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

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(Z. Naturforsch. **31 b**, 1096–1098 [1976]; received April 24, 1976)

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 ($NaClO_4$) at 30 ± 1 °C, in 75% aqueous dioxan.

The 1:1 formation constants (log K_1) 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 DUTT and co-workers[1]. 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 xylenol-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 ROSSOTTI[2], has been used to obtain values of $\bar{n}$ 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 $\bar{n}$ and pL values of the complexes.

(i) 0.8 ml of $HClO_4$ (0.02 M) + 1.0 ml of $NaClO_4$ (2 M) + 2.7 ml of H_2O + 0.5 ml of $NaNO_3$ (0.02 M) + 15.0 ml of dioxan.

(ii) 0.8 ml of $HClO_4$ (0.02 M) + 1.0 ml of $NaClO_4$ (2 M) + 2.7 ml of H_2O + 0.5 ml of $NaNO_3$ (0.02 M) + 10.0 ml of ligand (0.01 M) + 5.0 ml of dioxan.

(iii) 0.8 ml of $HClO_4$ (0.02 M) + 1.0 ml of $NaClO_4$ (2 M) + 2.7 ml of H_2O + 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 form[3,4].

The proton thus released by the nitroso-enolic form, leaves a negative centre for complex formation.

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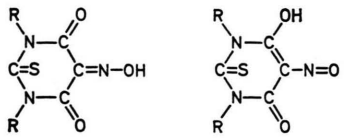

(R = tolyl, oximino-ketonic)

(R = tolyl, nitroso-enolic)

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.'[5] 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.*[6]. The β_n values were initially approximated from the data ($\bar{n}$, pL), with weight factor being unity; second approximations to the β_n values were then calculated, by attaching to them appropriate weight factors, computed from the 1st set of β_n values, and the process was repeated until successive cycles gave a change of less than one part per thousand in each β_n.

The weighted least squares treatment determines that set of β_n'S which make the function U

$$\left(U = \sum_{n=0}^{N} (y-x-nz)\,\beta_n x^n\right)$$

nearest to zero, by minimizing S

$$\left(S = \sum_{i=1}^{I} U^2(x_i y_i z_i) \text{ w.r.t.}\right)$$

variation in β_n.

We are reporting the S_{min} values for respective metal complexes. S_{min} has the same statistical distribution as χ^2 with k degrees of freedom, and with weight defined in accordance with SULLIVAN *et al.*[7], we can put $S_{min} = \chi^2$.

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

Cations	K_1*	K_2*	K_1**	K_2**	K_3**	S_{min}
La	2136	8318	1099	15071	316.0	0.14543
Pr	4467	5012	4313	5583	239.6	0.14200
Nd	5432	5892	5700	6002	—	0.32426
Sm	6607	5754	7858.9	4026.8	140.0	0.26893
Gd	3981	1660	6006	2163	481.0	0.104640
Dy	8710	3162	10303	3344.7	266.0	1.75580
Yb	18970	6252	19027	6982.2	205.0	0.084596
Yt	10502	3526	14000	4342	—	0.062520

* Correction term method.
** Weighted least squares method.

Discussion

POWELL and co-workers[8-11] in the studies with tripositive lanthanons and α,β-substituted, mono and dihydroxy 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[12], 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: $P^* = {}^*K_{n-1}/{}^*Kn = SRT$, at ionic strength other than zero: $P = K_{n-1}/Kn = ({}^*K_{n-1}/{}^*Kn)\,(u) = SRT\,f\,(u)$ where P* 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 assymmetry 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.

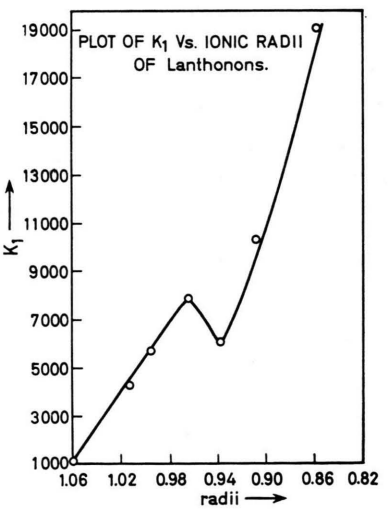

Fig. 1.

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[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.

Authors are thankful to Dr. Y. R. MIDHA, Research Fellow, Department of Physics, University of Delhi, Delhi, for formulating the computer programme for the calculation of formation constants. One of the authors (D. P. GOEL) is thankful to U. G. C. for financial assistance.

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