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Spectrophotometric Studies and Analytical Application of Ce(III) Chelates with 1-(2-Pyridylazo)-2-naphthol (*PAN*)

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A sensitive procedure for spectrophotometric determination of cerium(III) has been developed. At *pH* 10.2 cerium reacts with 1-(2-pyridylazo)-2-naphthol in 40% ethanol to form a red complex which has an absorption maximum at 545 nm. The molar absorptivity at 545 is $3.95 \cdot 10^3 \text{mol}^{-1}$. Maximum stability of the complex was attained in pure ethanol. The stoichiometries and structures of the chelates were studied applying conductometric titration, visible spectrophotometry and IR spectrophotometry. The IR spectra revealed that coordination takes place through the N=N, C—OH and pyridyl group.

(Keywords: Cerium determination; Spectrophotometry)

Spektrophotometrische Untersuchungen und analytische Anwendung von Ce*(III)-Chelaten mit 1-(2-Pyridylazo)-2-naphthol (PAN)*

Es wurde eine empfindliche Methode zur spektrophotometrischen Bestimmung von Cer(III) entwickelt. Bei einem *pH* von 10,2 reagiert Cer mit 1-(2-Pyridylazo)-2-naphthol in 40% Ethanol unter Bildung eines roten Komplexes mit einem Absorptionsmaximum bei 545 nm ($\varepsilon = 3\,950$). Der Komplex besitzt in reinem Ethanol ein Maximum an Stabilität. Die Stöchiometrien und Strukturen der gebildeten 1:1- und 1:2-Chelate wurden mittels konduktometrischer Titration, Elektronen- und IR-Spektrometrie untersucht. Die IR-Daten zeigen, daß die Koordination über N=N, C—OH und Pyridyl erfolgt.

Introduction

Recently several organic reagents have been suggested for the spectrophotometric estimation of Ce(III), among which are alizarin viridine, alizarin heliotrope and alizarin maroon[1], salicylidenebenzoichydrazide[2], 1-anthraquinonyl oxamic acid and its nitro derivative[3], vanilidenebenzoichydrazide and cinnamylidenebenzoichydrazide[4], some *p*-benzoquinone derivatives[5], salocylhydrazones of salicylaldehyde, vaniline and anisylaldehyde[6], and B-phenoxyvinylphosphonic acid[7].

Pyridylazo dyes—particularly 1-(2-pyridylazo)-2-naphthol (*PAN*)—have assumed importance in analytical chemistry as metallochromic indicators and colorimetric reagent for the microdetermination of many metal ions. *Puschel* et al.[8] investigated the nature of the complexes of *PAN* with iron, cobalt and nickel.

The formation of a chelates between *PAN* and manganese, cadmium, mercury, gallium and yttrium was reported[9]. Also, *PAN* was used to determine In(III)[10], V(IV)[11] and U(VI)[12] with satisfactory results. *Shibata*[13] found that *PAN* reacts very sensitively with rare earth metal to form deep red complexes in alkaline solution. All types of complexes formed between *PAN* and the rare earth metals can be extracted with ether except those of lanthanum, cerium and scandium. This paper describes the spectrophotometric studies on composition, stability and analytical application of Ce(III) chelates with *PAN* in pure ethanol as well as in a buffer solution containing 40% ethanol.

Experimental

Reagents and Apparatus

The solution of *PAN* (Merck) was prepared in ethanol. A stock solution of cerium(III) was prepared from cerium nitrate in water. The metal content of the solution was determined by conventional methods[14]. *Britton* and *Robinson* buffer solutions of *pH* range 2–12 were prepared as given by *Britton*[15].

All absorbance measurements were recorded at room temperature (20 ± °C) on a Unicam S.P. 8–100. The IR spectra of the chelates were made on a Unicam S.P. 3–200 as KBr disc. The *pH* of solutions were measured with an Accumet model 230 A*pH* meter using a glass electrode.

Preparation of the Metal Complexes

The solid complexes with stoichiometric ratios 1 : 1 and 1 : 2 were prepared by mixing a solution of *PAN* with a Ce(III) solution in pure ethanol at *pH* 10.2 containing 40% ethanol. The reaction mixture was then refluxed for 30 min on a water bath. On cooling the complexes separated as fine crystals. The solid was then filtered off and washed several times with ethanol, dried and preserved in a desicator over dried silica gel.

Recommended Procedure

Transfer 1.0 ml of cerium(III) nitrate solution containing about 80 μg cerium(III) into a 10.0 ml volumetric flask. Add 5.0 ml of buffer solution of *pH* 10.2, 2 ml $10^{-3} M$ ethanolic solution of *PAN* and 2.0 ml ethanol. Mix it thoroughly and read the absorbance of the formed complex at 545 nm against a reagent blank. The amount of the cerium present is calculated from a previously prepared calibration curve. On the other hand, 50 μg cerium(III) can be determined in pure ethanolic solution by reading the obsorbance of the complex at 525 nm against reagent blank.

Results and Discussion

The effect of the following parameters on the formation reaction of the Ce(III)-*PAN* complex were evaluated at a constant ionic strength of 0.1, regulated by a 1 *M* sodium perchlorate solution.

Effect of pH and PAN Concentration

The absorption spectra of *PAN* and its complex with Ce(III) at *pH* 10.2 and in pure ethanol, measured against a reagent blank, are presented in Fig. 1.

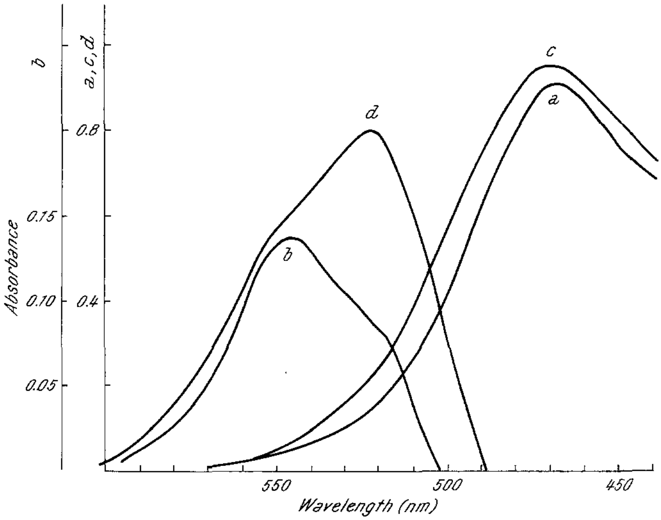


Fig. 1. Absorption spectra (I) at *pH* 10.2: *a* *PAN* conc. $5 \cdot 10^{-5}$ *M*. *b* Ce-*PAN* complex from *PAN* conc. $2 \cdot 10^{-4}$ *M* and Ce(III) conc. $1 \cdot 10^{-4}$ *M*. (II) In pure ethanol: *c* *PAN* conc. $5 \cdot 10^{-5}$ *M*. *d* Ce-*PAN* complex from *PAN* conc. $2 \cdot 10^{-4}$ *M* and Ce(III) conc. $1 \cdot 10^{-4}$ *M*

It is observed that at *pH* values below 8.2 the complex formed shows a maximum absorption at 600 nm. The rise of *pH* values above 8.2 causes a gradual hypsochromic shift and at *pH* 10.2 the maximum absorption is at 545 nm with a shoulder near 525 nm. At higher *pH* values (> 10.2) no shift of this maximum is observed but the absorbance decreases gradually. The formation of two complexes at least [1 : 1 and 1 : 2 Ce(III)-*PAN* complexes] is obvious, one predominating at *pH* range 6.0–6.5 and the second at *pH* range 8.2–10.2, as shown in Fig. 2.

At *pH* 10.2, the molecular extinction coefficient is about $3.95 \cdot 10^{3}\,\mathrm{l\,mol^{-1}\,cm^{-1}}$ (at 545 nm). This *pH* value was selected as the optimum *pH* for the Ce(III) determination.

Absorption spectra of a solution containing *PAN* and an excess of Ce(III) ion are given at different *pH* values. All the measurements at *pH* > 7 were done immediately after complex formation to avoid any cerium hydroxide precipition upon standing. Here we can see the formation of one complex with λmax at 545 nm and a shoulder near 520 nm (predominating at *pH* range 8.2–10.2). As shown in Fig. 2, it is most probable that in the presence of an excess of Ce(III) ions the 1 : 1 Ce(III)-*PAN* complex is formed.

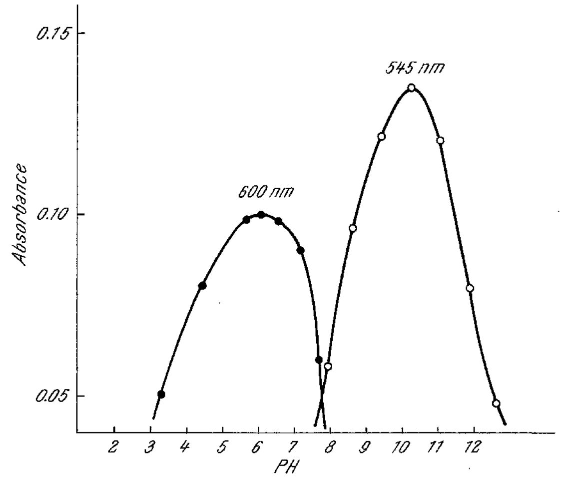


Fig. 2. *pH*-Absorbance plots measured at 545 and 600 nm; *PAN* conc. $2.0 \cdot 10^{-4} M$ and Ce(III) conc. $1.0 \cdot 10^{-4} M$

In pure ethanol, the Ce(III)-*PAN* complex exhibits a band with λmax at 525 nm and a shoulder near 550 nm. The band shows an increase in intensity with increasing concentrations of either *PAN* or Ce(III) ion. The molecular extinction of this complex has an actual high value $\sim 6.1 \cdot 10^3 \mathrm{l\,mol^{-1}\,cm^{-1}}$ (at 525 nm).

Stoichiometry of the Complexes

The composition of the complexes formed were examined by the molar ratio[16] and continuous variation[17] at *pH* 10.2 and in pure ethanol. The results obtained indicate the probable formation of two types of complexes with stoichiometric ratios 1 : 1and 1 : 2 Ce(III) : *PAN*.

The values of the apparent stability constants were evaluated for different media in order to find out the optimum conditions for maximum stability. The mean values of log *B* as well as the value of $-\Delta G°$

Table 1. *The apparent stability constants of Ce(III)-PAN complexes*

Type of complex	Log β			$-\Delta G^\circ$ kcal/mol		
	Pure ethanol	Buffer + ethanol	Buffer + ethanol + $NaClO_4$	Pure ethanol	Buffer + ethanol	Buffer + ethanol + $NaClO_4$
1 Ce^{3+} : 1 *PAN*	4.30	3.66	3.48	5.80	4.94	4.69
1 Ce^{3+} : 2 *PAN*	8.91	6.95	6.78	12.02	9.38	9.15

are given in Table 1. The values of ΔG° have been determined using the relation $\Delta G^\circ = -RT \ln B$. Maximum stability is attained in pure ethanol and the change in ionic strength by the addition of different concentrations of $NaClO_4$ (1 *M*) to the ethanol-buffer mixture shows no effect on the stability constant.

Beer's Law and Sensitivity of the Reagent

Series of standard solutions of Ce(III) were prepared and complexed with *PAN* at *pH* 10.2 and pure ethanol. The results obtained show a linear relationship between absorbance and concentration (in accordance with *Beer*'s Law) in the range 2.3 to 16.2 μg/ml Ce(III) at *pH* 10.2 and in the range 1.2 to 9.2 μg/ml Ce(III) in pure ethanol. From the constancy of the *A/C* values (in which *A* is the absorbance at concentration *C*), it is shown that Ce(III) can be determined with an error equal to 1.4 and 3.03 at *pH* 10.2 and pure ethanol respectively.

Effect of Interfering Ions

The reagent forms coloured complexes with a number of cations such as Co^{2+}, Ni^{2+}, Hg^{2+}, In^{3+}, Cd^{2+}, Fe^{3+}, U^{6+}, and V^{4+}. Other common ions such as Br^-, NO_3^-, Cl^-, F^-, NO_2^-, CH_3COO^-, CO_3^{2-}, SO_4^{2-}, ClO_4^-, Na^+, K^+ and NH_4^+ have been proved not to disturb the determination of cerium.

Table 2. *Sensitivities of methods for spectrophotometric determination of cerium*

Method	Medium	λ max	ε 10^3 l mol^{-1} cm^{-1}	Ref.
B-Phenoxyvinylphosphonic acid	*pH* = 12	322	3.60	[7]
Alizarin complexone	*pH* = 4.5–5.0	530	3.00	[18]
1-(2-Pyridylazo)-2-naphthol	*pH* = 10.2	545	3.95	—
1-(2-Pyridylazo)-2-naphthol	ethanol	525	6.10	—

Comparison with Other Reagents

A comparison of the molar absorptivities of Ce(III) complexes of B-phenoxyvinylphosphonic acid[7] and alizarin complexon[18] with those of *PAN* is given in Table 2. From this result, *PAN* is one of the most sensitive reagents for cerium.

Conductometric Measurements

A solution of 10^{-4} *M* of metal nitrate was titrated with a 10^{-3} *M* solution of *PAN* in pure ethanol. The conductance—molar ratio curves are characterized by breaks denoting the formation of 1 : 1 and 1 : 2 types of complexes with the Ce(III) ions.

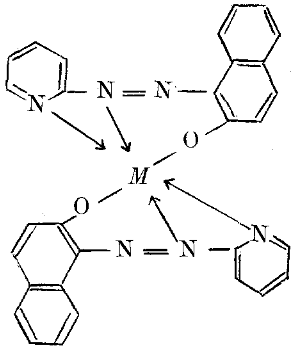
From this result it is concluded that the reaction between the metal ion and *PAN* occurs via the formation of a covalent linkage with the oxygen of the OH group. The complex formation appears to be accompanied by the liberation of the proton from the OH group as deduced from the increase of the electrical conductance when the reagent is added to the metal ion solution.

IR Spectra of the Solid Chelates

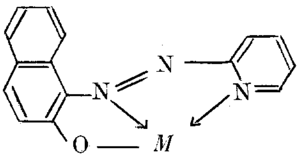
In order to throw more light on the structure of the chelates, the IR spectra of the chelates are compared with that of the free ligand. The IR spectrum of the ligand exhibit bands at 2 900, 1 500 and 1 685 cm^{-1} due to C—OH, —N=N— and —C=N— within the pyridine ring. These bands are shifted to 3 450, 1 630 and 1 820 cm^{-1} when the ligand is bonded with the metal ion. This revealed that the coordination of the *PAN* to the cerium took place through the nitrogen atom of each azo group and of the pyridine ring.

Generally, the IR spectra and the conductometric measurements certify that *PAN* would behave as a tridentate ligand coordinating via the nitrogen atom of each azo group and of the pyridine ring and a covalent linkage with the oxygen of the OH group is formed. The mode of bonding of Ce(III) ion with the *PAN* in the 1 : 1 and 1 : 2 types of complexes can be represented by the following structures:

1 : 2 Complex



1 : 1 Complex



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