

Spectrophotometric Study of the Complexation of Samarium(III) with Disodium 2-(2-Hydroxy-3-Sulfo-5-Nitrophenylazo)naphthalene-1,8-Dihydroxy-3,6-Disulfonate in the Presence of Cetyltrimethylammonium Bromide

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Abstract—The complexation of samarium(III) with disodium 2-(2-hydroxy-3-sulfo-5-nitrophenylazo)naphthalene-1,8-dihydroxy-3,6-disulfonate (*R*) was studied in the presence and absence of cetyltrimethylammonium bromide (CTMABr). Monoligand SmR and mixed-ligand SmR-CTMABr complexes were formed at pH 6 and showed light absorption maxima at 531 and 529 nm, respectively. The formation constants ($\log K_1$) of SmR and SmR-CTMABr complexes were 4.06 ± 0.04 and 4.99 ± 0.04 , respectively. The ratios of components in monoligand and mixed-ligand complexes were found to be 1 : 2 and 1 : 1 : 1, respectively. Beer's law was obeyed in solutions containing 1.20–7.20 and 1.20–9.60 $\mu\text{g/mL}$ Sm, respectively. A procedure for the photometric determination of samarium in monazite was developed.

For the photometric determination of rare-earth elements (REEs), organic reagents of different classes are used [1]. Among these, azo derivatives of chromotropic acid [2] are the most efficient for the determination of REEs.

To improve the analytical parameters of the reaction, mixed-ligand complexes of REEs are used [3].

In this work, we studied the effect of cetyltrimethylammonium bromide (CTMABr) on the complexation of samarium(III) with disodium 2-(2-hydroxy-3-sulfo-5-nitrophenylazo)naphthalene-1,8-dihydroxy-3,6-disulfonate (H_4R).

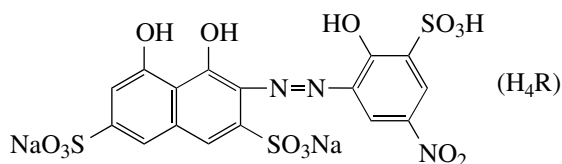
EXPERIMENTAL

The reagent was synthesized following the procedure reported in [4]. Its composition and structure were established by elemental analysis and IR spectroscopy.

Calc. (%): C, 31.53; H, 1.48; N, 6.90; S, 15.76; O, 36.78.

Found (%): C, 31.22; H, 1.43; N, 6.86; S, 15.70; O, 36.71.

IR (cm^{-1}): 1580 ($-\text{N}=\text{N}-$); 1585, 1590 (Naf-OH); 1045 (ArOH).



The reagent is readily soluble in water. A 1×10^{-3} M water-ethanol solution of CTMABr and a 2×10^{-3} M

samarium(III) solution prepared from samarium(III) nitrate were used. A titrimetric HCl solution (pH 1–2) and ammonia-acetate buffer solutions (pH 3–11) were used for attaining the required acidity of solutions. The pH of solutions was maintained using an I-130 potentiometer with a glassy electrode. The absorbance of solutions was measured using a Lambda 40 spectrophotometer (Perkin Elmer) and a KFK-2 ($l = 1$ cm) photocolormeter. The specific conductivity of solutions was measured using an N 5741 conductometer.

RESULTS AND DISCUSSION

The pH dependence of Sm complexation showed that the highest yield of SmR complex was observed at pH 6 ($\lambda_{\text{max}} = 531$ nm) (Table 1); the reagent exhibited an absorption maximum at 559 nm. In the presence of CTMABr, a ternary SmR-CTMABr compound ($\lambda_{\text{max}} = 529$ nm) was formed with an optimum yield at pH 6.

Monoligand SmR and mixed-ligand SmR-CTMABr complexes were formed rapidly. The ratios of reactants in complexes were found by the Starik-Barbanel method of relative yield, the slope method, and the method of isomolar series. The molar absorptivities of the complexes were calculated from saturation curves [5]. The ranges of Sm(III) concentrations over which Beer's law was obeyed were determined (Table 1).

The formation constants of monoligand and mixed-ligand samarium(III) complexes were calculated. The formation constant of SmR complex was calculated using the method of curve intersection [6]. $\log K_1$ was found to be 4.06 ± 0.04 ($n = 4$; $P = 0.95$) (Table 2).

Table 1. Main photometric characteristics of the reactions of samarium(III) with organic reagents (pH 6)

Reagent	λ_{\max} , nm	Sm-to-reagent ratio	$\epsilon_{\max} \times 10^{-3}$	Analytical range governed by Beer's law, $\mu\text{g/mL}$
Disodium 1,8-dihydroxynaphthalene-3,6-disulfonate-7-azobenzene [2]	530	1 : 1	0.6	0.6–2.6
H ₄ R	531	1 : 2	3.5 ± 0.01	1.2–7.2
H ₄ R + CTMABr	529	1 : 1 : 1	4.75 ± 0.01	1.2–9.6

Table 2. Data for calculating the $\log K_1$ of SmR complex (at a Sm-to-R molar ratio of 1 : 1; $c_{\text{Sm}} = 4.8 \times 10^{-5}$ M; $\Delta A_{\text{lim}} = 0.28$)

ΔA	$c_c \times 10^5$, M	$K_1 \times 10^{-4}$	$\log K_1$
0.07	1.20	1.1	4.04
0.11	1.89	1.05	4.02
0.15	2.57	1.2	4.08
0.17	2.91	1.2	4.08
			$\log K_{\text{av}} = 4.04 \pm 0.04$

Table 3. Specific conductivity ($m \times 10^{-3} \Omega^{-1} \text{cm}^{-1}$) of monoligand and mixed-ligand samarium complexes at pH 6

Complex	V_{R} , mL									
	1	2	3	4	5	6	7	8	9	10
SmR	1.00	1.00	0.99	0.94	0.90	0.86	0.85	0.84	0.83	0.83
SmR + CTMABr	1.00	0.96	0.91	0.87	0.82	0.78	0.75	0.71	0.70	0.69

Table 4. Permissible n-fold amounts of foreign substances (with respect to samarium) that do not interfere with the determination of samarium(III) as its monoligand (SmR) or mixed-ligand (SmR–CTMABr) complexes (error, 5%)

Ion or substance	SmR	SmR-CTMABr	Disodium 1,8-dihydroxynaphthalene-3,6-disulfonate-7-azobenzene [2]	Arsenazo III [8]
Na(I)	Does not interfere	Does not interfere		
K(I)	The same	The same		
Mg(II)	67	210		
Ca(II)	111	315	2	Slightly interferes
Ba(II)	76	170		
Zn(II)	181	508		
Cd(II)	311	540		
Mn(II)	31	430		
Ni(II)	161	460		
Co(II)	161	276		
Cu(II)	178	450		Interferes
Al(III)	15	211	1	300
Zr(IV)	25	118		Interferes
Th(IV)	3	15	0.5	The same
V(V)	28	83		
Mo(VI)	53	250		
W(VI)	27	450		
C ₂ O ₄ ²⁻	20	209	0.1	
EDTA	18	58		
Thiourea	211	594		
Citric acid	40	160		
Na ₂ HPO ₄ · 12H ₂ O	10	59	0.2	Interferes
F ⁻	50	89	0.5	The same

The formation constant of the mixed-ligand samarium(III) complex ($\log K_1 = 4.99 \pm 0.04$) was found from the curve of saturation of an 8×10^{-5} M SmR complex solution with a CTMABr solution using the method of curve intersection.

The obtained complexes were also examined by conductometric titration [7] (Table 3).

A comparison of the specific conductivities of monoligand and mixed-ligand samarium(III) complexes at pH 6 demonstrated that SmR–CTMABr complex was more stable.

The effects of foreign ions and masking agents on the complexation of samarium(III) in the presence and absence of CTMABr were studied (Table 4), and a procedure for determining samarium in monazite was developed.

Determination of samarium in monazite. A 0.1-g sample of monazite was dissolved in the mixture of 3 mL of HF, 1 mL of HCl, and 3 mL of HNO₃ in a glassy-carbon dish. The paste obtained was treated with 3–4 mL of HNO₃ at 50–60°C to the point of complete distillation of HF. The residue obtained was dissolved in water and transferred to a 100-mL volumetric flask; the solution was diluted to the mark with water. An aliquot portion of the obtained solution was placed in a 25-mL volumetric flask, 2.5 mL of a 2×10^{-3} M H₄R solution and 0.4 mL of a 1×10^{-3} M CTMABr solution were added, and the solution was diluted to the mark with a buffer solution of pH 6. The absorbance of solutions was measured in a cell with $l = 1$ cm at 490 nm against the solution of a blank experiment using the KFK-2 instrument. In the sample with a nominal con-

tent of Sm of 3.79%, $3.75 \pm 0.04\%$ Sm was found ($n = 5$; $P = 0.95$).

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