

Merrifield resin modified with thiacalixarene-tetraphosphonates: synthesis, characterization and europium sorption

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Tetrahydroxythiacalixarene tetraphosphonates were synthesized and chemically linked to chloromethylated polystyrene (Merrifield resin) surface via the Williamson reaction. In order to evaluate the effect of thiacalixarene platform structure on the properties of sorbents, phosphorylated resins with P=O groups attached to the polymer surface via methylene spacers were synthesized by the Arbuzov reaction of the iodomethylpolystyrene with trialkylphosphites. Composition and structure of the obtained materials was established by elemental analysis and IR spectroscopy. The sorbents obtained remove up to 99 % of Eu(III) ions from aqueous solutions of average mineralization level at pH of 5.5–6. The optimum contact time was established to be 2 h. Due to cooperative (macrocyclic) effect of P=O binding groups pre-organized at the upper rim of the thiacalixarene platform the resins exhibit better uptake parameters than the resins modified with para-unsubstituted, para-*tert*-butylsubstituted thiacalixarenes or the resins bearing the phosphonate groups directly bound to the Merrifield resin surface. Europium distribution coefficient for the best sorbents obtained was equal to 11.3.

Keywords: supramolecular chemistry, thiacalixarenes, phosphonates, Merrifield resin, lanthanides, sorption, radioactive wastes.

Синтезированы тетрагидрокситиакаликсарен-тетрафосфонаты, способные к химическому связыванию с поверхностью хлорметилированного полистирола (смолы Меррифилда) при помощи реакции Вильямсона. Для оценки влияния структуры тиакаликсарена на свойства сорбентов, с помощью реакции Арбузова между иодметилполистиролом и триалкилфосфонатами синтезированы фосфорилированные смолы с P=O группами, связанными с поверхностью полимера посредством метиленовых мостиков. Состав и структура полученных сорбентов охарактеризованы при помощи элементного анализа и ИК-спектроскопии. Полученные сорбенты позволяют извлекать до 99 % ионов Eu(III) из водных растворов средней минерализации при pH 5,5–6. Оптимальное время контакта сорбента с раствором — 2 часа. Благодаря кооперативному (каликсареновому) эффекту P=O групп, которые находятся на верхнем ободе тиакаликсаренов, для смол, модифицированных тиакаликсаренами получены лучшие параметры сорбции, чем для полимеров, модифицированных фосфонатными группами. Коэффициент распределения ионов европия для лучших образцов сорбентов составляет 11.3 л/г.

Смола Мерифілда модифікована тетрагідрокситіакаліксарен-тетрафосфонатами: синтез, властивості та сорбція іонів Європію. М.С.Лукашова, К.М.Беліков, К.Ю.Брильова, С.Г.Харченко, С.Г.Вишневецький, В.І.Кальченко.

Синтезовано тетрагідрокситіакаліксарен-тетрафосфонати, здатні до хімічного зв'язування з поверхнею хлорометильованого полістирену (смоли Меррифільда) за реакцією Вільямсона. Для оцінки впливу структури тіакаліксаренових платформ на властивості сорбційних матеріалів, за реакцією Арбузова між ідометилполістиреном та триалкілфосфонатами отримано фосфорильовані полімери з P=O групами, приєднані метиленовими групами до полімерної поверхні. Склад та структуру отриманих матеріалів встановлено за допомогою елементного аналізу та ІЧ-спектроскопії. Отримані сорбенти дозволяють вилучати до 99 % іонів Eu(III) з водних розчинів середньої мінералізації при pH 5,5–6. Оптимальний час контакту сорбенту з розчином — 2 год. Завдяки кооперативному (каліксареновому) ефекту P=O груп, що знаходяться на верхньому ободі тіакаліксаренів, для смол, модифікованих тіакаліксаренами, отримано кращі параметри сорбції, ніж для полімерів, модифікованих фосфонатними групами. Коефіцієнт розподілу іонів Європію для кращих зразків сорбентів становить 11.3 л/г.

1. Introduction

Development of nuclear energetics resulted in accumulation of large amounts of medium and high activity radioactive liquid wastes, which require effective methods of processing and safe storage [1, 2]. Long-lived actinides and lanthanides, including americium, plutonium and europium, are the most hazardous constituents of wastes [3, 4].

Selective separation of actinides and lanthanides from spent nuclear fuel, containing considerable amounts of metal ions, is a challenging scientific and technical problem. Industrial processes of actinide and lanthanide extraction use monodentate phosphororganic ligands like tributylphosphate, trialkylphosphine oxides, di-2-ethylhexylphosphoric acid and bidentate carbamoylphosphine oxides [5]. However, low extraction efficiency and poor selectivity are sufficient drawbacks of these compounds.

Calixarenes and thiacalixarenes, functionalized with receptor moieties of the

aforementioned ligands, are known to be highly selective macrocyclic extracting agents [6–8]. In the modified calixarenes, P=O groups are pre-organized to provide cooperative binding of actinide or lanthanide in the presence of coexisting metals [9, 10].

For the radionuclides removal various extraction [11, 12] and sorption [13, 14] techniques are proposed. Although sorption technology is advantageous over extraction schemes in hardware implementation, fabrication of highly selective porous sorbents with developed surface, high chemical and radiochemical stability, mechanical strength and reuse potential is a complicated issue.

The present work reports the method for chemical modification of Merrifield resin with tetrahydroxythiacalixarene tetraphosphonates **1–3**, exhibiting effective binding of actinide and lanthanide ions via cooperative effect of P=O groups on the upper rim or via chelating the ions by spatially close sulfur and oxygen atoms on the lower rim [15] (Fig. 1). The modified resins were shown to be effective sorption material for

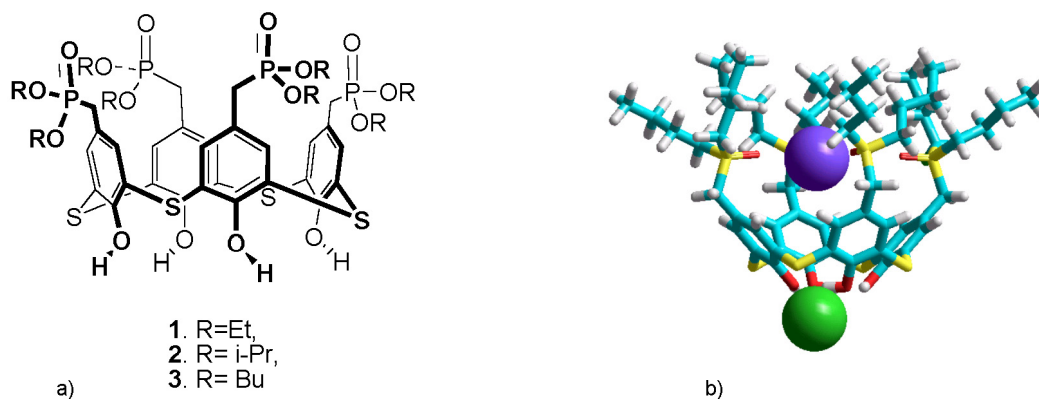
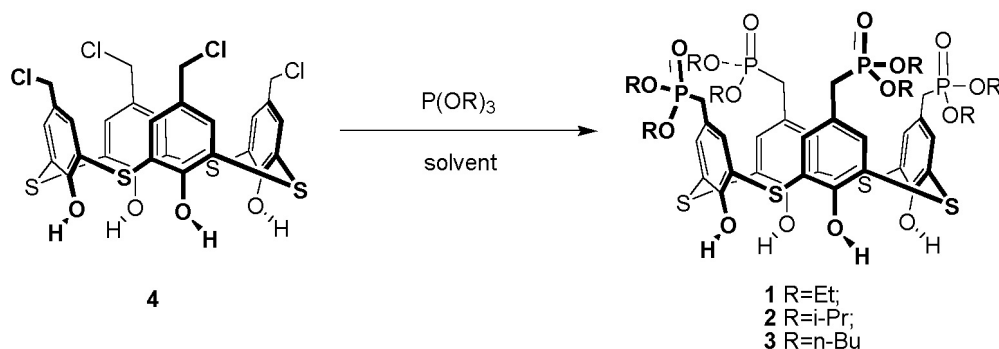


Fig. 1. Molecular structure of tetrahydroxythiacalix[4]arene tetraphosphonates **1–3** and schematic representation (a) their complexes with spherical lanthanide or actinide ions (b).



Scheme 1. Synthesis of tetrahydroxythiacalix[4]arene-tetraphosphonates 1–3.

Eu(III) recovery from natural waters with the average mineralization level.

2. Experimental

Materials and reagents

Tetrahydroxythiacalixarenes **5**, **6** were prepared according to the published procedures [15]. Chloromethyltetrahydroxythiacalixarene **4** was synthesized as described earlier [16]. Merrifield resin (200–400 mesh) with active chlorine content of 2.0 mmol/g was purchased from Polymer Labs. Dichloromethane was distilled over phosphorus pentoxide, DMF was distilled over calcium hydride. All reactions were carried out under dry argon.

¹H and ³¹P NMR spectra were recorded on a Varian VXR spectrometer operating at 300 MHz and 121.5 MHz, respectively. Chemical shifts are reported using internal tetramethylsilane and external 85 % H₃PO₄ as references. IR spectra were recorded in KBr tablets using Spectrum One (Perkin Elmer) spectrometer. Melting points were determined on a Boetius apparatus and are uncorrected.

For adsorption experiments, Eu(III) standard solution, prepared from Eu₂O₃ (Merck KGaA, Germany), was used. Ammonia solution (25 vol. %), nitric acid and hydrochloric acid were used for pH adjustment. Model solutions were prepared using deionized water. In the experiments with natural waters, groundwater containing (mg/L) 100 Ca²⁺, 30 Mg²⁺, 120 Na⁺, 11 K⁺, 1 Sr²⁺, 0.1 Fe(total), 44 Cl⁻, 12 NO₃⁻, 144 SO₄²⁻, 420 HCO₃⁻ was used.

Eu(III) concentration in solutions was monitored by method of inductively-coupled plasma atomic emission spectrometry (ICP-AES) using Trace Scan Advantage spectrometer (Thermo Jarrell Ash, USA). Bulk phase pH was measured by pH-150 instrument (Belarus). The surface morphology of sorbent particles was studied using MC-50

Micro optical microscope fitted with CAM V-200 video camera (Austria).

Determination of active chlorine content in the Merrifield resin

When exposed to moist air, active chloromethyl groups of Merrifield resins are hydrolyzed. So, quality control of the resin is needed before experiments. In the view of this, we suggested facile method for active chlorine determination, which was shown to be more convenient as compared to previously described techniques. The procedure includes treatment of the Merrifield resin with potassium iodide in absolute DMF at 70–80°C during 1 h followed by hydrolysis with sodium hydroxide for 4 h. Iodide concentration in the resulting mixture was determined by the Folgard method and recalculated into active chlorine.

Thiacalix[4]arene tetraphosphonates **1–3** were obtained with the yield of 70–90 % by the Arbuzov reaction between chloromethylthiacalixarene **4** and trialkylphosphites (Scheme 1) [16].

Phosphorus-containing thiacalixarenes **1–3** were precipitated from reaction mixture by hexane or pentane as colorless powders. Phosphorylated derivatives **1–3** are well soluble in chloroform, dichloromethane, benzene, toluene, chlorobenzene, trifluoroacetic acid and weakly soluble in alcohols, acetonitrile, hexane, pentane and petroleum benzene. Composition and structure of phosphorylated thiacalixarenes **1–3** were studied by elemental analysis and NMR spectroscopy. The presence of the signal attributed to OH groups of tetrahydroxythiacalixarenes **1–3** in a rather weak field (δ 9.39) confirms the cone conformation, stabilized by a circular system of intramolecular hydrogen bonds at the lower rim [16].

The general procedure for the synthesis of thiacalixarene phosphonates 1–3

At the first step, phosphorylation agent such as triethylphosphite, triisopropylphosphite, tributylphosphite (32.1 mmol) was added under stirring to the suspension of chloromethyltetrahydroxythiacalix[4]arene **4** (5.0 g, 7.3 mmol) in dry dichloromethane (750 mL). The reaction mixture was stirred at ambient temperature for 4 h. Then the solvent was evaporated under vacuum at room temperature. Further, hexane (150 mL) was added into the residual mixture. The obtained precipitate was quickly filtered off and washed with hexane (2×200 mL) under vigorous stirring. The synthesized products (colorless crystals) were dried under vacuum (0.01 mm Hg) at 50°C for 2 h.

5,11,17,23-Tetrakis-(diethoxyphosphorylmethyl)-25,26,27,28-tetrahydroxythiacalix[4]arene 1.

6.7 g, 85 %. M.p. 117–120°C. ^1H NMR (300 MHz, CDCl_3): δ 1.24 (*t*, 24H, $J = 7.0$ Hz, CH_3), 2.92 (*d*, 8H, $J = 21.3$ Hz, $\text{CH}_2\text{-P}$), 4.01 (*m*, 16H, $\text{CH}_2\text{-O}$), 7.55 (*s*, 8H, H-ar.), 9.38 (*s*, 4H, OH); ^{13}C NMR (75 MHz, CDCl_3): δ 16.39 (*d*, $J = 5.0$ Hz, $\text{P-O-CH}_2\text{-CH}_3$), 32.30 (*d*, $J = 140$ Hz, P-CH_2), 62.29 (*d*, $J = 6.4$ Hz, P-O-CH_2), 120.86 (*s*, C-ar.), 125.21 (*d*, $J = 8.9$ Hz, C-ar.), 140.35 (*d*, $J = 5.6$ Hz, C-ar.), 156.86 (*s*, C-ar.); ^{31}P NMR (121 MHz, CDCl_3): δ 25.7. Calc. for $\text{C}_{44}\text{H}_{60}\text{O}_{16}\text{P}_4\text{S}_4$, %: C, 48.17; H, 5.51; P, 11.29; S, 11.69. Found, %: C, 47.90; H, 5.31; P, 11.26; S, 11.48.

5,11,17,23-Tetrakis-(diisopropoxyphosphonylmethyl)-25,26,27,28-tetrahydroxythiacalix[4]arene 2.

8.0 g, 90 %. M.p. 107–110°C. ^1H NMR (300 MHz, CDCl_3): δ 1.12 and 1.25 (two *d*, 48H, $J = 6.3$ Hz), 2.88 (*d*, 8H, $J = 21.3$ Hz, $\text{CH}_2\text{-P}$), 4.55 (*m*, 8H, CH-O), 7.55 (*d*, 8H, $J = 2.6$ Hz, H-ar.), 9.30 (*s*, 4H, OH); ^{31}P NMR (121 MHz, CDCl_3): δ 23.7. Calc. for $\text{C}_{52}\text{H}_{76}\text{O}_{16}\text{P}_4\text{S}_4$, %: C, 51.65; H, 6.33; P, 10.25; S, 10.61. Found, %: C, 51.40; H, 6.17; P, 10.06; S, 10.50.

5,11,17,23-Tetrakis-(dibutoxyphosphorylmethyl)-25,26,27,28-tetrahydroxythiacalix[4]arene 3.

6.91 g, 72 %. M.p. 101–105°C. ^1H NMR (300 MHz, CDCl_3): *elita* 0.80 (*t*, 24H, $J = 6.8$ Hz, CH_3), 1.30 (*m*, 16H, $\text{CH}_2\text{-CH}_3$), 1.54 (*m*, 16H, $\text{CH}_2\text{-CH}_2\text{-CH}_3$), 2.95 (*d*, 8H, $J = 21.3$ Hz, $\text{CH}_2\text{-P}$), 3.95 (*m*, 16H, $\text{CH}_2\text{-O}$), 7.56 (*s*, 8H, H-ar.), 9.41 (*s*, 4H, OH). ^{31}P NMR (121 MHz, CDCl_3): δ 25.9. Calc. for $\text{C}_{60}\text{H}_{92}\text{O}_{16}\text{P}_4\text{S}_4$, %: C, 54.53; H, 7.02; P,

9.38; S, 9.71. Found, %: C, 54.23; H, 6.97; P, 9.26; S, 9.70.

The general procedure for modification of the Merrifield resin with tetrahydroxythiacalixarenes

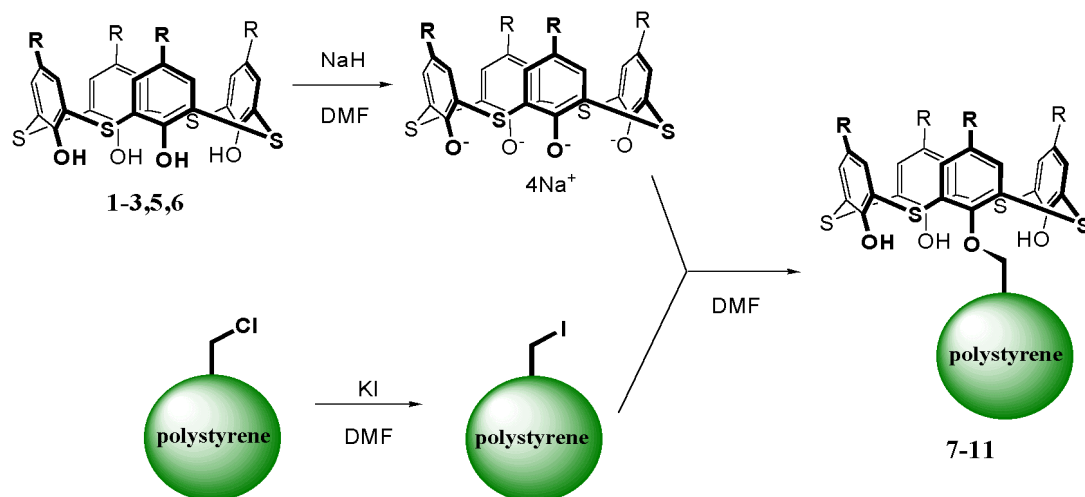
The Merrifield resin (1.00 g) was suspended in absolute DMF (20 ml) and potassium iodide (0.32 g, 2.0 mmol) was added into the suspension. The mixture was stirred at 70–80°C for 1 h. The resulting iodomethylpolystyrene was reacted with solution of tetrahydroxythiacalixarene **1–3,5,6** sodium salts, which were obtained by treatment of the corresponding tetrahydroxythiacalixarene (1.5 mmol) with sodium hydride (0.144 g, 6.0 mmol) in DMF (15 mL). The reaction mixture was stirred at 70–80°C for 72 h. The modified resin was filtered off, successively washed with DMF (×10 mL), 2 % hydrochloric acid solution (3×10 mL), distilled water (3×20 mL) and methanol (3×15 mL), dried under vacuum at 0.1 mm Hg to constant weight. Content of the thiacalixarene, covalently attached to the polymer matrix, was determined by elemental analysis.

The general procedure for phosphorylation of the Merrifield resin

Potassium iodide (0.30 g, 2.0 mmol) was added to suspension of the Merrifield resin (1.00 g) in absolute DMF (20 mL) and the mixture was stirred at 70–80°C for 1 h. The polymer was filtered off and dried under vacuum at 0.1 mm Hg to constant weight. The phosphorylation agent (triethylphosphite, triisopropylphosphite, tributylphosphite) (50 mmol) was added to the obtained polymer. The resulting suspension was heated under argon atmosphere at 125–150°C for 48 h. The synthesized resin was filtered off and successively washed with DMF (3×10 mL), 2 % hydrochloric acid solution (3×10 mL), distilled water (3×20 mL) and methanol (3×15 mL), dried under vacuum at 0.1 mm Hg to constant weight. The content of grafted phosphonate groups was determined by elemental analysis.

The sorption study

The study of sorption properties of the obtained materials towards Eu(III) ions was undertaken in batch mode in both single-component model solutions and spiked natural waters. For the experiment, the prepared sorbent was put in contact with 20 mL of feed solution with Eu(III) concentration of 10 mg/L. The required pH values were adjusted by adding nitric acid or ammonia solutions. Eu(III) concentration was



Scheme 2. Synthesis of thiacalixarene-containing Merrifield resins 7–11.

measured in both initial and supernatant solutions. The equilibration time was established to be 3 h. The sorption recovery value was estimated according to Eq. 1:

$$R = \frac{C_0 - C_e}{C_0} \cdot 100, \quad (1)$$

where C_0 — ion concentration in the initial solution, C_e — equilibrium concentration.

The sorption kinetics was studied in model solutions. In the experiments, 0.1 g of the sorbent was contacted with 20 mL of single-component solution with Eu(III) concentration of 10 mg/L. The study was undertaken at determined optimum pH level of bulk phase.

The dependence of recovery rate on contact time of the modified sorbent with the feed solution was simulated by second order equation (2):

$$\frac{dq}{dt} = k_2(q_e - q)^2, \quad (2)$$

where q — amount of the ions adsorbed per mass of the sorbent at time t , mg/g; q_e — amount of the adsorbed ions per mass of the sorbent at equilibrium, mg/g; t — contact time, min; k_2 — the second order sorption rate constant, $\text{g} \cdot \text{mg}^{-1} \cdot \text{min}^{-1}$.

Eq. 2 is linearized to Eq. 3 to give values of q_e and k_2 from dependence of t/q on t :

$$\frac{t}{q} = \frac{t}{q_e} + \frac{1}{k_2 q_e^2}. \quad (3)$$

To determine sorption capacity value, Eu(III) concentration was varied within the range of 10–250 mg/L at constant pH of

5.5–5.6. The experimental data were treated by Langmuir isotherm equation written in linear form (4):

$$\frac{C}{A} = \frac{1}{K_L A_\infty} + \frac{C}{A_\infty}, \quad (4)$$

where C — ion concentration in solution at equilibrium, mg/L; A — equilibrium sorption capacity, mg/g; A_∞ — maximum sorption capacity, mg/g; K_L — Langmuir constant, L/mg.

The distribution coefficient values were calculated according Eq. 3:

$$D = \frac{V}{m} \cdot \frac{C_0 - C_e}{C_e}, \quad (5)$$

where D — distribution coefficient, L/g; C_0 — ion initial concentration, mg/L; C_e — ion concentration at equilibrium, mg/L; V — feed solution volume, L; m — sorbent weight, g.

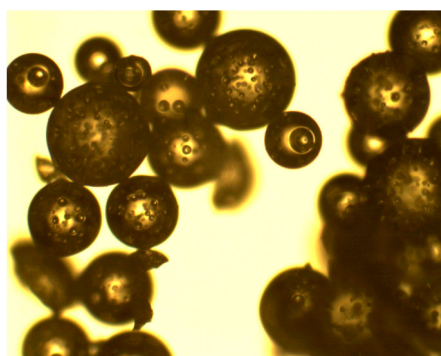
3. Results and discussion

Peculiarities of synthesis and characterization

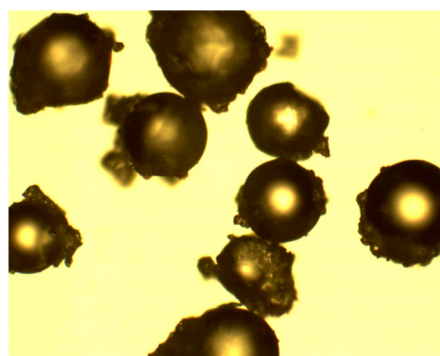
Porous silica gels and Merrifield resins, possessing developed surface with chemically active functional groups, are the most widely used substrates for synthesis of thiacalixarene-containing sorbents [17–20]. Thus, it was shown that chlorine atoms of CH_2Cl groups on the surface of Merrifield resin react with hydroxyl groups of *p*-tert-butyltetrahydroxythiacalixarene **6** via Williamson reaction in the presence of base and sodium iodide as an activator [21]. This reaction results in formation of strong chemi-

Table 1. Characterization of thiacalixarene-containing Merrifield resins 7–11.

Resin	Calixarene functional group	Elemental analysis				Thiacalixarene content, mmol/g of polymer	Bands in IR spectra, cm ⁻¹	
		C	H	S	P		ν_{OH}	$\nu_{\text{P=O}}$
7	CH ₂ P(O)(OEt) ₂	78.6	6.9	2.1	1.10	0.16	3375	1248
8	CH ₂ P(O)(OPr- <i>i</i>) ₂	86.4	7.2	0.9	2.1	0.12	3358	1249
9	CH ₂ P(O)(OBu) ₂	77.5	7.3	2.7	2.0	0.18	3363	1251
10	H	85.2	6.8	4.5	–	0.30	3296	–
11	<i>t</i> -Bu	84.9	8.2	9.7	–	0.28	3339	–



a)



b)

Fig. 2. Microphotography of the modified Merrifield resins 11 (a) and 14 (b) (magnified 150 times).

cal bonding Ar–O–CH₂ between matrix and lower rim of thiacalixarene.

An attempt to use this method for modification of Merrifield resin with phosphorous-containing thiacalixarenes 1–3 has turned out to be unsuccessful. However, thiacalixarenes 1–3 as well as *p*-unsubstituted and *p*-*tert*-butyl substituted tetrahydrothiacalixarenes 5 and 6 react easily when potassium iodide is used as an activator to substitute chlorine atom in CH₂Cl group by active iodine atom.

Modification of the Merrifield resin was undertaken by successive addition of potassium iodide and sodium salt of tetrahydrothiacalixarene 1–3, 5, 6 obtained by treatment with sodium hydride. The reactions were performed in DMF at 70–80°C for 72 h (Scheme 2).

Composition and structure of thiacalixarene-containing resins 7–11 was confirmed by elemental analysis, IR-spectroscopy and microscopy (Table 1 and Fig. 2a).

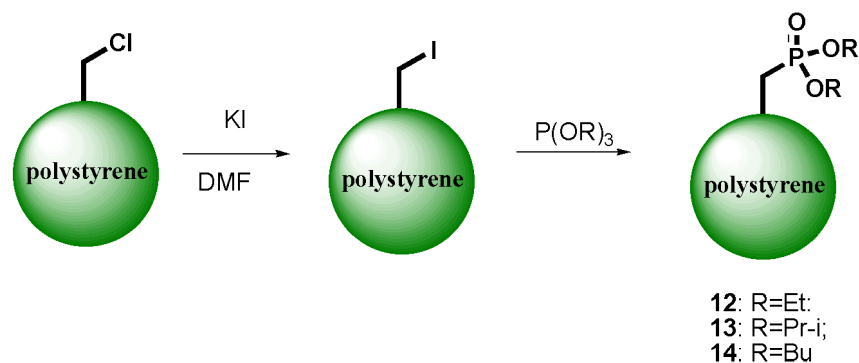
According to elemental analysis data, the content of thiacalixarenes 1–3, 5, 6 in obtained resins 7–11 is within the range of 0.12–0.30 mmol/g (Table 1). Phosphorylated thiacalixarenes 1–3 exhibit somewhat lower affinity to the resin surface as compared to

thiacalixarenes 5, 6 bearing hydrogen atoms or *tert*-butyl groups in *p*-position.

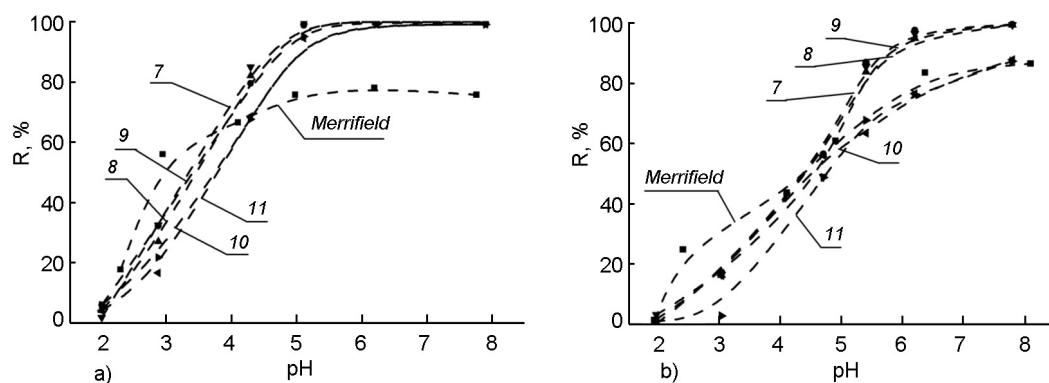
In the IR spectra of obtained materials 7–11 the shift of hydroxyl groups $\nu_{\text{acc}}(\text{OH})$ absorption band toward higher frequencies by 59 cm⁻¹ (3280 cm⁻¹) as compared to the spectra of tetrahydrothiacalixarenes 1–3, 5, 6 was observed. This shift indicates violation in circulation system of intramolecular bonds formed by OH groups, as a result of partial alkylation of hydroxyl moieties on the lower rim of the macrocycle. Also, a weak absorption bands attributed to ether groups $\nu(\text{ArOCH}_2)$ and sulfide bond of the macrocycle $\nu(\text{Ar-S-Ar})$ are observed at 1025 cm⁻¹ and 702 cm⁻¹, respectively. In the IR spectra of phosphorous-containing materials 7–9 the P=O group characteristic band is present at 1250 cm⁻¹.

In order to evaluate the effect of thiacalixarene platform structure on sorption properties of materials 7–11 we synthesized Merrifield resins 12–14 with P=O groups attached to the polymer surface via methylene spacers.

Phosphorylated resins 12–14 (Scheme 3 and Fig. 2b) were synthesized by the Arbuzov reaction of the iodomethylpolystyrene with trialkylphosphites. The reaction is performed at 125°C with an excess of the phos-

Scheme 3. Synthesis of phosphorylated Merrifield resins **12–14**.Table 2. Characterization of phosphorylated Merrifield resins **12–14**.

Resin	Calixarene functional group	Elemental analysis			P=O content, mmol/g of polymer	IR spectra $\nu_{\text{P=O}}$, cm^{-1}
		C	H	P		
12	Et	72.6	5.9	5.4	1.2	1248
13	Pr-i	70.5	6.3	6.1	1.6	1249
14	Bu	73.5	4.9	4.6	1.0	1251

Fig. 3. Effect of pH on sorption of Eu(III) ions from model solutions (a) and natural water (b) by thiacalixarene-containing Merrifield resins **7–11**.

phorylation agent. Composition and structure of the obtained materials was established by elemental analysis and IR spectroscopy method (Table 2). According to the elemental analysis results, content of P=O groups in the resin is within the range of 1.0–1.6 mmol/g. In the IR spectra of compounds **12–14** the characteristic $\nu(\text{P=O})$ band is observed at 1120 cm^{-1} .

Sorption properties of the modified resins

Sorption efficiency of the prepared resins towards Eu(III) ions was studied at different pH and Eu(III) concentration. It was shown that Eu(III) uptake achieves maximum at pH 5.5–6 giving a values of 96–99 % in both model solutions (Fig. 3a) and natural waters (Fig. 3b) for thiacalixarene-containing Mer-

Table 3. Sorption kinetics of Eu(III) ions by the Merrifield resins modified with thiacalixarene-tetraphosphonate (**8**) or phosphonate (**13**) moieties as treated by pseudo-second order model.

Resin	(8)	(13)
r^2	0.99	0.97
q_e , mg/g	43	25
k^2 , $\text{g}\cdot\text{mg}^{-1}\cdot\text{min}^{-1}$	0.01	0.04

rifield resins **7–11** and 96–98 % in the case of phosphorylated Merrifield resins **12–14** (Fig. 4). As it is seen from Fig. 3 and Fig. 4, there is notable difference between thiacalixarene-modified Merrifield resin and the P=O-capped polymer uptake behavior. Obvi-

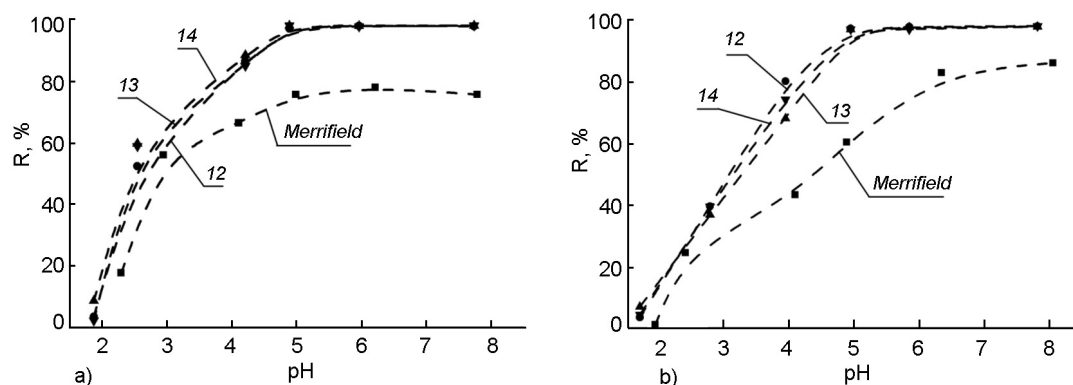


Fig. 4. Effect of pH on sorption of Eu(III) ions from model solutions (a) and natural water (b) by phosphorylated Merrifield resins **12–14**.

ously, this trend indicates strong cooperative effect of thiacalixarene moieties attached to the surface of Merrifield resin.

A series of sorption kinetic experiments were also performed. The optimum contact time was established to be 2 h (Fig. 5). The data obtained are summarized in Table 3. As it can be seen, the sorption kinetics is well described by pseudo-second order model (2). It can be assumed that the sorption process occurs in two steps. First, a rapid Eu(III) ions complexation by calixarene receptor molecules takes place on the sorbent surface, while the second step involves physical adsorption by polymeric support. However, the isolated contributions of the steps cannot be determined.

Equilibrium sorption capacity A , correlation coefficients r^2 and europium distribution coefficients D for Merrifield resins **7–14** are presented in Table 4. The obtained sorption isotherm shows good correlation with Langmuir theory. Evidently, sorption process occurs via formation of ion monolayer on the sorbent surface at energetically

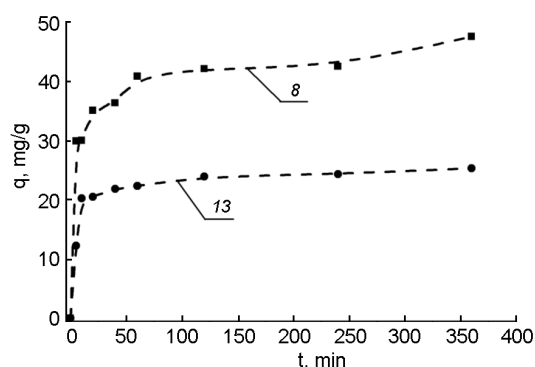


Fig. 5. Sorption kinetics of Eu(III) ions by the Merrifield resins modified with thiacalixarene-tetraphosphonate (**8**) or phosphonate (**13**) moieties.

equivalent sorption sites. As it can be seen, the resins **7–9** modified with thiacalixarene-phosphonates **1–3** exhibit better sorption performance comparing to resins **10, 11**, modified with *p*-unsubstituted or with *p*-*tert*-butyl substituted thiacalixarenes

Table 4. Equilibrium sorption capacity A and europium distribution coefficients D for Merrifield resins **7–14**.

Resin	Calixarene functional group	Single-component solution			Natural water		
		r^2	$A_{in} / [ES SA g EBB 3K], \text{ mg/g}$	$D, \text{ L/g}$	r^2	$A_{\infty}, \text{ mg/g}$	$D, \text{ L/g}$
7	$\text{CH}_2\text{P}(\text{O})(\text{OEt})_2$	0.95	37.2	5.1	0.97	41.4	4.4
8	$\text{CH}_2\text{P}(\text{O})(\text{OPr-i})_2$	0.98	71.4	11.3	0.99	76.9	4.6
9	$\text{CH}_2\text{P}(\text{O})(\text{OBu})_2$	0.89	31.3	11.3	0.91	37.3	5.3
10	H	0.98	24.8	2.3	0.95	26.0	5.5
11	<i>t</i> -Bu	0.96	37.0	7.1	0.99	17.5	3.6
12	Et	0.92	25.0	5.1	0.98	23.8	1
13	Pr-i	0.97	35.5	0.8	0.99	33.5	3.4

5, **6** with polymer **8** having superior sorption performance among the tested materials. In model solutions, resin **11** exhibits sorption characteristics, comparable to those obtained for polymers **7** and **9**. However, in the natural water, the values of A_{if} and D decrease substantially, pointing out poor specificity of butyl-substituted calixarenes in scavenging Eu(III) ions. The resins **12–14** possessing phosphonyl groups directly attached to the polymer surface were shown to be less effective as comparing with resins **7–9**. This trend can be explained in terms of the cooperative binding of europium cation with four P=O groups preorganized on the thiacalixarene macrocyclic platform.

Estimation of the P=O/Eu ratio in resins **7–9** and **12–14** turned out to be impossible in the view of additional Eu(III) sorption by polystyrene matrix.

4. Conclusions

Merrifield resins, possessing chemically linked tetrahydroxythiacalixarene phosphonate moieties were shown to be effective sorbents for selective removal of Eu(III) from aqueous solutions with average mineralization level at pH 5.5–6. Due to cooperative (macrocyclic) effect of the upper rim P=O groups the thiacalixarene tetraphosphonate resins exhibit better uptake parameters than the resins chemically modified with *p*-unsubstituted or *p*-*tert*-butylsubstituted thiacalixarenes or the resin bearing the phosphonate groups directly bound to the polymer surface.

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