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POTENTIOMETRIC DETERMINATION OF STABILITY CONSTANTS OF COMPLEXES OF RARE EARTH ELEMENTS WITH ARYLHYDRASONS OF BENZOYLACETONE

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The stability constants of the complexes of rare earth elements – La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu with arylhydrazones of benzoylacetone have been determined by the method of potentiometric titration, which change in the following sequence: Lu > Yb > Tm > Er > Ho > Dy > Tb > Gd > Eu > Sm > Nd > Pr > Ce > La. The stability of the complexes depends on the electron-donor and electron-acceptor character of the functional groups included in the ligands: –Cl>–SO₃H>–NO₂.

Keywords: rare earth elements, arylhydrazones, benzoylacetone, stability constants.

Today, rare earth elements (REE) and their compounds play an important role in many high-technological applications and their commercial value is enormous. Typical products that rely on the unique magnetic, optical or chemical properties of rare earth elements include hybrid electric cars, catalytic converters, electric windmills, compact fluorescent light bulbs and computer disk drives. Rare earth metals are also widely used in the production of various lasers, radar equipment, precision munitions and weapon systems [1].

Arylhydrazons of β -diketones and their complexes attracted a lot of attention due to their high synthetic potential for organic and inorganic chemistry and various useful properties. For example, arylhydrazones of β -diketones can be used in the development of functional materials associated with intelligent hydrogen bonding, photoelement structural switching, self-organized layers, liquid crystals, semiconductors, ionophores, indicators, spectrophotometric reagents

for the determination of metal ions, catalysts, photoluminescent materials, optical recording media, etc [2].

Therefore, studying the stability of complexes of rare earth elements with arylhydrazones of benzoylacetone is an actual problem for the purpose of using these complexes for the determination of REE in various industrial and natural objects.

In the present work, the stability constants of complexes of rare earth element (REE) with arylhydrazones of benzoylacetone: sodium(*E*)-5-chloro-3-(2-(1,3-dioxo-1-phenylbutane-2-ylidene)hydrazinyl)-2-hydroxybenzenesulfonate (NaH₂L¹), disodium(*E*)-3-(2-(1,3-dioxo-1-phenylbutane-2-ylidene)hydrazinyl)-2-hydroxy-5-sulfobenzene-sulfonate (Na₂H₂L²) and sodium(*E*)-3-(2-(1,3-dioxo-1-phenylbutan-2-ylidene)hydrazinyl)-2-hydroxy-5-nitrobenzenesulfonate (NaH₂L³) are under study.

Experimental part

The ligands (L) – NaH_2L^1 , $\text{Na}_2\text{H}_2\text{L}^2$ and NaH_2L^3 were previously obtained by the azocombination of diazotized derivatives of *o*-aminophenol with benzoylacetone in a slightly alkaline medium [3]. The individuality of compounds was proved by the methods of ^1H , ^{13}C NMR and IR spectroscopy. The purity of the reagents was monitored spectrophotometrically by the absorption spectra of NaH_2L^1 , $\text{Na}_2\text{H}_2\text{L}^2$ and NaH_2L^3 solutions and by paper chromatography.

The initial solution of REE ($c_{\text{REE}}=1\cdot 10^{-1}$ mol/L) was prepared by dissolving REE their oxides in 20 ml of dilute HCl (1:1) with slight heating by the method [4]. In connection with the presence of the $-\text{SO}_3\text{H}$ group the ligands were dissolved in water. pH-metric titration of mixtures of solutions of reagents NaH_2L^1 , $\text{Na}_2\text{H}_2\text{L}^2$ and NaH_2L^3 and metals (complexes) was carried out in an aqueous medium. The volume of titrated solutions was 50 ml with the content of $c_{\text{L}}=2\cdot 10^{-2}$ mol/L, $c_{\text{REE}}=1\cdot 10^{-3}$ mol/L. The ionic strength of the solutions was kept constant ($\mu=0.1$) by introducing the known amount of KCl. The titrant was a solution of $2\cdot 10^{-2}$ mol/L free of carbon dioxide. Solutions were mixed with a magnetic stirrer. The pH value was measured on the Ionomer I-130 with a glass and flowing silver chloride electrode.

Determination of stability constants of complexes. The dissociation constants of the reagents NaH_2L^1 , $\text{Na}_2\text{H}_2\text{L}^2$ and NaH_2L^3 were determined by potentiometric titration using the Schwarzenbach equation [5]. Titration was carried out at 25°C . The ionic strength of the solutions was kept constant ($\mu=0.1$ mol/L) by introducing the known amount of KCl. The following dissociation constants for the reagents were calculated: $\text{pK}_1=5.73\pm 0.01$, $\text{pK}_2=9.33\pm 0.03$ for NaH_2L^1 , $\text{pK}_1=5.41\pm 0.04$, $\text{pK}_2=8.94\pm 0.02$ for $\text{Na}_2\text{H}_2\text{L}^2$ and $\text{pK}_1=4.98\pm 0.03$, $\text{pK}_2=8.53\pm 0.01$ for NaH_2L^3 [3].

It is seen that with the introduction of functional groups to *meta*-position of molecules with respect to the azo-group, the acidic properties of these molecules increase and a correlation between pK of the reagents and the Hammett's substituents constants σ_{p} 0.78 ($-\text{NO}_2$), 0.45 ($-\text{SO}_3\text{H}$) and 0.23 ($-\text{Cl}$) is possible [6]. Based on the results

of quantum chemical calculations, it can be assumed that pK_1 characterizes the deprotonation of the $-\text{OH}$ group located in the *ortho* position of the aromatic part of the molecule, and pK_2 from the hydrazone form ($=\text{N}-\text{NH}-$).

To determine the step stability constants, the Bjerrum method was used [7, 8]:

$$[\text{L}] = \frac{(2-m) \cdot c_{\text{H}_2\text{L}} - [\text{H}^+] + [\text{OH}^-]}{[\text{H}^+] \cdot K_1 + 2[\text{H}^+]^2 \cdot K_1 K_2},$$

$$\alpha_{\text{L(H)}} = 1 + [\text{H}^+] \cdot K_1 + [\text{H}^+]^2 \cdot K_1 K_2$$

$$\bar{n} = \frac{c_{\text{L}} - [\text{L}] \cdot \alpha_{\text{L(H)}}}{c_{\text{REE}}},$$

here $c_{\text{L}}=2\cdot 10^{-3}$ mol/L, REE: $\text{H}_2\text{L}=1:2$, K_1 and K_2 are the protonation constants of the reagent, m is the neutralization point.

Plots of $\bar{n}-\text{pL}$ are constructed. The inverse ligand concentrations ($-\lg \text{L} = \text{pL}$) at the points $\bar{n}=0.5$ and $\bar{n}=1.5$ are equal to the logarithms of the step stability constants $\lg K_1$ and $\lg K_2$, respectively. To determine the exact value of the stability constants ($\lg \beta_1 = \lg K_1$; $\lg \beta_2 = \lg K_1 + \lg K_2$), the titration results are processed by the least squares method [9] and presented in Table.

Results and discussions

The results of potentiometric titration showed that the stability constants of ligand complexes with REE change in the following sequence (Table): $\text{Lu} > \text{Yb} > \text{Tm} > \text{Er} > \text{Ho} > \text{Dy} > \text{Tb} > \text{Gd} > \text{Eu} > \text{Sm} > \text{Nd} > \text{Pr} > \text{Ce} > \text{La}$.

Comparison of the stability constants of the reagent complexes shows that the functional groups introduced into the aromatic part of the molecule do not affect the change of sequence in a stability of complexes. Thus, the nature of the change in the stability of REE complexes with arylhydrazones of benzoylacetone is related to the ion hydrolysis constants and ionic radius [10], as well as electronic configuration of REE. In addition, NaH_2L^1 complexes are characterized by higher stability. This is due to the lower negative inductive effect of $-\text{Cl}$ (NaH_2L^1) relative to $-\text{SO}_3\text{H}$ ($\text{Na}_2\text{H}_2\text{L}^2$) and $-\text{NO}_2$ (NaH_2L^3), as well as the partially positive mesomeric effect of the chlorine atom (NaH_2L^1). The effect of the electron-acceptor properties of

the introduced functional group on the stability of complexes can be illustrated by the dependence of $\lg\beta_2=f(pK_1)$ and $\lg\beta_2=f(pK_2)$, shown in Figures 1 and 2.

Figures 1 and 2 show that the characters of the variation of the logarithmic functions of $\lg\beta_2=f(pK_1)$ and $\lg\beta_2=f(pK_2)$ are the same and the stability of the corresponding complexes increases with increasing basic properties of the

ligands. It observed that considered reagents form more stable complexes with lutetium(III). This is probably due to the electronic configuration and the ionic radius of lutetium(III).

Comparison of the stability constants of REE complexes with acetylacetone and REE complexes with arylhydrazones of benzoylacetone (Table) shows that complexes with NaH_2L^1 , $\text{Na}_2\text{H}_2\text{L}^2$ and NaH_2L^3 are more stable.

The stability constants of complexes of REE with NaH_2L^1 , $\text{Na}_2\text{H}_2\text{L}^2$ and NaH_2L^3

REE	<i>i</i>	$\lg\beta_i$				Ionic radius, REE^{3+} , pm [11]
		NaH_2L^1	$\text{Na}_2\text{H}_2\text{L}^2$	NaH_2L^3	Acetylacetone [7]	
La	1	6.29±0.01	6.23±0.03	6.19±0.03	4.96	103.2
	2	12.72±0.05	12.68±0.06	12.66±0.05	8.41	
	3	—	—	—	10.91	
Ce	1	6.57±0.02	6.50±0.05	6.44±0.07	5.30	101.0
	2	12.98±0.04	12.92±0.05	12.88±0.05	9.27	
	3	—	—	—	12.65	
Pr	1	6.62±0.01	6.64±0.04	6.55±0.06	5.27	99.0
	2	13.09±0.03	13.06±0.04	12.94±0.04	9.17	
	3	—	—	—	12.7	
Nd	1	6.79±0.03	6.71±0.04	6.67±0.05	5.3	98.3
	2	13.24±0.03	13.17±0.06	13.12±0.06	9.4	
	3	—	—	—	12.6	
Sm	1	7.31±0.06	7.21±0.06	7.14±0.07	5.59	95.8
	2	13.63±0.05	13.54±0.04	13.48±0.04	10.05	
	3	—	—	—	12.95	
Eu	1	7.69±0.06	7.56±0.05	7.47±0.03	5.87	94.7
	2	14.01±0.05	13.89±0.06	13.82±0.07	10.35	
	3	—	—	—	13.64	
Gd	1	7.80±0.04	7.65±0.02	7.56±0.06	5.90	93.8
	2	14.10±0.07	13.96±0.04	13.88±0.06	10.38	
	3	—	—	—	13.79	
Tb	1	7.98±0.06	7.82±0.05	7.71±0.05	6.02	92.3
	2	14.26±0.07	14.11±0.04	14.02±0.05	10.63	
	3	—	—	—	14.04	
Dy	1	8.04±0.04	7.86±0.03	7.74±0.06	6.03	91.2
	2	14.31±0.06	14.14±0.06	14.05±0.05	10.70	
	3	—	—	—	14.04	
Ho	1	8.11±0.06	7.92±0.07	7.79±0.03	6.05	90.1
	2	14.38±0.05	14.20±0.06	14.08±0.07	10.73	
	3	—	—	—	14.13	
Er	1	8.25±0.06	8.02±0.07	7.88±0.07	5.99	89.0
	2	14.50±0.04	14.28±0.02	14.16±0.05	10.67	
	3	—	—	—	14.05	
Tm	1	8.38±0.05	8.13±0.04	8.08±0.06	6.09	88.0
	2	14.71±0.05	14.48±0.07	14.36±0.06	10.85	
	3	—	—	—	14.33	
Yb	1	8.77±0.07	8.49±0.05	8.33±0.06	6.18	86.8
	2	15.01±0.03	14.76±0.04	14.62±0.05	11.04	
	3	—	—	—	14.64	
Lu	1	8.82±0.05	8.60±0.06	8.41±0.07	6.23	86.1
	2	15.13±0.04	14.87±0.04	14.72±0.05	11.00	
	3	—	—	—	14.63

Fig. 1. Dependence of $\lg\beta_2 = f(pK_1)$. Fig. 2. Dependence of $\lg\beta_2 = f(pK_2)$.

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NADİR TORPAQ ELEMENTLƏRİNİN BENZOİLASETONUN ARİLHİDRAZONLARI İLƏ KOMPLEKSLƏRİNİN DAVAMLILIQ SABİTLƏRİNİN POTENSİOMETRİK TƏYİNİ

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Potensiometrik titrləmə metodu ilə nadir torpaq elementlərinin – La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu benzoilasetonun arilhidrazonları ilə komplekslərinin davamlılıq sabitləri təyin edilmişdir və aşağıdakı sıra üzrə dəyişir: $\text{Lu} > \text{Yb} > \text{Tm} > \text{Er} > \text{Ho} > \text{Dy} > \text{Tb} > \text{Gd} > \text{Eu} > \text{Sm} > \text{Nd} > \text{Pr}$. Komplekslərin davamlılıqları liqandların tərkibində olan funksional qrupların elektron-donor və elektron-akseptor xarakterindən asılıdır: $-\text{Cl} > -\text{SO}_3\text{H} > -\text{NO}_2$.

Açar sözlər: nadir torpaq elementləri, benzoilaseton, arilhidrazonları, davamlıq sabiti.

ПОТЕНЦИОМЕТРИЧЕСКОЕ ОПРЕДЕЛЕНИЕ КОНСТАНТ УСТОЙЧИВОСТИ КОМПЛЕКСОВ РЕДКОЗЕМЕЛЬНЫХ ЭЛЕМЕНТОВ С АРИЛГИДРАЗОНАМИ БЕНЗОИЛАЦЕТОНА

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Методом потенциометрического титрования определены константы устойчивости комплексов редкоземельных элементов – La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu с арилгидразонами бензоилацетона, которые изменяются в следующей последовательности: $\text{Lu} > \text{Yb} > \text{Tm} > \text{Er} > \text{Ho} > \text{Dy} > \text{Tb} > \text{Gd} > \text{Eu} > \text{Sm} > \text{Nd} > \text{Pr} > \text{Ce} > \text{La}$. Устойчивость комплексов зависит от электроно-донорного и электроно-акцепторного характера функциональных групп, включенных в лиганды: $-\text{Cl} > -\text{SO}_3\text{H} > -\text{NO}_2$.

Ключевые слова: редкоземельные элементы, арилгидразоны, бензоилацетон, константы устойчивости.