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Complexing ability of 2,8,14,20-tetrabenzol-sulfo-calix[4]resorcinarene in relation to Cs⁺, Pd²⁺, Ce³⁺, Eu³⁺ ions in aqueous solution

The stability constants of complexes formed in a result of interaction «host-guest» of water-soluble calix[4]resorcinarene with metal ions (Cs⁺, Pd²⁺, Ce³⁺, Eu³⁺) in ratio 1:1 and thermodynamic parameters of their formation were calculated. The dependence of the Gibbs energy change of formation of complexes on the atomic number of the element was constructed. It is shown that the value of stability constants depends on the degree of deprotonation of the rim of the calix[4]resorcinarene. It is found that the guest-cations — Ce³⁺ and Eu³⁺ are characterized by high charge density, whereby they form the complexes which are relatively strong, and more hydrated.

Key words: water-soluble calix[4]resorcinarene, complex formation, pH-metric study, stability of complexes, thermodynamics.

In recent years a sharp increase in the number of publications devoted to the design of multifunctional ligands — hetero-ditopic receptors prone to the simultaneous binding of cations and anions [1–4] is observed, this interest is due to the possibility of their usage as sensors for monitoring biological systems and the environment, etc. The ability to bind cations by calixarenes is well known. The anions, anions that act, binding of metal ions, are included in the structure of hetero-ditopic receptors which are based on calixarenes. Despite the fact that the anion play a key role in chemistry and biology, receptors negatively charged particles are poorly studied, and the design of such compounds is a current trend in modern organic chemistry.

Calix[n]resorcinarenes form complexes with organic molecules and metal cations, including 4f- and 5f-elements, and are used in the creation of catalysts for chemical reactions, extractants, chemical sensors, ion-selective electrodes, the active compounds.

In the study of the complexation oxygen containing macrocyclic compounds with metal ions has been found that the formation of stable complexes depends, firstly, on the physical-chemical characteristics of the metal (size and charge of metal ion), and secondly, on the structure and size of the macrocycle (size of cavity of macrocycle, coplanarity of oxygen atoms, their symmetrical arrangement). All the above conditions determine the effectiveness of the interaction between the metal ion and macroheterocycles.

To understand the laws of these processes it is necessary to consider the thermodynamic aspects of the chelation process of «host-guest» in solution.

Calix[n]arenes and Calix[n]resorcinarenes are the most widely used class of artificial receptors, however, the thermodynamics of complexes is not well understood. 2,8,14,20-tetrabenzol-sulfo-calix[4]resorcinarene soluble in water fairly well and dissociates stepwise to forms anion [H_{4-n}L]ⁿ⁻ in an aqueous medium. The effectiveness of the host-guest complex formation increases as a result of the ionized groups on the rim of calix[n]resorcinarene [5].

The aim of this study is to evaluate the thermodynamic stability of the complexes formed by the interaction of macrocyclic receptor with cesium (+), palladium (2+), cerium (3+), Eu (3+) ions in an aqueous solution.

Experimental

Tetrabenzol-2,8,14,20-sulfo-calix[4]resorcinarene (hereinafter referred to as L) with gross formula: $C_{52}H_{40}O_{20}S_4$ (structural formula shown in Figure 1) was used as ligand. 2,8,14,20-tetrabenzol-sulfo-calix[4]-resorcinarene was synthesized by research group of Professor Bohari Yamin in the University Kebangsaan in Malaysia.

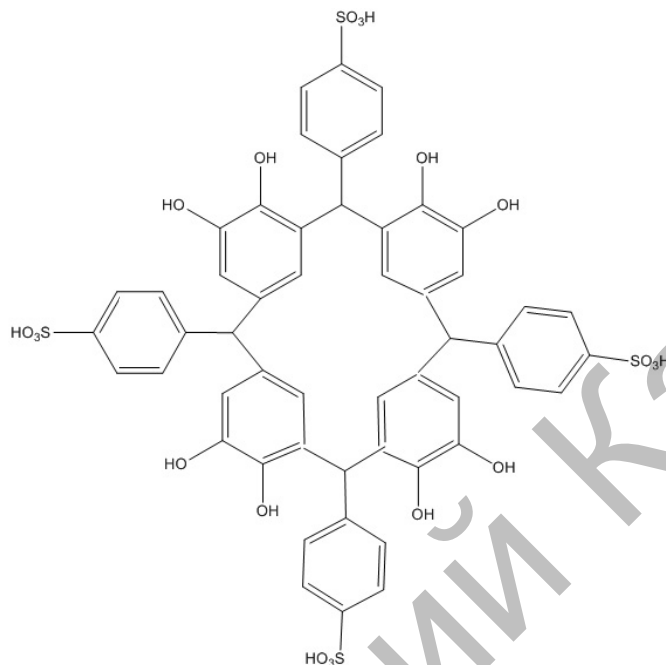


Figure 1. Structure of 2,8,14,20-tetrabenzol-sulfo-calix[4]resorcinarene

Relative molecular mass of this compound is $1109.09 \text{ g}\cdot\text{mole}^{-1}$, the results of elemental analysis, % are C (56.31), H (3.27), G (28.85), S (11.56).

Solutions containing ions of Cs^+ , Pd^{2+} , Ce^{3+} , Eu^{3+} with a concentration of $10^{-4} \text{ mole}\cdot\text{L}^{-1}$ were prepared by dissolving the corresponding salts accurately weighed CsI, PdCl_2 , $\text{Ce}_2(\text{SO}_4)_3$, $\text{Eu}_2(\text{CO}_3)_3$ in distilled water.

The ionic strength was created with the help of sodium nitrite (0; 0.1; 0.25; 0.5; 0.75; 1). Determination of the acidity constant of the ligand was carried out according to standard procedures by conductometric method [6].

pH titration was performed on a pH meter 827 Lab (Metrohm) with the help of 6.0256.600 combined electrode. The temperature was 298, 308, 318 K. The pH titration was carried out by the method of B'errum [7]. The ratio of M:L is 1:1 (on concentration and volume).

Approximation of Ulikh was used to calculate the enthalpy, Gibbs-Helmholtz equation — to calculate the entropy and the Gibbs — Gibbs free energy.

Results and discussion

The constant value of acidity equal to $5.62 \cdot 10^{-7}$ was calculated according to the conductivity depending on the concentration of ligand solutions. According to the classification of Lewis, it can be attributed to the group of bases which form characterized by higher strength complexes.

It is known that the calix[4]resorcinarene are a group of universal macrocyclic compounds capable to form complexes by type guest–host with neutral molecules and ions, and supramolecular aggregates, a specific supramolecular structure having catalytic activity. Chemical modification of these macrocycles yields new complex compounds with Cs^+ , Pd^{2+} , Ce^{3+} , Eu^{3+} ions. If we judge on the ability of complexing Cs^+ , Pd^{2+} , Ce^{3+} , Eu^{3+} ions, it should be noted that the cesium (1+) and palladium (2+) ions have a low propensity to form complexes. And cerium (3+) and europium (3+) ions belonging to the group of lanthanides react with molecules of the macrocyclic ligands and the bond preferably ionic character.

It is known [3] that the set of complexes between ionized calix[4]resorcinarenes and cations can be divided into two types: cell-like and inclusive, and as a result of polycenter electrostatic interaction between

the positively charged cations and negatively charged groups allegedly calix[4]resorcinarene complex formation should occur without any noticeable dive the metal ion into the cavity of calix[4]resorcinarenes.

The ionization calixarene rim occurs as a result of deprotonation of H₄L, leading to an increase of complexing ability with metal ions. Table 1 shows the stability constants of complexes (lgK), which are the equilibrium constants between guests-metal ions and anions [H_{4-n}L]ⁿ⁻, where n = 1–4 in aqueous solution:



Also Table 1 shows the characteristics of the ions of metal-complexing agents.

Table 1

Characteristics of ions of metal-complexing agents, lgK of complexes formed by the interaction with ligand

Complexing ion	Ionic radius (r), nm	Ion charge	Electronic configuration of the atom	lgK (298 K, I=0.1)
Cs ⁺	0.181 (CN=6) 0.202 (CN=12)	1	4s ² 3d ¹⁰ 4p ⁶ 5s ² 4d ¹⁰ 5p ⁶ 6s ¹	0.66
Pd ²⁺	0.078 (CN 4) 0.100 (CN 6)	2	4s ² p ⁶ d ¹⁰ 5s ⁰	0.70
Eu ³⁺	0.109 (CN 6)	3	4s ² p ⁶ d ¹⁰ f ⁷ 5s ² p ⁶ 6s ²	0.84
Ce ³⁺	0.115 (CN 6) 0.134 (CN 9)	3	4s ² p ⁶ d ¹⁰ f ¹ 5s ² p ⁶ d ¹ 6s ²	1.02

The results in Table 1 show that with the increasing polarizability of complexing ions the strength of formed complexes enhances.

Influence of ionic strength on the stability constants. The following figure 2 shows the stability constants of the complexes formed by the interaction of Cs⁺, Pd²⁺, Ce³⁺, Eu³⁺ ions with 2,8,14,20-tetrabenzol-sulfo-calix[4]resorcinarene.

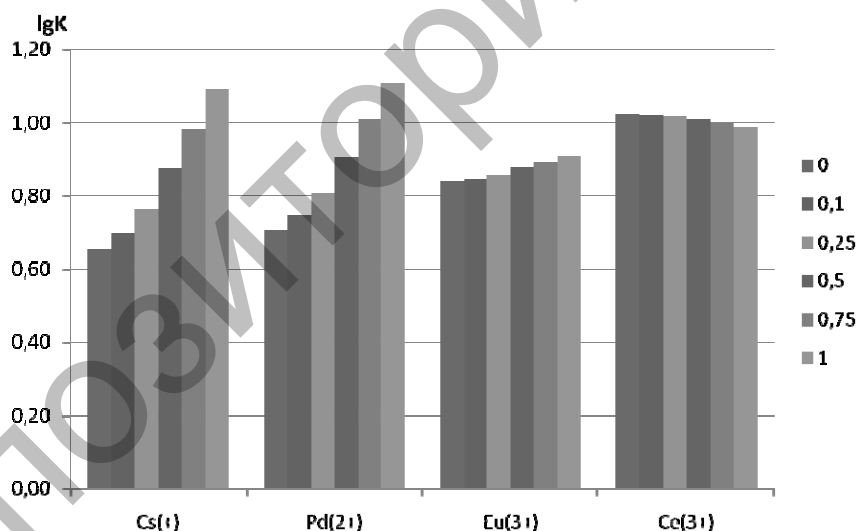


Figure 2. Dependence of the stability constants of complexes 2,8,14,20-tetrabenzol-sulfo-calix[4]resorcinarene with Cs⁺, Pd²⁺, Eu³⁺, Ce³⁺ ions under the influence of ionic strength

It is known that the effect of forming a bond «metal-ligand» is determined by interaction of metal ions with a solvent and ligand. With increasing charge and decreasing the radius of the ion-metal increases its complexing ability, which can be seen from the data, with the most stable complexes which are formed with ions of cerium (3+) and europium (3+).

The binding energy is determined as well as by the steric and electronic factors. The greater is ligand size, the more probably the occurrence of steric hindrance to the coordination of the ligand, since other ligands presenting in the system (in this case — nitrate ions, water molecules) are also involved in the complex formation. In our case, this pattern is observed for complexes Ce (3+), increasing the concentration of the supporting electrolyte reduces the strength of the formed complexes.

The reverse situation is noted in the case of cesium (+), palladium (2+), europium (3+) ions. This can be attributed to the stabilizing effect of the supporting electrolyte, caused by dehydration of the ligand and metal, as well as the formation of a negatively charged sphere of the outer contour of the complex, separating it from the solvent molecules in the bulk solution.

Moreover, cerium ion is most polarizing from the four-studied ions of metal-complexing agents hence it will be very active to attract ions of the supporting electrolyte compared to the ligand ions and palladium (2+) and cesium (+), Eu (3+) ions are less polarizable, so they increasing number of nitrate ions in the bulk solution will not have such a high impact, wherein for ions of palladium (2+) stability constants are higher at medium ionic strength, and for cesium (+) ions at high ionic strength.

Effect of temperature on the stability constants. Figure 3 shows the constant temperature resistance complexes dependence at constant ionic strength of $I = 1$.

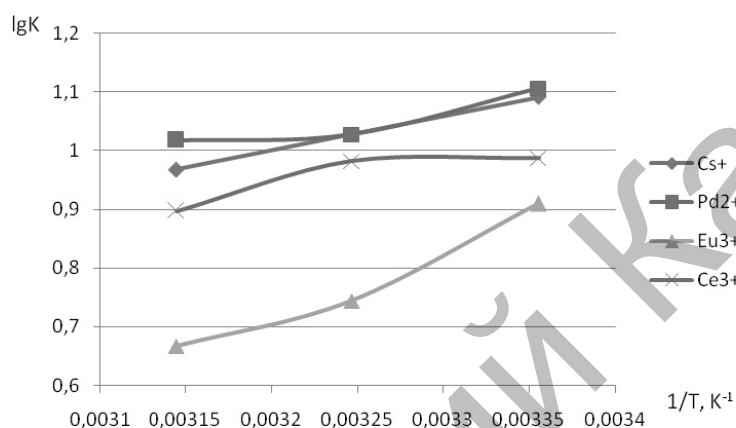


Figure 3. Dependence of the stability constants of complexes 2,8,14,20-tetrabenzol-sulfo-calix[4]resorcinarene with Cs⁺, Pd²⁺, Eu³⁺, Ce³⁺ ions from temperature

In all cases, the increase in temperature leads to the decrease in the stability of complex compounds. The value of the Gibbs energy of complexation was estimated based on the data on the stability constants. The dependence of the change in Gibbs free energy from the atomic number of element is shown in Figure 4 ($T = 298 \text{ K}$, $I = 1$).

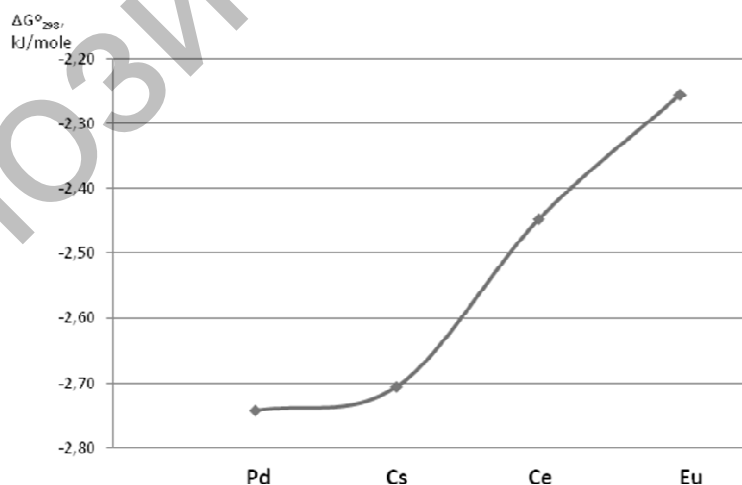


Figure 4. Dependence of Gibbs energy of formation from the atomic number of element

Thermodynamic parameters were calculated on the basis of the temperature dependence of the stability constants (Table 2).

Thermodynamic parameters of reactions of Cs^+ , Pd^{2+} , Ce^{3+} , Eu^{3+} metal ions complexes formation at 298 K

Thermodynamic parameters	Metal ion	I					
		0	0.1	0.25	0.5	0.75	1
$\Delta_r H_T^o$, $\text{kJ}\cdot\text{mole}^{-1}$	Cs^+	10.14	4.16	-4.82	-49.70	-34.74	-19.78
	Pd^{2+}	34.52	27.8	17.73	0.94	-15.84	-32.63
	Ce^{3+}	9.43	9.07	8.54	7.66	6.78	5.90
	Eu^{3+}	-109.36	-120.80	-86.55	-86.44	-93.46	-92.58
$\Delta_r G_T^o$, $\text{kJ}\cdot\text{mole}^{-1}$	Cs^+	-1.62	-1.73	-1.89	-2.16	-2.44	-2.71
	Pd^{2+}	-1.74	-1.84	-1.99	-2.24	-2.49	-2.74
	Ce^{3+}	-2.08	-2.10	-2.12	-2.17	-2.21	-2.25
	Eu^{3+}	-2.54	-2.53	-2.51	-2.49	-2.47	-2.45
$\Delta_r S_T^o$, $\text{J}\cdot\text{mole}^{-1}\cdot\text{K}^{-1}$	Cs^+	146.10	148.30	6.34	7.10	8.06	9.01
	Pd^{2+}	5.97	147.94	6.75	7.53	8.31	9.09
	Ce^{3+}	60.50	148.63	74.03	88.78	103.53	118.28
	Eu^{3+}	8.15	8.08	8.15	8.07	7.97	7.90

Transition from endothermic to exothermic effect with increasing ionic strength indicates metal-ligand bond strength increase; negative values of Gibbs energy change of complex formation also confirm a relatively high resistance to dissociation of the complex in solution. It can be assumed that polycenter electrostatic interactions of cations of cesium and palladium with negatively charged rim require greater desolvation calix[4]resorcinarene (according to equation (1)) than the interaction with cations of cerium and europium.

Conclusion

In general, increasing the concentration of the supporting electrolyte leads to an increase in entropy systems containing ions of Cs^+ and Pd^{2+} , is apparently due to the fact that in these cases the formation of complexes cell-like type since this process is entropically favorable process ($\Delta S > 0$). While guests-cations of Ce^{3+} and Eu^{3+} are characterized by high charge density, whereby they form the complexes are relatively strong, and more hydrated.

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2,8,14,20-Тетрабензол-сульфо-каликс[4]резорцинареннің сулы ерітіндіде Cs^+ , Pd^{2+} , Ce^{3+} , Eu^{3+} иондарына қатысты комплекс түзу қабілеті

Суда еритін каликс[4]резорцинареннің металл иондарымен (Cs^+ , Pd^{2+} , Ce^{3+} , Eu^{3+}) әрекеттесуі нәтижесінде «ие-қонақ» (1:1 қатынасында) комплекстердің тұрақтылық константалары және түзілу процестерінің термодинамикалық параметрлері есептелді. Комплекстердің түзілуінің Гиббс

энергиясы өзгеруінің элементтің реттік нөмірінен тәуелділігі тұрғызылды. Тұрақтылық константасының шамасы каликс[4]резорциареннің жиегінің депротондану дәрежесіне тәуелді екені көрсетілді. Ce^{3+} и Eu^{3+} қонақ-катиондарының заряд тығыздығы жоғары болғандықтан, олар түзетін комплекстер салыстырмалы тұрақты және гидратталуы жоғарырақ болады.

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Комплексообразующая способность 2,8,14,20-тетрабензол-сульфо-каликс[4]резорциарена по отношению к ионам Cs^+ , Pd^{2+} , Ce^{3+} , Eu^{3+} в водном растворе

Были рассчитаны константы устойчивости комплексов и термодинамические параметры процессов комплексообразования «хозяин-гость» (в соотношении 1:1) при взаимодействии водорастворимого каликс[4]резорциарена с ионами металлов (Cs^+ , Pd^{2+} , Ce^{3+} , Eu^{3+}). Построена зависимость изменения энергии Гиббса образования комплексов от порядкового номера элемента. Показано, что величина константы устойчивости зависит от степени депротонизации ободка каликс[4]резорциарена. Установлено, что гости — катионы Ce^{3+} и Eu^{3+} характеризуются высокой плотностью заряда, за счет чего образуемые ими комплексы являются относительно прочными и более гидратированными.

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