

The 1:2 Hafnium-Sodium Alizarin 3-Sulphonate Chelate

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With 4 figures

Abstract

Formation of a 1:2 hafnium-Alizarin Red S chelate (λ_{\max} 520 m μ) has been described. The composition has been arrived at employing absorptiometric measurements using the mole and slope ratio methods. The value of stability constant ($\log K$) as determined by the mole ratio method is 10.2. The system obeys BEER's law from 0.79 ppm. to 35.6 ppm. of hafnium between pH 1.0 and 2.5.

Sodium alizarin 3-sulphonate (Alizarin Red S) abbreviated as ARS forms coloured chelates with the metals of third, fourth, fifth and sixth group of the periodic table. BANERJI and DEY¹⁾ studied the composition and stability of the hafnium-Alizarin Red S chelate but they employed only one method, viz., method of continuous variations using absorbance measurements. However, it is very useful to investigate such systems employing different methods to arrive at the composition. Besides the study of the composition and stability of this chelate the study of the analytical application is also worthwhile. Hence with this end in view the reinvestigation of hafnium-Alizarin Red S chelate using other methods and its analytical application has been described in this communication.

Experimental

Instruments

For photometric studies a Unicam SP 500 spectrophotometer using glass cells of 1 cm. thickness was employed. A Klett Summerson colorimeter (test tube model) was also employed for studying the effect of the foreign ions.

pH measurements were performed using a LEEDS and NORTHRUP direct reading pH indicator using glass and calomel electrode system supplied by the same manufacturer.

Materials

Solutions of Alizarin Red S (BDH AnalaR) and hafnium oxychloride (JOHNSON and MATHEY) were prepared in double distilled water. Other chemicals used were also of AnalaR grade.

¹⁾ S. K. BANERJI and A. K. DEY, Bull. chem. Soc. Japan **35**, 2051 (1962).

Results and Discussion

Nature of the complexes formed: BANERJI and DEY¹⁾ employed the method of VOSBURGH and COOPER²⁾ to determine the nature of the complexes formed in solution between hafnium and Alizarin Red S. It was found that only one complex having λ_{\max} at 520 m μ is formed.

Stoichiometry of the components: The ratio of the metal:reagent has been established by the mole ratio method³⁾ and the slope ratio method⁴⁾. For the mole ratio method a series of solutions were prepared containing a constant amount of Alizarin Red S and increasing ratio of metal to chelating agent. The absorbances of the solutions were measured against distilled water blanks at 500 m μ and 520 m μ , at pH 1.5.

For slope ratio method two series of solutions were prepared. In the first series varying amounts of Alizarin Red S were added to a constant excess of hafnium oxychloride. The other series contained a constant excess of the reagent and varying concentrations of hafnium. Absorbance readings of the solutions were noted against distilled water blank at two different wavelengths.

The results of the mole ratio method (Fig. 1) and the slope ratio method (Fig. 2) shows that the ratio of hafnium to Alizarin Red S in the chelate is 1:2 and hence may be represented as $\text{HfO}(\text{ARS})_2$. These results confirms the results obtained by BANERJI and DEY¹⁾.

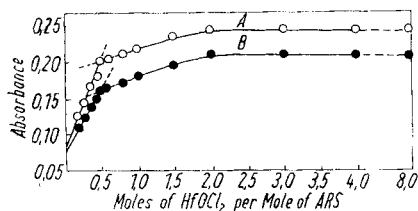


Fig. 1. Determination of the composition from absorption spectra studies using mole ratio method. Curve A: Concentration of ARS $2.0 \cdot 10^{-4}$ M; Curve B: Concentration of ARS $1.0 \cdot 10^{-4}$ M

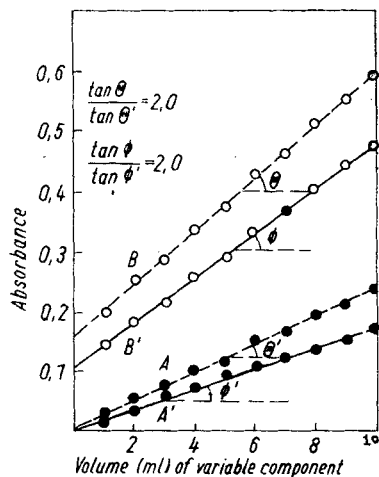


Fig. 2. Determination of the composition from absorption spectra studies using slope ratio method. A, A' ARS varying, B, B' HfOCl_2 varying, Broken line 500 m μ . Solid line 520 m μ . 10 ml. ($1.00 \cdot 10^{-3}$ M) excess component \times ($3.33 \cdot 10^{-4}$ M) variable component \times (15-x) ml. H_2O

²⁾ W. C. VOSBURGH and G. R. COOPER, J. Amer. chem. Soc. **63**, 437 (1941).

³⁾ J. H. YOE and A. L. JONES, Industr. Engng. Chem. (Anal) **16**, 111 (1944).

⁴⁾ A. E. HARVEY and D. L. MANNING, J. Amer. chem. Soc. **72**, 4488 (1950).

Evaluation of the stability constant

The stability constant has also been calculated by the mole ratio method through a calculation of the degree of dissociation of the chelate using the following expression:

$$K_d = (xc) / (nxc)^n / c(1 - \alpha).$$

The values of $\log K$ as determined by BANERJI and DEY and also from the mole ratio method are given in table 1. The free energy change of formation has also been calculated with the help of the expression

$$\Delta F^\circ = -RT \ln K,$$

the terms having their usual meaning.

Table 1
Stability Constants

Method employed	pH	log K	ΔF° at 25° (K. Cals)
Method of DEY et al.	1.8–2.7	10.4 ± 0.3	-14.4 ± 0.4
Mole ratio method	1.5	10.2 ± 0.2	-14.1 ± 0.2

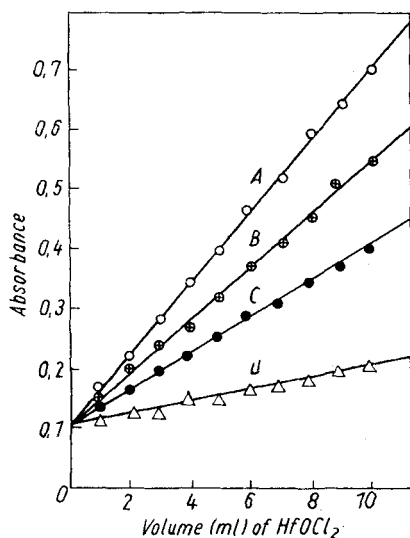


Fig. 3. Adherence to BEER'S Law. (Total volume 25 ml.) Curve A: 10 ml. ($1.0 \cdot 10^{-3}$ M) ARS. ml. ($5.00 \cdot 10^{-4}$ M) $HfOCl_2$; (15-x) ml. water; Curve B: 10 ml. ($1.0 \cdot 10^{-3}$ M) ARS. ml. ($2.50 \cdot 10^{-4}$ M) $HfOCl_2$ (15-x) ml. water; Curve C: 10 ml. ($1.0 \cdot 10^{-3}$ M) ARS. ml. ($1.66 \cdot 10^{-4}$ M) $HfOCl_2$ (15-x) ml. water; Curve D: 10 ml. ($1.0 \cdot 10^{-3}$ M) ARS. ml. ($1.11 \cdot 10^{-4}$ M) $HfOCl_2$ (15-x) ml. water

Adherence to BEER'S Law

Several mixtures containing (1, 2, 3, ... 10 ml.) of hafnium oxychloride and 10 ml of Alizarin Red S were prepared and their pH was adjusted to 1.5. The total volume was kept 25 ml. in each case and their absorbance readings were noted with a Unicam SP 500 spectrophotometer at 520 m μ . It was found that the system adheres to BEER'S law from 0.79 ppm. to 35.6 ppm. of hafnium (Fig. 3).

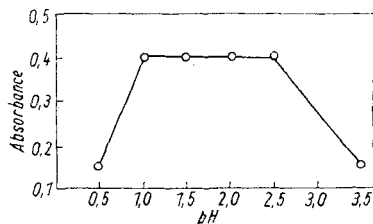


Fig. 4. Influence of pH on the intensity of the chelate. Conc. of ARS $4.00 \cdot 10^{-4}$ M, Conc. of $HfOCl_2$ $1.00 \cdot 10^{-4}$ M

Influence of pH on the intensity of the chelate

The effect of pH on the intensity of the chelate was studied and it was found that a mixture containing $4.0 \cdot 10^{-4}$ M Alizarin Red S and $1.0 \cdot 10^{-4}$ M hafnium oxychloride retained its absorbance values, i. e., 0.400 between pH 1.0 and 2.5 (Fig. 4).

Effect of added foreign ions

The effect of various cations and anions was studied with a KLETT SUMMERSON photoelectric colorimeter with KLETT filter No. 52 (transmission 485–550 $m\mu$) and their tolerance limits were calculated. It was found that copper, iron(II), iron(III), aluminium, chromium(VI), magnesium, beryllium, cerium(III), cerium(IV), molybdenum, vanadium(V), uranium(VI), fluoride, carbonate, acetate, oxalate, citrate, tartrate and borate interferes at all concentrations, whereas, sodium, potassium, lithium, silver, barium, strontium, calcium, chloride, bromide, iodide, chlorate, nitrite, nitrate, sulphite, sulphate, thiosulphate, can be tolerated in large excess.

Sensitivity. The sensitivity as defined by SANDELL⁵⁾ is 0.178 γ/cm^2 at 520 $m\mu$ and the practical sensitivity based on the absorbance value of 0.010 units is 1.78 γ/cm^2 .

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⁵⁾ E. B. SANDELL, Colorimetric determination of traces of metals 3rd edit, Intersci. Publ., New York (1959), p. 83.

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