Influence of the Concentrations of Potassium, Sodium, and Ammonium Ions on the Cesium Sorption with Mixed Nickel Potassium Ferrocyanide Sorbent Based on Hydrated Titanium Dioxide

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Received December 5, 2012

Abstract—The effect of single-charged cations (Na^+ , K^+ , NH_4^+) on the cesium sorption with mixed nickel potassium ferrocyanide sorbent based on hydrated TiO_2 was studied. The K^+ and Na^+ ions exert no effect at their concentrations of up to 0.5 M; the Cs^+ distribution coefficients from KCl and NaCl solutions are $(1.1 \pm 0.5) \times 10^5$ and $(8 \pm 3) \times 10^4 \text{ mL g}^{-1}$, respectively. The sorbent is highly specific to Cs^+ in the presence of ammonium ions. The sorption mechanisms were studied. The concentration ranges in which Cs^+ and NH_4^+ are sorbed by independent mechanisms (Cs^+ , by the ferrocyanide phase; NH_4^+ , by the phase of hydrated TiO_2) and in which the Cs^+ distribution coefficient decreases owing to competitive filling of the ferrocyanide phase with ammonium ions were determined. At cesium concentrations in solution exceeding 50 mg L^{-1} , Cs^+ and NH_4^+ are absorbed jointly owing to coprecipitation in the mixed ferrocyanide phase in the pore space of the sorbent.

Keywords: sorption, cesium, ferrocyanide, specificity, selectivity, mechanism

DOI: 10.1134/S1066362213040103

One of the objectives of modern chemical technology is preparation of selective sorbents capable to recover microcomponents from multicomponent salt solutions (natural or artificial) with the aim, on the one hand, to concentrate and subsequently use the valuable components of the solution and, on the other hand, e.g., to purify natural waters to the environmentally safe level without affecting their salt composition. This problem is also topical for radiochemical technology, namely, for treatment of highly saline liquid radioactive wastes and for recovery of useful individual radionuclides from multicomponent solutions. Therefore, study of the selectivity of the radionuclide sorption is of interest for the development of new sorbents.

The best sorbents for cesium recovery are transition metal ferrocyanides [1]. Their selectivity was studied in numerous works [2–8]. Milyutin [9] reported the separation factors of the Cs^+ – H^+ , Cs^+ – Na^+ , Cs^+ – Ca^{2+} , and Cs^+ – Mg^{2+} pairs for a wide range of inorganic sorbents including several kinds of ferrocyanides. It was shown that the Cs^+ sorption with transition metal ferrocyanides is not quite selective and that the selectivity of ferrocyanide sorbents depends on the procedure of

their preparation (precipitation followed by granulation, impregnation, preparation of composite sorbents, chemical deposition onto a support). The majority of published papers dealt with the Cs^+ sorption from solutions containing Na^+ ions. Data on the selectivity of the Cs^+ sorption with ferrocyanides in the presence of K^+ and NH_4^+ ions are virtually lacking, despite the fact that specifically these ions will exert the strongest effect on the Cs^+ sorption because of the closeness of their ionic radii to that of Cs^+ . The affinity series for ferrocyanides can be presented as $\text{Na}^+ < \text{K}^+ < \text{NH}_4^+$.

This study deals with the influence of the K^+ , Na^+ , and NH_4^+ concentrations on the sorption of Cs^+ with mixed nickel potassium ferrocyanide sorbent based on hydrated TiO_2 (T-55 sorbent). The sorbent preparation procedure is described in [10].

EXPERIMENTAL

The effect of the K^+ , Na^+ , and NH_4^+ ions on the specificity of T-55 sorbent to Cs^+ was studied without isotopic carrier (the Cs^+ concentration is determined by the concentration of the microcomponent, ^{137}Cs). Batch experiments were performed with ^{137}Cs -spiked

Fig. 1. Cs^+ distribution coefficient on T-55 sorbent as a function of the activity of single-charged cations. (a) K^+ and (b) Na^+ .

aqueous solutions. The concentrations of the interfering ions were set with NaCl, KCl, and NH_4Cl solutions. The active concentration of the cations was varied from 9.88×10^{-5} to 0.3 M, and the ionic strength, from 0.0001 to 0.5 M. The phase contact time was 1 week. Samples were analyzed radiometrically with a UMF-2000 α, β -radiometer equipped with a semiconductor detector.

Because of the revealed effect of NH_4^+ on the Cs^+ recovery with the sorbent, the sorbent specificity to Cs^+ was additionally studied in a wider range of NH_4^+ concentrations (up to 2 M) and at different Cs^+ concentrations (without isotopic carrier and at Cs^+ concentrations of 10^{-3} and 100 mg L^{-1}). The Cs^+ concentration was set with a CsCl solution. The choice of Cs^+ concentrations is associated with the presence of three types of sorption sites in T-55 sorbent [10], characterized by different distribution coefficients of Cs^+ and different ranges of Cs^+ concentrations in which these sites realize their capacity, and also with different mechanisms of Cs^+ sorption. It was of interest to study the selectivity of each kind of sorption sites.

To calculate the activity coefficients f and activities (a , M) of the ions, we used the improved Debye–Hückel equation [11]

$$\log f = Az_i^2 \mu^{1/2} / (1 + aB\mu^{1/2}),$$

where μ is the solution ionic strength; z_i , ion charge; A and B , constants depending on temperature and dielec-

tric permittivity of the solvent (for water at 298 K, $A = 0.512$, $B = 0.328$); a , empirical constant taking into account the ion size and characterizing the mean distance at which the solvated ions approach each other, assuming that they are hard spheres.

The calculated activity coefficients f are well consistent with the tabulated values of the activity coefficients of ions in aqueous solutions at 25°C and equal ionic strengths [12].

To study the variation of the selectivity to NH_4^+ in the course of surface modification of hydrated TiO_2 (T-5 grade) to obtain mixed nickel potassium ferrocyanide (T-55 sorbent), we obtained isotherms of the NH_4^+ sorption from NH_4Cl solutions without Cs^+ . The ratio of the solution volume to the sorbent weight was 50 mL/75 mg. To determine the NH_4^+ concentration in the solution, we used an I-160MI laboratory ion meter equipped with an ELIS-121 NH_4 electrode. T-5 sorbent (Thermoxid Research and Production Company) was used in the ammonium form and preliminarily calcined at 400°C .

We also studied the dependences of the NH_4^+ distribution ratios on the Cs^+ concentration in the solution. The initial NH_4^+ concentration in the solution was 0.05 M. The Cs^+ concentration was varied from 1×10^{-5} to 10000 mg L^{-1} . The ratio of the solution volume to the sorbent weight was 50 mL/100 mg. T-5 and T-55 sorbents after sorption were examined by IR spectrometry using a Vertex-70 IR–Raman spectrometer with RAM-II attachment (Bruker, Germany).

RESULTS AND DISCUSSION

A study of the effect of single-charged cations on the Cs^+ specificity of T-55 sorbent showed that only NH_4^+ cation competed with Cs^+ in sorption. The logarithm of the Cs^+ distribution coefficient ($\log K_d$) on T-55 sorbent is plotted in Fig. 1 vs. logarithm of the activity ($\log a$) of K^+ and Na^+ ions in solution.

We revealed no effect of K^+ and Na^+ ions in the examined concentration range (up to 0.5 M) on the Cs^+ sorption with mixed nickel potassium ferrocyanide sorbent based on hydrated TiO_2 . The Cs^+ distribution coefficients determined from KCl and NaCl solutions coincide within the uncertainty and amount to $(1.1 \pm 0.5) \times 10^5$ and $(8 \pm 3) \times 10^4 \text{ mL g}^{-1}$, respectively.

The results we obtained are well consistent with published data on sorption of alkali metal and ammonium ions on transition metal ferrocyanides. As shown

Fig. 2. Cs^+ distribution coefficient on T-55 sorbent as a function of the activity of NH_4^+ ions in solution. (a) ^{137}Cs without isotopic carrier; Cs^+ concentration, mg L⁻¹: (b) 10^{-3} and (c) 100.

in [1, 13], ferrocyanides sorb alkali metal ions owing to the zeolite effect, which is manifested the more strongly, the closer the diameter of the sorbate ion to the channel cross section size in the structure of the ferrocyanide. The maximal zeolite effect is observed for the Cs^+ cation. The NH_4^+ ion is the closest in size to the Cs^+ ion (the effective diameter of the hydrated cation is 0.25 nm for Cs^+ , 0.25 nm for NH_4^+ , 0.3 nm for K^+ , and 0.4–0.45 nm for Na^+ [12]); therefore, the NH_4^+ ion exerts a stronger effect on the Cs^+ sorption than do cations of the other elements under consideration.

Figure 2 shows how the Cs^+ distribution coefficient on T-55 sorbent depends on the activity of NH_4^+ ions in solution.

Without isotopic carrier, at NH_4Cl concentrations in solution in the range 0.0001–0.01 M, we revealed no effect of NH_4^+ ions on the Cs^+ sorption. Least-squares processing of points corresponding to higher concentrations of NH_4^+ ions gives a linear regression equation for the correlation between $\log K_d$ and $\log a$. The slope close to unity (0.9 ± 0.1) suggests that the effective

Fig. 3. Isotherms of NH_4^+ sorption from NH_4Cl solutions with (1) T-5 and (2) T-55 sorbents at $20 \pm 2^\circ\text{C}$.

Fig. 4. NH_4^+ distribution coefficient on (a) T-5 and (b) T-55 sorbents as a function of Cs^+ concentration in solution.

charge of the Cs^+ ion in the ion-exchange event is close to unity. It was also noted that, at the Cs^+ concentration in solution of 10^{-3} mg L⁻¹, NH_4^+ ions started to suppress the Cs^+ sorption at a concentration higher by an order of magnitude (0.1 M), with the slope also equal to unity within the determination uncertainty. At a Cs^+ concentration of 100 mg L⁻¹ and, presumably, in the entire concentration range over 50 mg L⁻¹, the NH_4^+ ions do not affect the Cs^+ sorption.

Figure 3 shows the isotherms of NH_4^+ sorption from NH_4Cl solutions with T-5 and T-55 sorbents. Figure 4 shows how the distribution coefficients of NH_4^+ on T-5 and T-55 sorbents depend on the Cs^+ concentration in solution. The characteristics of the Cs^+ sorption in the presence of NH_4^+ ions in solution and without them, obtained by statistical processing of the curves, are given in Table 1.

We found that T-5 sorbent is unselective and recovers NH_4^+ with a higher distribution coefficient than Cs^+ . Presumably, the increased sorbent affinity for NH_4^+ is due to the “memory effect” and to the size of the crys-

Table 1. Characteristics of Cs⁺ and NH₄⁺ sorption from NH₄Cl solutions with T-5 and T-55 sorbents

Sorbent	Cs ⁺ sorption		NH ₄ ⁺ sorption ⁺	
	[Cs ⁺] in solution, mg L ⁻¹	log K _d of Cs ⁺ [mL g ⁻¹]	log K _d of NH ₄ ⁺ without Cs ⁺ [mL g ⁻¹]	log K _d of NH ₄ ⁺ in the presence of Cs ⁺ [mL g ⁻¹]
T-5	10 ⁻⁷ –10	1.8 ± 0.5	3.6 ± 0.1	2.5 ± 0.1
	10–1000	~1		
T-55	2 × 10 ⁻⁷ –5 × 10 ⁻⁴	4.8 ± 0.2	2.5 ± 0.1	2.5 ± 0.1
	5 × 10 ⁻³ –5	4.2 ± 0.1		
	50–500	2.3 ± 0.2		

tal lattice of hydrated TiO₂, formed in the course of the synthesis. The procedure used for preparing T-5 sorbent yields the sorbent in the ammonium form. On calcining the sorbent at 400°C, the ammonia is removed, but on contact with an NH₄Cl solution the NH₄⁺ ion in the presence of which the sorbent structure was formed tends to occupy its site. Similar effects were noted in [14] where it was shown that silica gels primarily sorbed the substance that had been initially present in the reaction mixture in the course of the synthesis.

Figure 5 shows the IR spectra of T-5 and T-55 sorbents after the sorption from solutions containing 0.05 M NH₄⁺ and 10⁻⁴ mg L⁻¹ and 10 g L⁻¹ Cs⁺. The IR spectra of all the sorbents contain a broad absorption band at 2800–3800 cm⁻¹, characteristic of stretching vibrations of the OH groups of titanium hydroxide, participating in hydrogen bonding. The strong absorption peak at 1635 cm⁻¹ is due to bending vibrations of adsorbed water molecules. T-55 sorbent also exhibits

absorption bands at 2060 and 2092 cm⁻¹, characteristic of the ferrocyanide phase. In the IR spectra of T-5 and T-55 sorbents after sorption from 0.05 M NH₄⁺ solution, irrespective of the chosen Cs⁺ concentration, there are absorption peaks in the region of 1400 cm⁻¹, corresponding to N–H bonds in the NH₄⁺ ions, which also confirms the NH₄⁺ uptake by the sorbents.

As compared to T-5 sorbent, T-55 sorbent is highly specific to Cs⁺ in the presence of NH₄⁺ (Table 1). The results we obtained suggest that the sorption of Cs⁺ and NH₄⁺ with T-55 sorbent in a definite concentration range occurs by different mechanisms, and therefore the Cs⁺ distribution coefficient is independent of the NH₄⁺ concentration (Figs. 2, 4). At Cs⁺ concentrations in solution of up to 50 mg L⁻¹ and NH₄⁺ concentrations of up to 0.01 and 0.1 M, the NH₄⁺ ions are sorbed by sorption sites of hydrated TiO₂:

whereas Cs⁺ is sorbed by sites of the ferrocyanide phase:

With an increase in the NH₄⁺ concentration in the solution, the sorption sites of hydrated TiO₂ becomes filled, and NH₄⁺ starts to compete with Cs⁺ for filling of sorption sites of the ferrocyanide phase:

Fig. 5. IR spectra of sorbents after NH₄⁺ sorption from 0.05 M NH₄⁺ solutions with different Cs⁺ concentrations. Sorbent: (1, 2) T-5 and (3, 4) T-55. Cs⁺ concentration: (1, 3) 10⁻⁴ mg L⁻¹ and (2, 4) 10 g L⁻¹.

Table 2. Static exchange capacities (SECs) of sorption sites of T-5 and T-55 sorbents for Cs^+ , determined in tap water with pH 7.8 ± 0.2 [the content of hardness salts, alkali metals, and anions in tap water met SanPiN (Sanitary Rules and Regulations) 2.1.4.1074–01; the total hardness was $2.4 \text{ mg-equiv L}^{-1}$, and the Ca^{2+} concentration was $30 \pm 5 \text{ mg L}^{-1}$]

Sorbent	Sorption site	SEC of site, mg L^{-1}
T-5	H_3O^+	0.1
	OH^-	≥ 20
T-55	$\text{K}_2\text{Ni}[\text{Fe}(\text{CN})_6]$	0.001
	$\text{K}_2(\text{TiO})[\text{Fe}(\text{CN})_6]$	14.6
	OH and $\text{Cs}_2\text{Ni}[\text{Fe}(\text{CN})_6]$ deposited in the pore space of the sorbent	255

Difference between Figs. 2a and 2b in the NH_4^+ concentration at which the competition becomes noticeable may be due to different specificities and capacities of the sorption sites (Table 2) in different concentration ranges.

At high cesium concentrations in solution, the presumable mechanism of the Cs^+ sorption with T-55 sorbent is deposition of poorly soluble nickel cesium ferrocyanide in the sorbent pores, rather than the ion exchange. In the presence of NH_4^+ in the solution, Cs^+ and NH_4^+ can coprecipitate in the form of mixed ferrocyanides.

Thus, T-55 sorbent is highly specific to Cs^+ in the presence of single-charged Na^+ , K^+ , and NH_4^+ cations and can be efficient for treatment of highly saline liquid radioactive wastes. Studies showed that the concentration of Na^+ and K^+ ions does not affect the Cs^+ sorption. In definite ranges of Cs^+ and NH_4^+ concentrations (2×10^{-7} – $5 \times 10^{-4} \text{ mg L}^{-1}$ and up to 0.01 M; 5×10^{-3} – 5 mg L^{-1} and up to 0.1 M, respectively), NH_4^+ ions do not affect the Cs^+ sorption, and Cs^+ and NH_4^+ are sorbed by different mechanisms. At higher concentrations of the components, the NH_4^+ ion, which, as compared with Na^+ and K^+ ions, is closer to Cs^+ in the ionic radius, competes with Cs^+ in sorption, which leads to a decrease in the Cs^+ distribution coefficient. At Cs^+ concentration in solution exceeding 50 mg L^{-1} , Cs^+ and NH_4^+ are taken up jointly owing to coprecipitation in the form of mixed ferrocyanides in the pore space of the sorbent.

ACKNOWLEDGMENTS

The study was financially supported by the Ministry of Education and Science of the Russian Federation within the framework of Federal Target Program “Scientific and Scientific-Pedagogical Personnel of Innovative Russia” for the years 2009–2013 (agreement no. 14.A18.21.0313).

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