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Note

Calorimetric studies on mixed ligand chelates: Ln^{3+} – EDTA – kojic acid systems

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Enthalpy changes for metal–ligand interactions are often obtained from variations of the formation constant with temperature. Standard heat changes in such reactions are of the order of 20–40 kJ $mole^{-1}$ and would change the stability constant values by about 0.1–0.2 log units for a temperature change of 10 K. Since most measurements of formation constants involve uncertainties of this order, the enthalpy changes so calculated would be largely unreliable. These can, therefore, be obtained more accurately by direct calorimetric measurements. Though data on a number of binary systems have already appeared in the literature[1, 2], mixed ligand chelation has not received sufficient attention.

Recently, Kugler and Carey[3] have obtained enthalpy data on the mixed ligand chelates of thorium–EDTA/DCTA with a number of secondary ligands such as tiron, catechol etc. by direct calorimetric measurements. The formation constants for a number of such mixed ligand systems involving lanthanide ions have been obtained in this laboratory by a potentiometric titration procedure[4]. The attachment of a secondary ligand such as kojic acid to the primary Ln^{3+}–EDTA complexes was found to take place in the pH range 5.5–8.5. This paper now describes the determination of enthalpy and entropy changes in some Ln^{3+}–EDTA–kojic acid systems by direct calorimetric measurement.

EXPERIMENTAL

Reagents

Rare earth oxides (purity > 99.9%) obtained from Rare Earth Products, U.K., were used as such. Their solutions in nitric acid were further standardised by titration with EDTA using xylenol orange as indicator.

Kojic acid, B.D.H. reagent (bio-chemical grade) was recrystallised from hot alcohol and dried in vacuum.

Apparatus

The calorimetric set up, fabricated by us for this purpose, has been described previously[5]. The sensing element was a 2 KΩ Fenwal thermistor and electrical calibration was done using a 15 Ω manganin heater (wound over a glass frame and coated with araldite) fed by a constant current source (250 mA). The bridge imbalance was fed to a Rikādenki recorder operated on 1 mV range. The sensitivity obtained was ~16 mV $^{\circ}C^{-1}$.

Procedure

100 ml of the Ln^{3+}–EDTA (1 : 1) solution, adjusted to pH 6.5–7.0, was taken in the Dewar flask. The ionic strength was maintained at 0.1 M by addition of potassium nitrate. An equivalent amount of kojic acid (sodium salt, pH ~9.5) was placed in a thin-walled glass bulb immersed in the solution of the primary complex. After equilibration, the bulb was gently broken and the temperature change during mixed ligand chelation was recorded. The final pH after mixing was around 8.5 indicating that the reaction was complete. The observed heat changes were corrected for the blank, carried out in the absence of the lanthanide ions.

Alternatively, to a 1 : 1 : 1 mixture of holmium, EDTA and kojic acid in the Dewar flask, the requisite amount of alkali was added by breaking the bulb to obtain the heat change for the reaction of the type

$LnY + HA + OH \rightleftharpoons Ln \cdot Y \cdot A + H_2O$

This was corrected for the heat of ionisation of kojic acid and heat of dilution of alkali, both determined in separate experiments. The corrected enthalpy change thus obtained agreed with that obtained earlier.

The stability constants for the mixed ligand chelates were obtained in 20% alcohol–water medium. They were corrected for a 100% aqueous system by assuming the relationship $\log K = a\, pK$ (ref. 6) and from the known values of the pK of kojic acid in aqueous and 20% alcohol media. ΔS° values were obtained from the resulting

TABLE 1

THERMODYNAMIC PARAMETERS FOR Ln^{3+}–EDTA–KA SYSTEM

$\mu = 0.1$ M, temperature = 300 K.

Metal ion	*ΔH° (kJ mole^{-1})*	*ΔG° (kJ mole^{-1})*	*ΔS° (J mole^{-1} K^{-1})*
La	− 8.8		
Pr	−10.5	−23.1	10.3
Sm	−16.0	−23.5	6.0
Gd	−16.4	−23.1	5.7
Ho	−16.4	−24.0	6.0
Tm	−18.5	−24.0	4.3
Lu	−17.6	−24.0	5.0

ΔG° values for purely aqueous medium and ΔH° values obtained in this study. These are summarised in Table 1.

RESULTS AND DISCUSSION

Mixed ligand chelation, i.e. attachment of kojic acid to the primary Ln^{3+}–EDTA complex, has been found to take place exothermally for all the lanthanide ions studied, whereas the concomitant entropy changes have small, positive values.

The association of two oppositely charged ions is normally expected to occur with liberation of heat and decrease in entropy. Graddon and Ong[7], in their study of base adducts of Cu β-diketonates in non-aqueous media, have obtained such values. In aqueous medium, the ions are heavily hydrated and complexation (inner sphere type) is accompanied by destruction of their respective hydration sheaths. The heat and entropy changes have, therefore, to be ascribed to a "reaction" part and a "dehydration" part[8]. The dehydration of the metal ion involves breaking of large number of $M–H_2O$ bonds. This process more than compensates for the heat evolved during the "reaction" part and the overall result is a small endothermic effect. The release of water molecules from the tightly bound hydration sheath, however, brings about a large positive entropy change and complexes become stabilised by an entropy rather than enthalpy effect.

In the case of mixed ligand chelation, complexation with the primary ligand like EDTA probably brings about a significant dehydration of the lanthanide ion, still leaving a residual charge thereon. The attachment of the secondary ligand thus mainly represent the "reaction" part and is accompanied by a favourable heat change, but only a small entropy increase. The mixed ligand chelates of Th–EDTA/DCTA with salicylic acid and 8-hydroxyquinolinesulphonic acid show a similar trend[3].

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