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Rare Earth Chelates of 2-(*p*-Sulphophenylazo)-1:8-Dihydroxy-Naphthalene-3:6-Disulphonate (SPADNS)

Kailash N. Munshi* and Arun K. Dey

Rare earths react with SPADNS to form violet coloured water soluble complexes at *p*H 6·0. The colour formation does not depend upon reaction time and is instantaneous. The absorbance values are not changed by keeping the mixtures at room temperature even after 24 hr. Spectral studies show the formation of only one 1 : 1 complex in all the cases with the λ_{max} of the various chelates lying between 550 mμ to 565 mμ at *p*H 6·0. The values of the apparent conditional stability constants have been calculated by three different methods and the results are fairly in good agreement with each other. The values of log *K* for the various lanthanoid chelates of SPANDS lie between 4·4 to 5·8 (*p*H 6·0; 25°). Position of the chelate ring has also been suggested on the basis of the charge on the complexes determined by electrophoresis experiments.

The use of 2-(*p*-sulphophenylazo)-1 : 8 dihydroxy-naphthalene-3 : 6 disulphonic acid in colorimetric determination was described by Banerjee[1,2] who determined Th, Zr and fluoride. Datta[3] used it as an indicator in the complexometric determination of Zr, while Fleury[4] studied the lake formation between Th(IV) and SPADNS and developed a photometric method of determining Th. Recently Saxena and Dey[5] obtained two complexes of Pd(II) with SPADNS at different *p*H values. Garg, Shrivastawa and Dey[6] studied Al(III)-SPADNS chelate in detail.

The use of SPADNS for the determination of rare earths was suggested for the first time[7] by the authors, but details of the characteristics of the chelate were not described. This paper describes the composition, stability and other features of the lanthanoid chelates of SPADNS.

EXPERIMENTAL

Instruments : Absorbance measurements were made with Unicam SP 500 spectrophotometer using 1 cm. thickness of the solution. Hydrogen ion concentration were measured with a L and N *p*H indicator with a glass-calomel electrode system.

* Department of Chemistry, Nagpur University, Nagpur.

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Materials : Standard solutions of rare earth metals (Johnson, Matthey and Co.) were prepared from either the oxides dissolved in HCl or the chlorides in water acidulated with HCl. The required concentrations were obtained by suitable dilutions.

The reagent solution was prepared by taking an accurately weighed quantity of a pure sample of SPADNS (BDH) and dissolving it in distilled water.

Conditions of Study : All measurements were done at 25°. The *p*H was adjusted by adding suitable amounts of dilute NaOH or HCl. The total volume was kept 25 ml. in all the cases. Only eight members of the rare earth family, i.e., praseodymium, neodymium, samarium, gadolinium, holmium, thulium, ytterbium and lutetium were taken for study.

RESULTS AND DISCUSSION

Characteristics of SPADNS : The effect of *p*H on SPADNS was studied over the *p*H range 1–12·5 with solutions containing $4{\cdot}0\times10^{-5}M$. Only very little shift from 510 to 520 mμ in λ_{max} was observed.

Characteristics of the Colour of the Chelates : Rare earths react with SPADNS to form violet-coloured, water soluble complexes at *p*H 6·0. The colour formation is instantaneous and is stable for 24 hours. However, the mixtures were kept for half an hour for equilibration. The colour intensity remains constant between 20° and 60°. There is no appreciable change in absorbance values when the order of the addition of the reagents is changed.

Spectral Studies of the SPADNS Chelates : Three series of mixtures containing six mixtures each is prepared by taking $2\times10^{-4}M$ of the components and varying the metal : reagent ratio as 4 : 1, 1 : 1, 1 : 4. The absorption spectra from 400–630 mμ reveal the existence of only one complex in all the cases at different *p*H values, i.e., 4·5, 5·0, 5·5, 6·0, 6·5 and 7·5. The results indicate that from *p*H 5·5 to 6·5 the λ_{max} is constant in different systems, while at other *p*H values above and below the results were confusing and no definite proof of a stable complex existing was obtained. Hence, it was concluded that only one complex is formed with SPADNS and lanthanons and that too is stable between *p*H 5·5 to 6·5. The wavelength of the maximum absorption of SPADNS chelates of the Pr, Nd and Lu is 550 mμ, for Gd and Tm is 560 mμ and for Sm, Ho and Yb it is 565 mμ, between *p*H 5·5–6·5.

p*H Range of Stability of the Chelates* : It is a range of *p*H within which the λ_{max} of the chelates remains unchanged. The absorption spectra containing 4 ml of $2{\cdot}0\times10^{-4}M$ rare earth solution and 16 ml of $2{\cdot}0\times10^{-4}M$ SPADNS solution (total volume 25 ml) show that all the chelates are stable between *p*H 5·0 and 6·5.

Composition of the Chelates : SPADNS forms 1 : 1 (metal : reagent) complexes with the rare earths. This composition is confirmed by the results obtained by the method of continuous variations[8] and also by the method of mole ratio[9]. These results were further confirmed by measuring the absorbances at different wavelengths also, since only one complex is formed at *p*H 6·0.

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Evaluation of Stability Constant : The values of apparent conditional stability constant K, have been calculated by three different methods and the results are fairly in agreement to each other:

(*a*) the method of Anderson and coworkers modified by Dey and coworkers[10,11],

(*b*) the mole ratio method as suggested by Harvey and Manning[12],

(*c*) the method of continuous variations[8] using non-equimolecular solutions.

The values of log K as obtained by these methods are given below :

TABLE 1

Apparent Conditional Stability Constant (log K) of the Chelates

pH = 6·0; Temperature = 25°

Composition of the chelates 1 : 1

Chelate	Wavelength of study (mμ)	log K	Method
Pr(III)—SPADNS	550	5.2±0.2	(*a*)
		5.6±0.1	(*b*)
		5.8±0.1	(*c*)
Nd(III)—SPADNS	550	4.7±0.2	(*a*)
		5.5±0.1	(*b*)
		5.5±0.3	(*c*)
Sm(III)—SPADNS	565	4.4±0.1	(*a*)
		5.4±0.1	(*b*)
		5.3±0.1	(*c*)
Gd(III)—SPADNS	560	4.5±0.1	(*a*)
		5.3±0.1	(*b*)
		5.1±0.2	(*c*)
Ho(III)—SPADNS	565	5.1±0.1	(*a*)
		5.7±0.1	(*b*)
		5.5±0.3	(*c*)
Tm(III)—SPADNS	560	4.8±0.1	(*a*)
		5.5±0.1	(*b*)
		5.3±0.1	(*c*)
Yb(III)—SPADNS	565	4.4±0.1	(*a*)
		5.4±0.1	(*b*)
		5.1±0.2	(*c*)
Lu(III)—SPADNS	550	4.5±0.1	(*a*)
		5.3±0.1	(*b*)
		4.9±0.1	(*c*)

(*a*) Anderson and coworker's method modified by Dey and coworkers.

(*b*) Mole ratio method.

(*c*) Method of continuous variations.

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Position of the Chelate Ring : There can be two possible positions for chelation in SPADNS :

(*i*) The metal ion may be coordinated through the two oxygens of the hydroxyl groups in 1 and 8 positions or

(*ii*) The metal ion may be coordinated between a nitrogen of the azo group and the oxygen of the hydroxyl group.

The anionic nature of the lanthanoid chelate was indicated by electrophoresis experiments as well as by complete adsorption of the colour of the chelate by ion exchange resin Amberlite IR-45(OH) and by the ionization of the free SPADNS solution at different *p*H values, the position (*i*) can better be suggested for the position of the chelate ring in the 1 : 1 rare earth chelates of the SPADNS.

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Chemical Laboratories,
University of Allahabad,
Allahabad.

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