

## INTERACTION OF SAMARIUM(III) WITH 2,2',3,4-TETRAHYDROXY-3'-SULFO-5'-NITROAZOBENZENE IN THE PRESENCE OF CATIONIC SURFACTANTS

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**Abstract.** The effect of surfactants (CS) - chloride cetylpyridinium (CPCI), cetylpyridinium bromide (CPBr) and cetyltrimethylammonium bromide (CTABr) on the complexation of samarium (III) with 2,2',3,4-tetrahydroxy-3-sulfo-5'-nitroazobenzene (R)-investigated and optimal conditions for the formation of multiligand complexes were found. It was found that in the presence of cationic surfactants, multi-ligand complexes are formed with the ratio of the components Sm(III): R: CS = 1: 1: 1. The chemical-analytical characteristics of binary and multi-ligand complexes of samarium (III) have been determined by the spectrophotometric method. Under optimal conditions for the formation of multi-ligand complexes, ligand-ligand interactions between the reactant and the CS were investigated and it was established that ionic associates with a 1: 1 ratio are formed. By the method of conductometric titration, the specific electrical conductivity of the complexes was investigated. A concentration interval obeying Beer's law has been established and the effects of foreign ions and masking substances on the determination of samarium(III) in the form of multi-ligand complexes have been studied. A method for spectrophotometric determination of samarium microquality in monocyte has been developed.

**Keywords:** samarium (III), spectrophotometric determination, complexation, chloride cetylpyridinium, cetylpyridinium bromide, cetyltrimethylammonium bromide.

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### 1. Introduction

The effect of surfactants (CS) - chloride cetylpyridinium (CPCI), cetylpyridinium bromide (CPBr) and cetyltrimethylammonium bromide (CTABr) on the complexation of samarium (III) with 2,2',3,4-tetrahydroxy-3-sulfo-5'-nitroazobenzene (R)-investigated and optimal conditions for the formation of multiligand complexes were found. It was found that in the presence of cationic surfactants, multi-ligand complexes are formed with the ratio of the components Sm(III): R: CS = 1: 1: 1. The chemical-analytical characteristics of binary and multi-ligand complexes of samarium (III) have been determined by the spectrophotometric method. Under optimal conditions for the formation of multi-ligand complexes, ligand-ligand interactions between the reactant and the CS were investigated and it was established that ionic associates with a 1: 1 ratio are formed. By the method of conductometric titration, the specific electrical conductivity of the complexes was investigated. A concentration interval obeying Beer's law has been established and the effects of foreign ions and masking substances on the determination of samarium(III) in the form of multi-ligand complexes have been studied. A method for spectrophotometric determination of samarium microquality in

monocyte has been developed.

Rare earth elements (REEs) are widely used in chemical and nuclear engineering, as well as in ferrous and non-ferrous metallurgy. The growing importance of REEs in modern engineering and technology makes it necessary to develop simple, rapid and highly sensitive analytical methods for determining traces of these elements. To determine trace amounts of REE, the spectrophotometric method is most often used (Yatsimirskiĭ *et al.*, 1996).

It is known that different classes of organic reagents are used for spectrophotometric determination of REE, among them nitrogen- and oxygen-containing chelate-forming reagents are considered the most effective (Yatsimirskiĭ *et al.*, 1996; Soylak & Türkoğlu, 2000; Aliyeva *et al.*, 2009; Du *et al.*, 1994; Hajieva *et al.*, 2005; Ivanov *et al.*, 1999). In the presence of cationic surfactants and hydrophobic amines, the degree of protonization of acid-chromophore reagents decreases and at the same time the interval of interaction with metals with mixing into a more acidic medium is expanded (Pilipenko & Tananoiko, 1983; Ivanov *et al.*, 2003; Nagiev *et al.*, 2003; Nagiev *et al.*, 2007).

In this paper, the effect of cationic surfactants - cetylpyridinium chloride (CPCI), cetylpyridinium bromide (CPBr) and cetyltrimethylammonium bromide (CTMABr) on the complexation of samarium (III) with 2,2',3,4-tetrahydroxy-3'-sulfo-5'-nitroazobenzene were investigated and a method for spectrophotometric determination of samarium microquantity in monocyte was developed.

## 2. Experimental part

**Apparatus.** The optical density of the solutions was measured on a computer-assisted Lambda-40 spectrophotometer (Perkin Elmer) and on a KPK-2 photoelectrocolorimeter in cuvettes with a layer thickness of 1.0 cm. The acidity of the solutions was controlled using a pH-meter pH-121 with a glass electrode. The electrical conductivity of the solutions was measured on the METTLER TOLEDO conductometer.

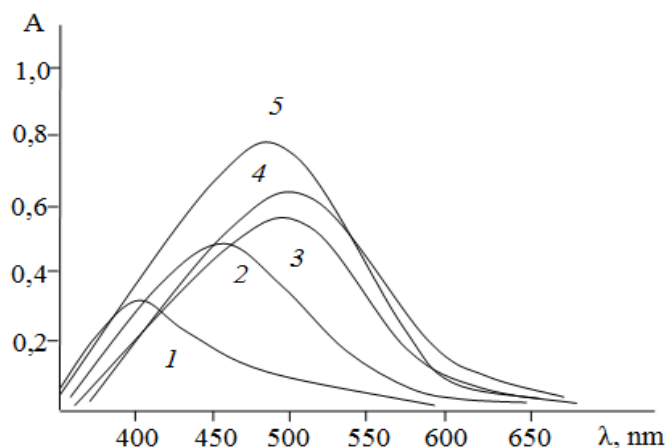
**Reagents:** Standard  $1.0 \times 10^{-2}$  M samarium (III) solution was prepared by dissolving the calculated  $\text{Sm}(\text{NO}_3)_6 \cdot 6\text{H}_2\text{O}$  in water according to the procedure (Korostelev, 1964). Working  $1.0 \times 10^{-3}$  M solutions were prepared by diluting the initial solution with distilled water. The work used  $1.0 \times 10^{-3}$  M aqueous solutions of 2,2',3,4-tetrahydroxy-3'-sulfo-5'-nitroazobenzene (R) and cationic surfactants (CS). 2,2',3,4-Tetrahydroxy-3'-sulfo-5'-nitroazobenzene is synthesized by a well-known technique (Busev, 1972) and identified by IR and NMR spectroscopy. All used reactants had a qualification not lower than b.d.a. To create the required pH value of the medium, acetate-ammonia buffer solutions (pH 3.0-11.0) and fixal HCl (pH 0-2.0) were used.

## 3. Results and their discussion

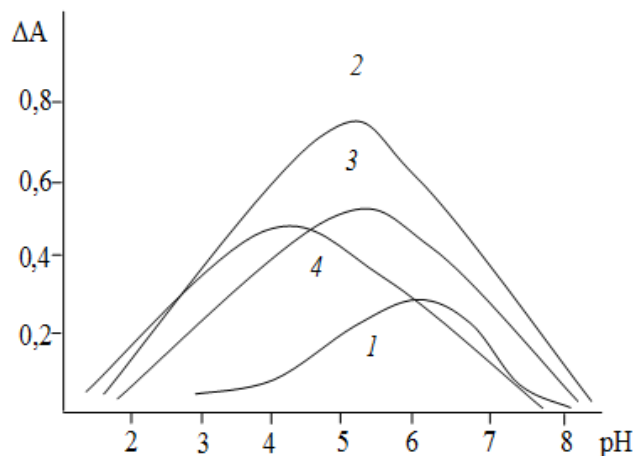
Previously (Huseynov, 2007) it was shown that in an aqueous solution at pH 4.5-6.5 the reagent is in the form  $\text{H}_3\text{R}^{2-}$  and has a maximum light absorption at 429 nm. Under these conditions, samarium (III) with the reactant forms a colored complex with maximum light absorption at 457 nm. In the presence of cationic surfactants, mixed-ligand complexes of  $\text{Sm}(\text{III})\text{-R-CS}$  are formed, while a bathochromic shift is observed compared to the spectrum of the Binary Complex  $\text{Sm}(\text{III})\text{-R}$  (Fig. 1). The

maximum light absorption of the Sm(III)-R-CPCl, Sm(III)-R-CPBr and Sm(III)-R-CTMABr complexes is observed at 483, 490 and 486 nm, respectively.

The study of the dependence of optical density on the pH of the solution showed that during the formation of multi-ligand complexes Sm(III)-R-CS, the maximum yield shifts to a more acidic medium compared to the binary complex Sm(III)-R (Fig. 2). Thus, the yield of the Sm(III)-R complex is maximum at a pH of 6.0-6.5, Sm(III)-R-CPCl and Sm(III)-R-CPBr - at a pH of 5.0-5.5, Sm(III)-R-CTMABr - at a pH of 4.0-4.5 (Table 1).



**Figure 1.** Absorption spectra of complexes of Sm at optimal pH value: 1 -R, 2 - Sm(III)-R, 3 - Sm(III)-R-CPCl, 4 - Sm(III)-R-CPBr, 5 - Sm(III)-R-CTMABr  
 $C_{Sm}=4,0 \cdot 10^{-5}M$ ,  $C_R=1,0 \cdot 10^{-4}M$ ,  $C_{CS}=6,0 \cdot 10^{-5}M$ ,  
 $\lambda_{40}$ ,  $l=1,0$  cm



**Figure 2.** Dependence of optical density of complex solutions of Sm(III) on pH at  $\lambda_{max}$  on the background of control solution: 1 - Sm(III)-R, 2 - Sm(III)-R-CPCl, 3 - Sm(III)-R-CPBr, 4 - Sm(III)-R-CTMABr.  
 Conditions are shown on fig.1

To select the optimal conditions, the effect of the concentration of reactants, temperature and time on the formation of binary and multi-ligand complexes was studied. The yield of the Sm(III)-R complex is maximum at a concentration of  $1.0 \times 10^{-4}$  M of reagent, and the yield of multi-ligand complexes at a concentration of

$8.0 \times 10^{-5}$  M of reagent and  $6.0 \times 10^{-5}$  M of CS. All samarium(III) complexes are formed immediately after mixing the component solutions and are stable. So, if the binary complex is stable for less than three hours and when heated to  $60^{\circ}\text{C}$ , then multi-ligand complexes are stable for more than two days and when heated to  $90^{\circ}\text{C}$ .

**Table 1.** Chemical-analytical characteristics of samarium(III) complexes with 2,2',3,4-tetrahydroxy-3'-sulfo-5'-nitroazobenzene

Complex	pH <sub>opt</sub>	$\lambda_{\text{max}}$ , nm	$\varepsilon \times 10^3$ (at $\lambda_{\text{max}}$ )	Ratio of components	Calibration graph linearity interval, $\mu\text{g/ml}$	$\lg \beta$
Sm-R	6,0-6,5	457	6,75 $\pm$ 0,02	1:1	0,50-6,00	5,52 $\pm$ 0,03
Sm-R-CPCI	5,0-5,5	483	15,50 $\pm$ 0,02	1:1:1	0,22-6,00	8,84 $\pm$ 0,05
Sm-R-CPBr	5,0-5,5	490	12,20 $\pm$ 0,02	1:1:1	0,45-7,20	8,48 $\pm$ 0,06
Sm-R-CTMABr	4,0-4,5	486	11,60 $\pm$ 0,03	1:1:1	0,45-7,20	8,42 $\pm$ 0,08

At the optimal pH value in the formation of multi-ligand complexes, ligand-ligand interactions between the reactant and cationic surfactants were investigated. It was found that in the presence of CS, bathochromic shifts in the absorption spectrum of the reagent at 16-30 nm are observed, which make it possible to predict the formation of ionic associates between the CS and the sulfo group of the reagent. By the method of intersection of curves, the stoichiometry and stability constants of the R-CS associates were determined (Table 2). With the influence of CS on the sulfogroups of the reagent, the maximum delocalization of the  $\pi$  system of the reagent occurs, as a result of which the negative inductive effect of the sulfo group increases, and this in turn leads to a bathochromic shift of the absorption band.

By the method of conductometric titration, the specific electrical conductivity of R-CS associate solutions and the formation of corresponding multi-ligand samarium (III) complexes at pH<sub>opt</sub> (Table 3) were investigated.

**Table 2.** Chemical-analytical characteristics of R-CS associates at pH<sub>opt</sub> in the formation of multi-ligand complexes of samarium(III)

Associate	$\lambda_{\text{CS}}$ , nm	$\lambda_{\text{R-CS}}$ , nm	Ratio R:CS	$\lg K$
R-CPSI	261	459	1:1	3,61 $\pm$ 0,05
R-CPUBr	262	457	1:1	3,58 $\pm$ 0,06
R-DTMABr	207	445	1:1	3,53 $\pm$ 0,09

**Table 3.** Specific electrical conductivity ( $\text{m}10^{-4} \text{ Ohm}^{-1} \times \text{cm}^{-1}$ ) of solutions of R-CS associates in the formation of multi-ligand complexes at pH<sub>opt</sub>

V <sub>CS</sub> , ml	0,5	1,0	1,5	2,0	2,5	3,0	3,5	4,0	4,5	5,0
CS										
CPCI	3,65	3,67	3,60	3,57	3,55	3,54	3,53	3,52	3,52	3,52
CPBr	3,71	3,66	3,61	3,59	3,57	3,56	3,55	3,54	3,53	3,53
CTMABr	3,77	3,74	3,71	3,70	3,68	3,64	3,61	3,59	3,58	3,58

Methods of relative yield of Starick-Barbanel, equilibrium shift and isomolar series are used to determine the ratio of reacting components in the composition of the

resulting colored complexes of samarium (III) (Bulatov & Kalinkin, 1986). All methods showed that the ratio of components in the binary complex is Sm(III): R = 1: 1, and in the multi-ligand complex - Sm (III): R: KPAV = 1: 1: 1. Astakhov's methods determined the number of protons displaced by complexation and confirmed the specified ratios of components in the complexes (Astakhov *et al.*, 1961). The ratio of components in the composition of Ionic associations R-CS and in the multi-ligand complexes Sm(III)-R-CS shows that the mechanism of formation of binary Sm(III)-R and multi-ligand complexes Sm(III)-R-CS are the same. These data also prove the appearance of an electrostatic interaction between the CS and the sulfo group of the reagent during the formation of multi-ligand complexes.

The stability constants of binary and multiligand complexes of samarium(III) have been calculated. To calculate the stability constant of the Sm(III)-R complex, the curve intersection method was used and it was found that  $\lg\beta=5.52\pm 0.03$ . Taking into account the molar ratio of components in the composition of multi-ligand complexes, their stability constants were calculated and it was established that in the presence of CS the stability of complexes increases by about three orders of magnitude (Table 1).

Comparison of stability constants and specific electrical conductivity of solutions of R-CS associates with the stability constant of mixed-ligand complexes of Sm(III)-R-CS shows that the formation of multi-ligand complexes in solution depends on the ligand-ligand interaction between the reactant and the CS. With an increase in the stability constant of associates, the specific electrical conductivity of their solutions decreases and the stability constants of multi-ligand complexes increase. It has been previously investigated (Gadzhieva *et al.*, 2006) that the stability of AS associates with organic reagents depends on the mobility of chloride and bromide ions, as well as on the charge of the nitrogen atom in the groups  $-\text{N}(\text{CH}_3)_3-\text{NC}_5\text{H}_5$  in their composition.

The specific electrical conductivity of solutions of mixed- ligand complexes of samarium(III) complexes was also investigated by the method of conductometric titration. To this end, at optimal pH value, solutions of R-CS associates were titrated with samarium(III) solutions (Table 4). It can be seen that with an increase in the stability constant of the R-CS associates and sm(III)-R-CS multi-ligand complexes, the specific electrical conductivity of their solutions decreases.

**Table 4.** Specific electrical conductivity ( $\text{m} \cdot 10^{-4} \text{Ohm}^{-1} \cdot \text{cm}^{-1}$ ) of solutions of mixed-ligand complexes of samarium (III) at  $\text{pH}_{\text{opt}}$

$V_{\text{Sm(III), ml}}$ R-CS	0,5	1,0	1,5	2,0	2,5	3,0	3,5	4,0	4,5	5,0
R -CPCl	0,98	0,95	0,91	0,86	0,83	0,80	0,78	0,76	0,74	0,74
R -CPBr	0,99	0,97	0,95	0,88	0,86	0,83	0,80	0,78	0,76	0,76
R -CTMABr	1,03	1,00	0,97	0,94	0,91	0,89	0,8	0,84	0,83	0,83

The calibration graph is lined in the range of 0.50-6.0  $\mu\text{g/ml}$  Sm(III) for the Sm(III)-R complex, 0.22-6.0  $\mu\text{g/ml}$  for Sm(III)-R-CPCl and 0.45-7.20  $\mu\text{g/ml}$  for Sm(III)-R-CPBr and Sm(III)-R-DTMABr. The molar light absorption coefficients at  $\lambda_{\text{of}}$  the sm(III)-R-R-CPSI, Sm(III)-R-CPBr and Sm(III)-R-D-DTMABr complexes are respectively equal to  $(6.75\pm 0.02) \cdot 10^3$ ,  $(15,50\pm 0,02) \cdot 10^3$ ,  $(12,20\pm 0,02) \cdot 10^3$  and  $(11,60\pm 0,02) \cdot 10^3$ .

The influence of foreign ions and masking substances on the determination of samarium(III) in the form of binary and multi-ligand complexes has been studied. It was

found that in the presence of cationic surfactants, the selectivity of the reaction increases significantly (Table 5). The method for determining Sm(III) in the form of the multi-ligand complex Sm(III)-R-CTMABr has the highest selectivity.

**Table 5.** Permissible ratio by mass of foreign substances for the determination of samarium(III) with 2,2,3,4-tetrahydroxy-3'-sulfo-5'-nitroazobenzene in the presence of cationic surfactants (error 5%)

Ion or substance	R	R-CPCl	R-CPBr	R-CTMABr	Arsenazo III (Bulatov & Kalinkin, 1986)
Na (I)	Doesn't get in the way	Doesn't get in the way	Doesn't get in the way	Doesn't get in the way	
K (I)	Doesn't get in the way	Doesn't get in the way	Doesn't get in the way	Doesn't get in the way	
Mg (II)	38	140	135	180	
Ca (II)	97	220	230	295	Weakly Prevents
Ba(II)	42	114	127	192	
Zn(II)	9	72	83	125	
Cd(II)	185	205	213	263	
Mn(II)	14	82	80	124	
Ni(II)	16	91	87	140	
III Co(II)	10	192	204	270	
Cu(II)	Prevents	38	47	120	Prevents
Al (III)	Prevents	24	23	113	300
Zr (IV)	25	104	100	160	Prevents
Th (IV)	14	26	26	122	Prevents
V (V)	43	74	72	157	
Mo (VI)	6	22	24	105	
W (VI)	47	123	128	203	
	28	71	76	151	
EDTA	21	44	49	119	
Thiomocina	174	252	248	374	
Citric acid	33	95	93	110	
	19	31	37	60	Prevents
	23	62	70	82	Prevents

The developed methods for determining samarium (III) in the form of a multi-ligand complex Sm-R-CTMABr are used to determine it in monocyte.

**Definition of samarium in monocyte.** A monocyte sample of 0.10 g in a glasscarbon cup is dissolved when heated in a mixture of 3 ml of HCl + 1 ml of H<sub>2</sub>F<sub>2</sub> + 3 ml of HNO<sub>3</sub>. The resulting mass is treated with 3-4 ml of HNO<sub>3</sub> at 50-60 ° C until completely distilled with hydrogen fluoride. The resulting residue is dissolved in distilled water when heated, filtered, transferred to a flask with a capacity of 100 ml, brought to a mark and mixed well. The alicwot part of the resulting solution is placed in a flask with a capacity of 25 ml, 2.0 ml of 1.0 · 10<sup>-3</sup> solution of the reagent, 1.5 ml of 1.0 · 10<sup>-3</sup> solution of cetyltrimethylammonium bromide is added and diluted to the label with an acetate-ammonia buffer solution with a pH of 4.0. The optical density of the solution is measured on the KPK-2 MP device at λ = 490 nm against the background of the control experiment in the ditch l = 1.0 cm. graphics (Table 6).

**Table 6.** Results of the determination of samarium in monacyte (n= 5; P=0,95)

Sample	Sm content on the passport, %	Found Sm, %	S <sub>r</sub>
Monacyte	3,79	3,73±0,12	0,028

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