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Potentiometric Studies on the Complexes of Some Trivalent Rare Earths with 5-Chloropyridine-2,3-diol

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The complexes of some rare earths [Ce(III), Pr(III), Nd(III), Sm(III), Tb(III), Dy(III), and Ho(III)] with 5-chloropyridine-2,3-diol (*CPD*) were studied potentiometrically in 50% dioxane-water at a ionic strength of 0.1 *M* ($NaClO_4$) at 35 ± 0.1 °C. The proton-ligand stability constant of *CPD* and the stability constants of its complexes with the metals have been determined using the *Calvin-Bjerrum* technique as modified by *Irving* and *Rossotti*. The order of the stability constants is found to be Ce < Pr < Nd < Sm < Tb < Dy < Ho.

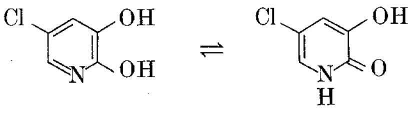
(Keywords: Stability constants)

Potentiometrische Untersuchungen der Komplexe einiger trivalenter Seltenerdmetalle mit 5-Chlorpyridin-2,3-diol

Es wurden die Komplexe von Ce(III), Pr(III), Nd(III), Sm(III), Tb(III), Dy(III) und Ho(III) mit 5-Chlorpyridin-2,3-diol (*CPD*) in 50% Dioxan-Wasser bei einer Ionenstärke von 0,1 *M* ($NaClO_4$) und einer Temperatur von 35 ± 0,1 °C potentiometrisch untersucht. Die Proton-Ligand-Stabilitätskonstante von *CPD* und die Stabilitätskonstanten der Metallkomplexe wurden nach der Methode von *Calvin-Bjerrum* mit der *Irving-Rossotti*-Modifikation bestimmt. Die Reihenfolge der Stabilitätskonstanten ergab sich folgendermaßen: Ce < Pr < Nd < Sm < Tb < Dy < Ho.

Introduction

5-Chloropyridine-2,3-diol (*CPD*) (**Ia**, **Ib**) has been used for the spectrophotometric determination of iron, palladium and osmium[1,2]. Studies of its complexes with some bivalent metal ions have been also been carried out potentiometrically[1]. A survey of the literature, however, reveals that no work has hitherto been done on its complexes with rare earths. The present investigation deals with the potentiometric studies of the complexes of Ce(III), Pr(III), Nd(III), Sm(III), Tb(III), Dy(III) and Ho(III) with *CPD* in 50% dioxane-water at a ionic strength of 0.1 *M* ($NaClO_4$) and at a temperature of 35 ± 0.1 °C.



Ia **Ib**

Materials and Methods

A pure sample of *CPD* was obtained from K & K laboratories and its solution was prepared in dioxane without further purification. The solutions of the metal perchlorates were prepared using metal carbonates or oxide of Anal R grade. All these perchlorate salt solutions were standardised complexometrically[3]. All other chemicals used were reagents of Anal R grade.

A Beckman *pH* meter (model SS-2) with a glass electrode assembly was used for *pH* measurements. The *pH* meter readings obtained for the dioxane-aqueous medium were corrected according to the method of *Van Uitert* and *Hass*[4].

A thermostat MLW (type NBE) GDR was used for constant temperature.

Tetramethyl ammonium hydroxyde (*TMAH*) was used as titrant. Its solution was standardized with potassium hydrogen phthalate.

The following solutions (total volume 20 ml) were titrated against *TMAH* (*M*/20).

(i) 1.0 ml $HClO_4$ (0.01 *M*) + 1.0 ml $NaClO_4$ (2.0 *M*) + 10 ml dioxane + 8 ml water.

(ii) 1.0 ml $HClO_4$ (0.01 *M*) + 1.0 ml $NaClO_4$ (2.0 *M*) + 10 ml *CPD* (0.01 *M*) in dioxane + 8 ml water.

(iii) 1.0 ml $HClO_4$ (0.01 *M*) + 1.0 ml $NaClO_4$ (2.0 *M*) + 1 ml metal perchlorate (0.01 *M*) + 10 ml *CPD* (0.01 *M*) in dioxane + 7 ml water.

The proton-ligand stability constant ($\log K_1^H$) and metal-ligand stability constant were calculated by the method of *Calvin-Bjerrum*[5,6] as modified by *Irving* and *Rossotti*[7].

Results and Discussions

The values of $\bar{n}_A$ at different corrected *pH* values were calculated from the titration curves of solutions (i) and (ii). The proton-ligand stability constant was calculated by plotting a graph $\bar{n}_A$ vs. *pH*. The proton-ligand stability constant value was also calculated by the plot of $\log (1 - \bar{n}_A)/\bar{n}_A$. The values found by these methods agree quite well. The mean value of the proton-ligand stability constant is 8.06. The second proton-ligand stability constant could not be determined potentiometrically since *CPD* is a considerably weaker base and exists almost entirely in the form **Ib**.

Our findings are in agreement with those already reported[1]. From the titration curves of solution (ii) and (iii) values for $\bar{n}$ and pL were calculated. The $\bar{n}$ values were plotted against the corresponding pL values. From these formation curves the values of the metal-ligand stability constants were calculated. The stability constants thus obtained were refined using other computational techniques$_8$ (see Table 1). It was not possible to evaluate values of $\log K_2$ as hydrolysis of metal complexes takes place at $\bar{n} < 1$.

Table 1. *Metal-ligand stability constant* ($\log K_1$) *of the complexes of CPD*

	Ce	Pr	Nd	Sm	Td	Dy	Ho
$\log K_1$	7.15	7.32	7.45	7.82	8.75	9.12	9.25

The order of the stability constants was found to be: Ce(III) < Pr(III) < Na(III) < Sm(III) < Td(III) < Dy(III) < Ho(III) which is in agreement with the findings of *Stagg* and *Powell*[9].

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