Hafnyl Ion - Sodium Alizarin 3-Sulfonate Chelate : A Spectrophotometric Study

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Considerable work on metal chelates involving sodium alizarin-3-sulfonate (trivial name Alizarin Red S, abbr. ARS), and their analytical applications have been reported from these

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laboratories[1-9]. From electrical conductance measurements[10] it has been concluded that the reagent behaves as a colloidal electrolyte and aqueous solutions of ARS show the characteristics of a true solution, only when very dilute.

Chelate formation of sodium alizarin-3-sulfonate with quadrivalent metals like zirconium and hafnium[11,12], and thorium[13] has been studied mainly with reference to the nature of lakes formed and position of the chelate ring in the structures. This paper describes the composition and stability of the hafnium chelate.

Experimental

Materials.—BDH reagent grade sodium alizarin-3-sulfonate (Alizarin Red S reagent) was used for the studies without any further purification. A solution of suitable concentration was prepared and standardized by determining the sulfur in the compound. Hafnyl chloride, obtained from M/S A. D. Mackay & Co. Inc., N. Y., was dissolved in water, hydrochloric acid being added to prevent hydrolysis and the hafnium in the solution was determined as hafnia. Freshly prepared solutions in redistilled water, free from carbon dioxide, were employed to avoid effects due to the hydrolysis of the metal salt.

Experimental Procedure. — A Unicam SP 500 spectrophotometer, operated by Doran mains unit on 220 V./50 cycl., single phase stabilized mains was used. Matched glass cells of 10 mm. thickness were used for absorbance measurements, which were noted against distilled water blanks.

pH measurements were made with a Leeds and Northrup pH meter with a glass-calomel electrode system. The experiments were performed in a room maintained at 25°C. The pH of all solutions were adjusted to 2.0 ± 0.2, by the addition of hydrochloric acid.

Results

Nature of the Complex in Solution. — The method described by Vosburgh and Cooper[14] was adopted. Mixtures were prepared containing various proportions of hafnyl chloride and sodium alizarin-3-sulfonate and the absorbances were measured at different wavelengths. The λ_{max} of each mixture is found to lie at the same spectral region of 520 mμ, which shows that only one complex is formed, under the conditions of study, in the system investigated here.

Stoichiometry of the Components.—The ratio of the metal : reagent in the complex has been established by the method of continuous variations. The total volume in each case was 50 ml. The absorbances were measured at 500 and 520 mμ. Various concentrations of the reactants were used and the results are summarized in Table I and some are graphically represented in Fig. 1. In Fig. 1, the difference of the absorbance of the mixture and that which would be shown by the chelating agent alone, if no chelation occurred, is plotted against the composition of the mixture. In Table I and in the legends of Fig. 1, c represents the concentration of hafnyl chloride and

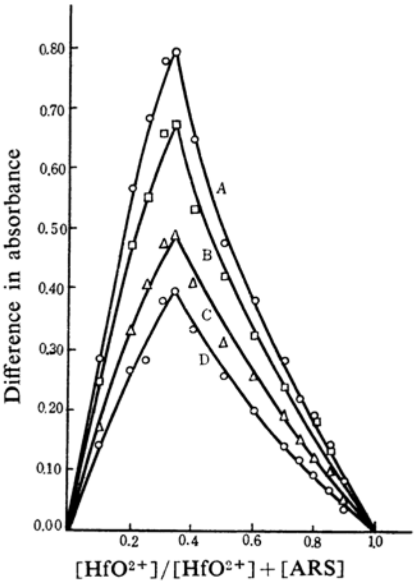

Fig. 1. Determination of the composition from absorption spectra studies at 500 mμ (equimolecular solutions).
Curve A $c=4.0\times10^{-4}$ M, $p=1$
Curve B $c=3.33\times10^{-4}$ M, $p=1$
Curve C $c=2.5\times10^{-4}$ M, $p=1$
Curve D $c=2.0\times10^{-4}$ M, $p=1$

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TABLE I. COMPOSITION OF HAFNIUM - ARS CHELATE

Fig.	Curve	$c\times10^4$ M	p	Wavelength mμ	Vol. of $HfOCl_2$ ml. at peak	Composition of the chelate Hf : ARS
1	A	4.00	1.0	500	16.7	1 : 2
	B	3.33	1.0	500	16.7	1 : 2
	C	2.50	1.0	500	16.7	1 : 2
	D	2.00	1.0	500	16.7	1 : 2
Not shown	A	4.00	1.0	520	16.7	1 : 2
	B	3.33	1.0	520	16.7	1 : 2
	C	2.50	1.0	520	16.7	1 : 2
	D	2.00	1.0	520	16.7	1 : 2
Not shown	A	3.33	1.5	500	21.4	1 : 2
	B	2.00	2.0	500	25.0	1 : 2
Not shown	A	3.33	1.5	520	21.4	1 : 2
	B	2.00	2.0	520	25.0	1 : 2

$p=c'/c$, where c' is the concentration of sodium alizarin sulfonate.

From the above table it is evident that the composition of the chelate is $HfO(ARS)_2$.

Influence of pH on the Stability of the Chelate.—The absorbances of mixtures containing 0.00009 M of hafnyl chloride and 0.00018 M of the reagent at different pH were measured at different wavelengths and it is seen that the λ_{max} lies at 520 mμ in the case of solutions having pH of 1.0 to 4.0, showing thereby that the chelate is stable in this range of pH.

Evaluation of the Stability Constant. — The stability constant has been calculated by the modified method of Anderson et al.[15] as described earlier[7-9]. In this case the stability constant K is given by

$$K=\frac{x}{(a-x)(b-2x)^2} \tag{1}$$

where x is the concentration of the complex at equilibrium and a and b are the initial concentration of the metal ion and the chelating agent, respectively. Taking two sets of concentrations with the same absorbance, i. e. the same value of x, we have:

$$K=\frac{x}{(a_1-x)(b_1-2x)^2}=\frac{x}{(a_2-x)(b_2-2x)^2} \tag{2}$$

Hence, from a knowledge of two sets of initial concentrations of a and b, the value of x can be calculated and therefrom K may be evaluated.

The value of $\log K$ in the system hafnyl chloride-sodium alizarin-3-sulfonate works out to be 10.4±0.3 at 25°C, and the corresponding free energy of formation ΔF° is -14.4 ± 0.4 kcal.

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