Potentiometric Determination of Stability Constants of Trivalent Metal Ion Complexes with Di-p-tolyl-thiovioluric Acid

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Potentiometric Determination, Stability Constants, Di-p-tolyl-thiovioluric Acid

The consecutive formation constants of 1:1, 2:1, 3:1 chelate species formed by the interaction of di-p-tolyl-thiovioluric acid (D-p-TOTVA) with the tripositive lanthanons and yttrium cations were determined potentiometrically at 0.1 µ (NaClO₄) at 30 ± 1 °C, in 75% aqueous dioxan.

The 1:1 formation constants (log K₁) for the complexes increase with the increase in the atomic number of the lanthanon (3), with a break at gadolinium.

The results indicate that the ligand bonds bidentately to heavier lanthanons (smaller ionic radii). However, definite dentate character of bonding to lighter (larger ionic radii) lanthanons could not be established.

Introduction

Formation constants of lanthanons with substituted pyrimidinols, have not been reported in the literature. The present study has been planned, with a view, to establish, relationship between the dentate character of the ligand and successive stability constant ratios.

Experimental

Instruments: A Beckman pH-meter, expandomatic, SS-2 model, in conjunction with a glass and calomel electrode assembly (0-14 pH range) was used for pH-measurements.

The pH-meter was standardised with potassium hydrogen phthalate, and phosphate buffers before performing the titrations.

Reagents: Di-p-tolylthiovioluric acid was prepared by the general method outlined by Durst and co-workers1. Solution of the ligand was prepared in freshly distilled dioxan. All the metal ion solutions were prepared from A. R. lanthanon nitrate samples, procured from Indian Rare Earths Ltd. They were standardised by EDTA, using xylene-orange as indicator; chemically pure sodium perchlorate (Riedel) was used to keep the ionic strength constant.

A 0.05 M solution of tetramethyl ammonium hydroxide (TMAH) in 75% dioxan (aqueous) was used as the titrant. It was standardised with a solution of potassium hydrogen phthalate. The dioxan used was purified by refluxing with sodium wire for 24 h and was freshly distilled over sodium before use. All other chemicals used were of reagent grade. All measurements were made at 30 ± 1 °C. Pre-saturated nitrogen (with 75% aq. dioxan) was passed through the solutions during titration.

pH titration procedure: The method of Bjerrum and Calvin, as modified by Irving and Rossoitt2, has been used to obtain values of n and pL.

The following solutions (total volume = 19.67 ml, due to contraction on mixing dioxan and water) were titrated potentiometrically against standard 0.05 M TMAH solution to find n and pL values of the complexes.

(i) 0.8 ml of HClO₄ (0.02 M) + 1.0 ml of NaClO₄ (2 M) + 2.7 ml of H₂O + 0.5 ml of NaNO₃ (0.02 M) + 15.0 ml of dioxan.

(ii) 0.8 ml of HClO₄ (0.02 M) + 1.0 ml of NaClO₄ (2 M) + 2.7 ml of H₂O + 0.5 ml of NaNO₃ (0.02 M) + 10.0 ml of ligand (0.01 M) + 5.0 ml of dioxan.

(iii) 0.8 ml of HClO₄ (0.02 M) + 1.0 ml of NaClO₄ (2 M) + 2.7 ml of H₂O + 0.5 ml of metal nitrate (0.02 M) + 10.0 ml of ligand (0.01 M) + 5.0 ml of dioxan.

Calculations: The ligand exhibits keto-enol tautomerism and the proton of -NOH group can be replaced by a metal ion in the oximino-ketonic form. However, in order to neutralise an alkali like TMAH, the original weakly acidic oximino-ketonic form has to tautomerise into the more acidic nitroso-enolic form3,4.

The proton thus released by the nitroso-enolic form, leaves a negative centre for complex formation.
From the titration curves of solutions (i) and (ii) the values of pK(OH) were calculated by plotting, log (a/1 — a) vs pH. (Where a is the degree of dissociation), when straight line, of intercept equal to pK and slope equal to unity was obtained. The dissociation constant has been found to be equal to 5.38 and the formation constants of various complexes are reported in Table I.

From the titration curves of solutions (i), (ii) and (iii), \( \bar{n} \) values of the metal complexes were determined at various pH values. The formation curves obtained by plotting the \( \bar{n} \) and \( pL \) values have been analysed for log \( K_1 \) and log \( K_2 \) of the different complexes by the 'correction term method.' The stability constants were computed on an IBM 360 FORTRAN IV computer using a weighted least squares program patterned after that of SULLIVAN et al. The \( \beta_n \) values were initially approximated from the data (\( \bar{n} \), \( pL \)), with weight factor being unity; second approximations to the \( \beta_n \) values, and the process was repeated until successive cycles gave a change of less than one part per thousand in each \( \beta_n \).

The weighted least squares treatment determines that set of \( \beta_n^s S \) which make the function

\[
U = \sum_{n=0}^{N} \left( y_n - x - nz \beta_n x^n \right)
\]

nearest to zero, by minimizing S

\[
S = \sum_{i=1}^{1} U^2(x_i y_i z_i) \text{ w.r.t.}
\]

variation in \( \beta_n \).

We are reporting the \( S_{\text{min}} \) values for respective metal complexes. \( S_{\text{min}} \) has the same statistical distribution as \( \chi^2 \) with k degrees of freedom, and with weight defined in accordance with SULLIVAN et al., we can put \( S_{\text{min}} = \chi^2 \).

Table I. Stability constants of the metal complexes with di-p-tolylthiovioluric acid.

<table>
<thead>
<tr>
<th>Cations</th>
<th>( K_1^* )</th>
<th>( K_2^* )</th>
<th>( K_1^{**} )</th>
<th>( K_2^{**} )</th>
<th>( S_{\text{min}} )</th>
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** Correction term method.  
** Weighted least squares method.

Discussion

POWELL and co-workers in the studies with tripotent lanthanons and \( \alpha,\beta \)-substituted, monodihydroxy carboxylic acids, have established that, the gadolinium break and a rather abrupt decline in \( K_1/K_2 \) ratios, as the lanthanon radii decreases beyond that of Sm\( ^{3+} \), is an indication of a change from tridentate to bidentate ligancy, combining with a nine coordinate (tricapped trigonal prism) hydrated lanthanon. They have cited BJERRUMS theory, that ratios of successive step formation constants depend principally upon individual formation and decomposition statistics relating to \( AB_{n-1} \) and \( AB_n \) chelate species; BJERRUMS theory can be in general expressed as: 

\[
P^* = \frac{K_{n-1}}{K_{n-1}S_{\text{RT}}} = \text{SRT} \text{, at ionic strength other than zero: } P = \frac{K_{n-1}}{K_{n}} = \left( \frac{K_{n-1}}{K_{n}} \right) (u) = \text{SRT f (u) where } P^* \text{ is the ratio of true thermodynamic step formation constant (at infinite dilution), S is the purely statistical consideration, T is the electrostatic factor, R is a general rest factor (including ligand asymmetry and steric effect).}

Pure statistical consideration predicts, \( K_1/K_2 \) values as 3.27 and 4.92 for a ligand functioning bidentately and tridentately in its association with nine coordinated lanthanon in aqueous media.

Our results indicate a clear break at gadolinium shown in a plot of \( K_1 \) vs ionic radii of lanthanons (Fig. 1). A perusal of the \( K_1 \) and \( K_2 \) values for lighter lanthanons (Ln–Nd) shows that \( K_1 \) values are quite small as compared to \( K_2 \), so that \( K_1/K_2 \) ratios are also quite small.
A reversal of the above trend is observed at Sm(III) where $K_1$ values are larger than $K_2$, and the $K_1/K_2$ ratio is almost constant at (3.0) for the heavier lanthanons (Sm–Yb); this is in keeping with trends observed by Powell and co-workers. The value of $K_1/K_2$ ratio for heavier lanthanons is near to the purely statistical value 3.27, suggesting that the dentate character of the ligand is bidentate.

The abnormally low value of $K_1/K_2$, for lighter lanthanons can be rationalized, as the two steps of complex formation are overlapping. This is suggested by the shape and the slope of the curve\textsuperscript{13}. Since the two steps of complex formation are not discernible in the case of lighter lanthanons, hence nothing conclusive can be said about the dentate character of the ligand, from $K_1/K_2$ values which are abnormally low as compared to the purely statistical value of 4.92. However, it is curious to note that as the radii decreases, $K_1$ values tend to become closer to $K_2$ and then they become larger than $K_2$ at the critical radii of Sm(III).

This may be a pointer to a change in ligancy, for ligands where the two steps are simultaneous.

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\end{thebibliography}