Helmholtz equation.

RESULTS AND DISCUSSION

Table 2 gives the values of β_1, β_2 and K_2 of Cf(III), Pm(III) and Tm(III) thiocyanate complexes along with other trivalent actinides and lanthanides

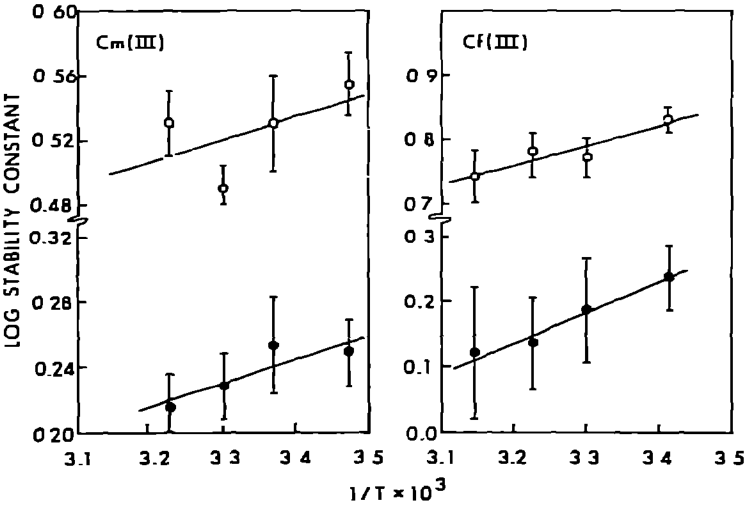

Fig. 2. Temperature variation of stability constants of the complexes of Cm(III) and Cf(III) with thiocyanate $\mu = 1.0$ (NH_4ClO_4—NH_4SCN) ●, log β_1; ○, log β_2.

TABLE 2

Stability constants of thiocyanate complexes of trivalent actinides and lanthanides at 30°C

μ = 1.0; NH_4ClO_4—NH_4SCN medium.

M (III)	β_1	β_2	K_2	Ref.
Pu	2.18 ± 0.17	4.10 ± 0.21	1.88 ± 0.18	2
Am	1.47 ± 0.21	4.19 ± 0.30	2.85 ± 0.47	2
Cm	1.53 ± 0.19	4.08 ± 0.23	2.66 ± 0.36	2
Cf	1.57 ± 0.24	6.12 ± 0.36	3.89 ± 0.60	Present work
La	1.32 ± 0.10	1.66 ± 0.10	1.26 ± 0.12	2
Pm	1.53 ± 0.20	1.75 ± 0.20	1.14 ± 0.19	Present work
Eu	1.36 ± 0.14	1.93 ± 0.18	1.42 ± 0.16	2
Tb	1.69 ± 0.12	2.19 ± 0.12	1.30 ± 0.12	2
Tm	1.18 ± 0.24	2.61 ± 0.26	2.22 ± 0.47	Present work
Lu	1.61 ± 0.20	2.25 ± 0.22	1.40 ± 0.21	2

determined under identical experimental conditions. Figure 3 shows the plot of β_1 and β_2 vs. Z, the atomic number of trivalent lanthanides, where a slight increasing trend with Z for both β_1 and β_2 has been observed. This behaviour is different from that observed for chloride complexing by Peppard et al. [11] and for nitrate complexes of trivalent lanthanides by Choppin and Strazik [12] where a small but perceptible decrease in stability constants was observed with increasing Z and the chloride and nitrate complexes of trivalent lanthanides have been shown to be outer-sphere type. The observed

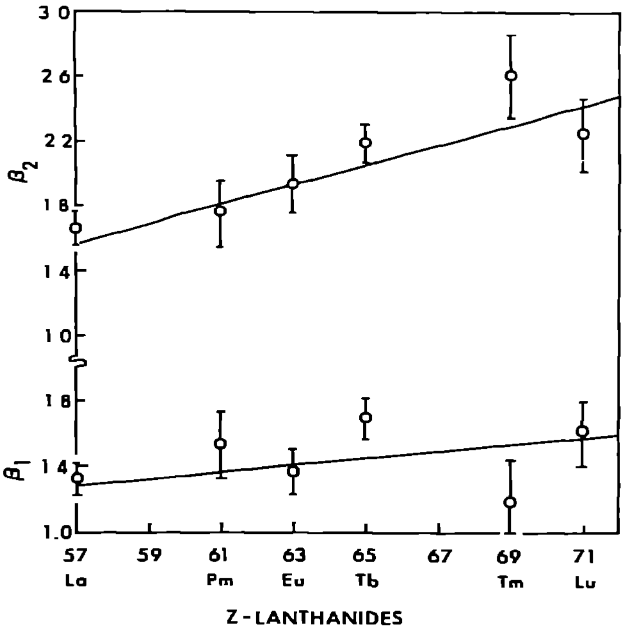

Fig. 3. Stability constants of the lanthanide thiocyanate complexes.

difference in the behaviour of lanthanide thiocyanate complexes probably results, at least partly, from inner-sphere complexing, conceivably because of the stronger complexing power of the SCN^- ion compared with that of Cl^- and NO_3^- ions. However, the rate constant of the non-radiative transfer of energy, k_t, and the duration of the luminescence period, τ_0, in case of rare-earth thiocyanate systems, suggest that outer-sphere complexes of europium(III) thiocyanate are present in moderate concentrations of SCN^- (up to 3.0 M) whereas between 3 and 10 M SCN^- concentration, inner-sphere complexes are formed. In addition, our thermodynamic data [2] for europium(III) thiocyanate complexes also gives small negative values of enthalpy and entropy for both the first and second complexes and it was interpreted that the two complexes are predominantly outer-sphere type. The apparently contradictory results can be understood in a better way if account is taken of the loss of rotational entropy of the thiocyanate ion on ligation with the metal ions. Phipps and Plane [13], while explaining the small negative entropy change observed in the association of SCN^- ion with $Cr(H_2O)_6^{3+}$, considered a negative contribution from the loss of rotational entropy (~16 e.u.) when the linear SCN^- ion combines with the metal ion. Considering the Eu(III)—SCN^- system in the light of the above discussion, the ligational entropy change associated with both the complexes may, in fact, be positive and therefore the small negative enthalpy and the positive entropy values associated with both Eu(III)—SCN^- complexes will indicate them to be more inner-sphere type. Similar values of small negative enthalpy and negative entropy have been obtained for the two Tm(III)—SCN^- complexes studied in the present work. Our observations of an increasing trend in β_1 and β_2 values of trivalent lanthanide thiocyanate complexes with Z as well as the thermodynamic parameters for the Eu(III) and Tm(III)—SCN^- systems discussed above support the view that both the species $MSCN^{2+}$ and $M(SCN)_2^+$ have more of the inner-sphere character if the rotational entropy loss is taken into consideration. The NMR and relaxation study [6] of the binding of SCN^- (0.05—3 M) to trivalent lanthanide ions gives N—Gd $\simeq$ 2.5 Å for $Gd(SCN)^{2+}$, $Gd(SCN)_2^+$ and $Gd(SCN)_3$ showing that SCN^- is in the first coordination sphere of the metal. This is further supported by a recent study on fluorescence spectra and lifetime measurement [7] of aqueous solutions of europium nitrate and perchlorate where, even at very low nitrate concentrations, inner-sphere complexes are formed whereas in the ClO_4^- medium up to a perchlorate concentration of 1.0 M and at a $[ClO_4^-]/[Eu(III)]$ ratio of 28, outer-sphere interactions have been inferred. Thiocyanate ions having stronger complexing ability should definitely show more inner-sphere character when complexed with trivalent lanthanides. The contrary conclusions drawn by Antipenko et al. [5] regarding the nature of Eu(III)—SCN^- complexes in moderate concentrations of thiocyanate (<3 M) probably require re-examination. The first and second thiocyanate complexes of trivalent actinides should also have a predominantly inner-sphere character. As seen from the K_2 values (Table 2), the trivalent actinide complexes are more stable than the trivalent lanthanide ones of comparable ionic radii, indicating the participation of 5 f orbitals in the metal—SCN^- bond formation of the trivalent actinides [2,4].

Table 3 gives the thermodynamic parameters of thiocyanate complexes of trivalent actinides and lanthanides. It can be seen from this table that the free energy values, ΔF_1, for Pu(III) are higher than the corresponding values of other trivalent actinides and lanthanides, probably due to a partial covalent character even in the first complex of Pu(III) with thiocyanate [2]. The comparatively higher free energy change is reflected in the positive entropy value ΔS_1. Though the ΔS_1 value for Am(III) is also positive, the stability of $AmSCN^{2+}$ is reduced by the more endothermic enthalpy value (ΔH_1). For other trivalent actinides and lanthanides, small negative values of both ΔH_1 and ΔS_1 are obtained which, as discussed earlier, indicate the complex $MSCN^{2+}$ to be of the inner-sphere type. The small negative enthalpy can arise due to the relative "softness" of the thiocyanate ligand as it ligates through nitrogen as against oxygen in ligands like carboxylates. As stated earlier, the ΔF_2 values for the trivalent actinides are higher than those of the trivalent lanthanides of comparable ionic radii. This higher value for the trivalent actinides is reflected either in the enthalphy or the entropy values depending on the hydration of these metal complex species. It is well known that hydration of the trivalent metal ions, both actinides and lanthanides, increase with their atomic number due to decreasing ionic radii (lanthanide, actinide contraction). Thus for Am(III), the higher ΔF_2 is reflected in the more exothermic enthalpy value (compared with trivalent lanthanide ΔH_2 values) whereas with the more heavily hydrated Cf(III) energy required to liberate larger number of water molecules gives somewhat endothermic ΔH_2 but a more positive ΔS_2 value. For the trivalent lanthanides, the thermodynamic parameters for the second complex follow the same pattern as for the first in the virtual absence of covalent character, even in the second complexes.

TABLE 3

Thermodynamic parameters of trivalent actinide and lanthanide thiocyanate complexes at 30°C and unit ionic strength

Reaction	ΔF (kcal mole^{-1})	ΔH (kcal mole^{-1})	ΔS (cal deg^{-1} mole^{-1})
Actinides			
$Pu^{3+} + SCN^- \rightleftharpoons PuSCN^{2+}$ *	—0.45 ± 0 05	+0.06 ± 0.18	+1.7 ± 0.6
$Am^{3+} + SCN^- \rightleftharpoons AmSCN^{2+}$ *	—0.17 ± 0.10	+0.60 ± 0.56	+2.5 ± 1.9
$AmSCN^{2+} + SCN^- \rightleftharpoons Am(SCN)_2^+$ *	—0.70 ± 0.10	—1.76 ± 0.88	—3.5 ± 2.9
$Cm^{3+} + SCN^- \rightleftharpoons CmSCN^{2+}$	—0 32 ± 0.03	—0.67 ± 0.28	—1.2 ± 0.9
$CmSCN^{2+} + SCN^- \rightleftharpoons Cm(SCN)_2^+$	—0.36 ± 0.03	+0.02 ± 0.75	+1.3 ± 2.5
$Cf^{3+} + SCN^- \rightleftharpoons CfSCN^{2+}$	—0.25 ± 0.11	—2.06 ± 0.29	—6.0 ± 1.0
$CfSCN^{2+} + SCN^- \rightleftharpoons Cf(SCN)_2^+$	—0.81 ± 0.11	+0.71 ± 0.59	+5.0 ± 2.0
Lanthanides			
$Eu^{3+} + SCN^- \rightleftharpoons EuSCN^{2+}$ *	—0.18 ± 0.06	—0.83 ± 0 20	—2 1 ± 0.7
$EuSCN^{2+} + SCN^- \rightleftharpoons Eu(SCN)_2^+$ *	—0.21 ± 0.06	—0.82 ± 0.31	—2.0 ± 1.0
$Tm^{3+} + SCN^- \rightleftharpoons TmSCN^{2+}$	—0.10 ± 0.12	—0.37 ± 0.24	—0.9.± 0.9
$TmSCN^{2+} + SCN^- \rightleftharpoons Tm(SCN)_2^+$	—0.48 ± 0.12	—1.17 ± 0.36	—2.3 ± 1.2

* Data from ref. 2.

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