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Brief Communications

Sorbents based on calix[4]arenes for extraction of technetium(VII) from acidic and alkaline media

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Sorption of Tc^{VII} from solutions of various compositions with new sorbents prepared by the noncovalent immobilization of (thia)calix[4]arenes on the Amberlite XAD-7^{TM} support was studied. The sorbents studied efficiently extract technetium(VII) from both acidic and alkaline media. The sorption capacity of the sorbent with thiacalix[4]arene groups is superior to that of the sorbents with calix[4]arene groups and several times higher than that of the sorbents previously proposed for the sorption of Tc^{VII}. Technetium(VII) is sorbed by this sorbent as 1 : 1 and 1 : 2 thiacalix[4]arene—NH_4TcO_4 and 1 : 1 and 1 : 2 thiacalix[4]arene—$NaTcO_4$ complexes.

Key words: sorbents, calix[4]arenes, thiacalix[4]arenes, extraction of technetium, polymer support Amberlite XAD-7^{TM}.

Increased interest in technetium (Tc) is due to its long half-life period. The fission products of uranium accumulate a large fraction of Tc (up to 0.9 kg per ton of U). Moreover, Tc^{VII} shows specific chemical behavior, first of all, the high migration activity in aqueous systems under oxidative conditions.[1] From the viewpoint of environmental problems, technetium is an important radionuclide, which can substantially increase the total radiation dose to the public resulted from the expansion of the world´s nuclear power sector. However, no efficient methods for the fractional isolation and utilization of Tc have not yet been proposed. Therefore, the development of efficient methods of its detection, concentrating, and isolation from solutions of various compositions remains urgent. Since natural objects contain Tc^{VII} in very low concentrations, the task of its concentrating seems primary.

It is known that technetium(VII) is efficiently extracted from aqueous solutions in a wide pH range by polymer sorbents containing groups of macrocyclic compounds, including calix[n]arenes and thiacalix[4]arenes.[2,3,4]

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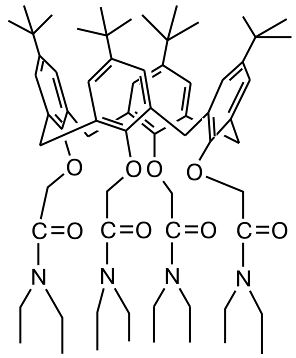

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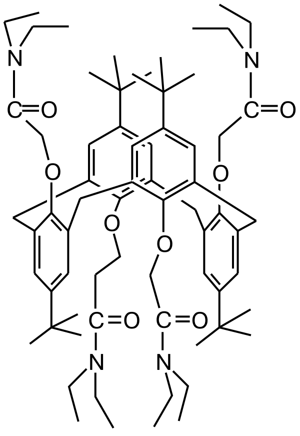

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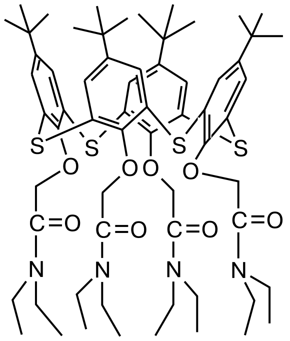

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A whole series of complexation agents based on calix[4]arenes capable of binding diverse cations with great selectivities has been synthesized in recent years.[5,6] In this connection, for the sorption of Tc^{VII} we proposed polymer sorbents of the new type, which are rather simply prepared by the noncovalent immobilization of calix[4]arenes on the polymer Amberlite XAD-7^{TM} that has proved an adequate support.

Sorbents *1—3*, which were prepared by the immobilization of calix[4]arenes on the support Amberlite XAD-7^{TM}, contain the following compounds: 5,11,17,23-tetrakis(*tert*-butyl)-25,26,27,28-tetrakis[(*N*,*N*-diethylcarbamoyl)methoxy]calix[4]arene in conformation *cone* (**1**), 1,3-*alternate* (**2**), and 5,11,17,23-tetrakis(*tert*-butyl)-25,26,27,28-tetrakis[(*N*,*N*-diethylcarbamoyl)methoxy]-2,8,14,20-tetrathiacalix[4]arene in conformation *cone* (**3**).

Calix[4]arenes **1—3** were synthesized according to the previous procedures,[7,8,9] and their constants and spectral data correspond to those presented in the literature.

Experimental

Preparation of sorbents. The corresponding calix[4]arene (0.15 g) was dissolved in propan-2-ol (5 mL) at 50 °C. Dried resin XAD-7^{TM} (1.5 g) was added by small portions to the solution with stirring. The obtained mixture was stirred for 60 min at 50 °C and dried for 2 h *in vacuo* (12 Torr) at 50 °C with stirring and in a desiccator at 100 °C to a constant weight. Sorbents *1—3* were obtained in an amount of 1.65 g each. The calculated content of calix[4]arenes on the resin was 0.26 mmol g^{-1}.

The sorption of Tc^{VII} was carried out under static conditions at the ratio of the solution volume and sorbent weight $V : m = 100$ mL g^{-1}. The time needed to establish the sorption equilibrium was 2 h, the initial concentration of Tc^{VII} was 10^{-5} mol L^{-1}, and ^{99}Tc was used as an aqueous solution of NH_4TcO_4. The determination of Tc^{VII} was carried out radiometrically in solution before and after sorption by the β-activity using a Beckman-4900 liquid scintillation spectrometer. The distribution coefficient (K_d, mL g^{-1}) of technetium(VII) was calculated from the data.

Results and Discussion

The study of the dependence of the amount sorbed on the nitric acid concentration showed that all the three sorbents efficiently sorbed Tc^{VII} from dilute solutions of HNO_3. Thiacalix[4]arene-containing sorbent *3* showed the best efficiency. Its distribution coefficient of Tc^{VII} at an HNO_3 concentration of 10^{-3}—10^{-1} mol L^{-1} is 10^3—10^5 mL g^{-1} (Table 1), which substantially exceeds those of calix[4]arene-containing sorbents *1* and *2* (for them K_d is $(1—3) \cdot 10^2$ mL g^{-1}). This suggests that the presence of sulfur atoms in a calix[4]arene molecule is an important conditions for efficient binding (in this case, sorption) of Tc^{VII}. The sorption of Tc^{VII} decreases rapidly for all the three sorbents with an increase in the HNO_3 concentration above 10^{-1} mol L^{-1}. It follows from this fact that, possibly, in the sorbent phase Tc^{VII} is bound by calix-

Table 1. Distribution coefficients (K_d) for the sorption of Tc^{VII} by sorbents *1—3* with noncovalently immobilized calix[4]arenes **1—3** from solutions of various compositions at 25 °C

Medium (C/mol L^{-1})	K_d		
	1	*2*	*3*
HNO_3 (10^{-3})	$2.7 \cdot 10^2$	$1.9 \cdot 10^2$	$1.3 \cdot 10^5$
HNO_3 (10^{-2})	$1.7 \cdot 10^2$	$3.3 \cdot 10^2$	$4.9 \cdot 10^3$
HNO_3 (0.1)	$1.1 \cdot 10^2$	$3.0 \cdot 10^2$	$3.3 \cdot 10^3$
HNO_3 (0.5)	—	$1.5 \cdot 10^2$	$3.2 \cdot 10^2$
HNO_3 (1)	31.0	$1.6 \cdot 10^2$	$1.0 \cdot 10^2$
NaOH (0.1)	62.3	$1.5 \cdot 10^2$	$4.4 \cdot 10^3$
NaOH (0.5)	$2.5 \cdot 10^2$	$3.0 \cdot 10^2$	$2.9 \cdot 10^5$
NaOH (1)	$2.7 \cdot 10^2$	$2.0 \cdot 10^2$	$1.9 \cdot 10^4$
NaOH (0.1) + $NaNO_3$ (0.1)	96.94	$1.5 \cdot 10^2$	$7.9 \cdot 10^3$
NaOH (0.5) + $NaNO_3$ (0.5)	82.1	$1.4 \cdot 10^2$	$1.3 \cdot 10^3$
NaOH (1) + $NaNO_3$ (1)	73.3	$1.4 \cdot 10^2$	$6.2 \cdot 10^2$
Water from Lake Karachai	64.0	$2.9 \cdot 10^2$	$9.2 \cdot 10^2$
Sea water	$3.0 \cdot 10^2$	$4.9 \cdot 10^2$	$8.7 \cdot 10^3$

[n]arenes as a pertechnate anion $\mathrm{TcO_4^-}$. It is possible that the decrease in sorption is caused by an increase in competition with the $\mathrm{NO_3^-}$ ion, whose concentration increases.

Since the sorbents with noncovalently immobilized groups can be considered as solid-phase extragents (SPE),[10,11] "slope of a straight line" method adopted in liquid extraction can be applied to determine the composition of the complex extracted to the sorbent phase. Therefore, to determine the solvate number of the Tc$^{\mathrm{VII}}$ complex with thiacalix[4]arene **3** extracted to the sorbent phase for its sorption from 10^{-3} mol L^{-1} $\mathrm{HNO_3}$, four sorbents with calculated amounts of thiacalix[4]arene of 0.05, 0.1, 0.15, and 0.2 mmol g^{-1} were prepared according to the above described procedure. The dependence of ratio of the distribution coefficient K_d on the content of thiacalix[4]arene **3** in the sorbent phase in the logarithmic coordinates is expressed by a straight line with a slope of 1 (Fig. 1). It can thus be inferred that the 1 : 1 thiacalix[4]arene **3**—Tc$^{\mathrm{VII}}$ complex is extracted by the sorbent phase at a technetium(VII) concentration of 10^{-5} mol L^{-1}.

The sorption isotherm of technetium(VII) from 0.1 *M* $\mathrm{HNO_3}$ (Fig. 2) by sorbent *3* containing noncovalently immobilized thiacalix[4]arene **3** is sigmoid in shape. According to the literature data, an isotherm of this type corresponds to the successive uptake of complexes of various compositions by the sorbent phase.[12] As shown above, the 1 : 1 {**3**—Tc$^{\mathrm{VII}}$} complex is extracted from 10^{-3} *M* $\mathrm{HNO_3}$ by the sorbent phase. Therefore, based on the character of the isotherm, we may assume that the 1 : 1 {**3**—Tc$^{\mathrm{VII}}$} complex is sorbed below the inflection point (at low Tc$^{\mathrm{VII}}$ concentrations), whereas the 1 : 2 complex is extracted above the inflection point. The isotherm makes it possible to estimate the capacity of the sorbent below ($1.2 \cdot 10^{-2}$ (mg of Tc) g^{-1}) and above ($6.5 \cdot 10^{-2}$ (mg of Tc) g^{-1}) the inflection point.

The study of the amount of Tc$^{\mathrm{VII}}$ sorbed by three sorbents as a function of concentration of the base and content of the salt additive (see Table 1) showed that their sorption capacity depends nonlinearly on the content of NaOH and $\mathrm{NaNO_3}$ in the solution. For sorbents *2* and *3*, the sorption maximum falls onto 0.5 *M* NaOH, but in 1 *M* NaOH the sorption of Tc$^{\mathrm{VII}}$ decreases. The amount of Tc$^{\mathrm{VII}}$ sorbed decreases in the same way upon the addition of $\mathrm{NaNO_3}$ to the studied solutions. It can be concluded that in fact the amount of Tc$^{\mathrm{VII}}$ sorbed as a function of the concentration of $\mathrm{Na^+}$ ions rather than that of the basicity of the medium. Therefore, $\mathrm{Na^+}$ ions participate in the mechanism of sorption of Tc$^{\mathrm{VII}}$. Evidently, the complexes of the calix[4]arenes with $\mathrm{NaTcO_4}$ are extracted by the sorbent phase. This explains the indirect dependence of the sorption of Tc$^{\mathrm{VII}}$ on the NaOH concentration: primarily an increase in [$\mathrm{Na^+}$] favors the sorption of technetium, but with the further increase in the NaOH concentration the sorption of Tc$^{\mathrm{VII}}$ decreases due to increasing competition with anions $\mathrm{OH^-}$. The same occurs when the concentration of ions $\mathrm{NO_3^-}$ increases upon the addition of sodium nitrate to the studied solutions.

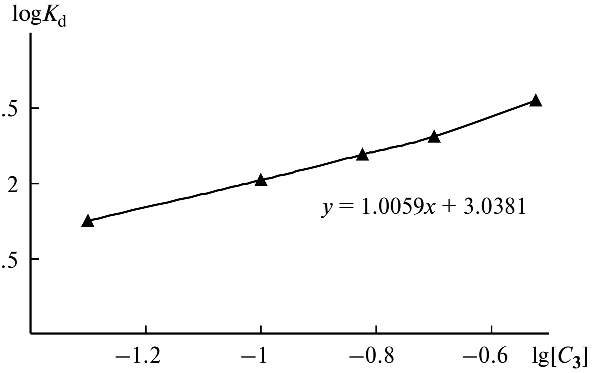

Fig. 1. Logarithm of the distribution coefficient for the sorption of Tc$^{\mathrm{VII}}$ *vs* logarithm of the content of thiacalix[4]arene **3** in XAD-7$^{\mathrm{TM}}$ (10^{-3} *M* $\mathrm{HNO_3}$, 25 °C).

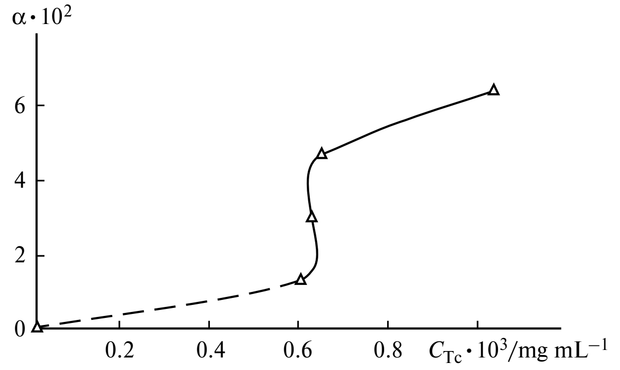

Fig. 2. Sorption isotherm of Tc$^{\mathrm{VII}}$ by sorbent *3* (0.1 *M* $\mathrm{HNO_3}$, 25 °C); α is the ratio of the amount of Tc (mg) to 1 g of the sorbent, and C_Tc is the Tc concentration in the solution after sorption.

Table 2. Compositions of solutions modeling natural waters

Sea water		Water from Lake Karachai[a]	
Compound	C_i^b/g L^{-1}	Ion	C_i^b/g L^{-1}
NaCl	11.05	$\mathrm{Na^+}$	2.0
$\mathrm{NaHCO_3}$	0.14	$\mathrm{K^+}$	0.012
$\mathrm{Na_2SO_4 \cdot 10\ H_2O}$	1.856	$\mathrm{Ca^{2+}}$	0.040
KCl	0.416	$\mathrm{Mg^{2+}}$	0.080
$\mathrm{CaCO_3}$	0.422	$\mathrm{Cl^-}$	0.060
$\mathrm{CaF_2}$	0.07	$\mathrm{HCO_3^-}$	0.0003
$\mathrm{MgNO_3 \cdot 6\ H_2O}$	1.326	$\mathrm{NO_3^-}$	0.013
$\mathrm{MgCl_2 \cdot 6\ H_2O}$	19.87	$\mathrm{NO_2^-}$	0.611
$\mathrm{Fe_2(SO_4)_3 \cdot 9\ H_2O}$	4.37	$\mathrm{SO_4^{2-}}$ [c]	0.122

[a] Nearby FGPU "PO Mayak."
[b] C_i is the concentration of an ion.
[c] Total amount.

It was shown that all the sorbents studied efficiently sorb Tc^{VII} from model solutions of water from the Lake Karachai and sea water at pH 8. The data in Table 1 indicate that the sorption of Tc^{VII} from water remains almost unchanged compared to the sorption from acidic and alkaline solutions. Therefore, the presence of alkaline and alkaline-earth metals and Fe^{3+}, as well as their counterions, in high concentrations (see Table 2), only slightly affects the efficiency of sorption of Tc^{VII} by the studied sorbents. This suggests their selectivity is high enough to find use in analytical practice.

Now we can compare the sorption properties of the novel sorbents based on calix[4]arenes with the most widely used granulated, fibrous, and inorganic sorbents. The distribution coefficients of Tc^{VII} for sorption from a weakly acidic medium (pH 3) by granulated AV-17, fibrous filled sorbent based on AV-17 (these sorbents manifested the highest sorption ability toward Tc^{VII}), and the inorganic sorbent GSK (crystalline CdS) have values of $1.1 \cdot 10^4$, $3.7 \cdot 10^4$, and 13.4 mL g^{-1}, respectively.[1] Under these conditions, the distribution coefficient K_d for the sorption of Tc^{VII} by sorbent *3* (see Table 1) is substantially higher ($1.3 \cdot 10^5$ mL g^{-1}).

Thus, it has been shown for the first time that the sorbents prepared by the noncovalent immobilization of calix[4]arenes (**1** and **2**) and thiacalix[4]arene (**3**) on the resin Amberlite XAD-7^{TM} efficiently extract technetium from both acidic and alkaline media. The capacity of the sorbent with noncovalently immobilized thiacalix[4]arene **3** exceeds that of the sorbents with immobilized calix[4]arenes **1** and **2** by two to three orders of magnitude and several times higher than the capacity of the sorbent proposed earlier for the sorption of Tc^{VII}. This allows us to recommend them, especially thiacalix[4]arene-containing sorbent *3*, for practical use. Based on the established value of the solvate number, the type of the sorption isotherm, and the dependence of the sorption of Tc^{VII} on [Na$^+$], we believe that Tc^{VII} is sorbed by this sorbent as complexes $\{\mathbf{3} \cdot NH_4TcO_4\}$ and $\{\mathbf{3} \cdot NaTcO_4\}$ and, possibly, $\{\mathbf{3} \cdot 2\, NH_4TcO_4\}$ and $\{\mathbf{3} \cdot 2\, NaTcO_4\}$.

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