ISSN 0040-5795, Theoretical Foundations of Chemical Engineering, 2018, Vol. 52, No. 4, pp. 581–586. © Pleiades Publishing, Ltd., 2018.
Original Russian Text © P.S. Gordienko, I.A. Shabalin, S.B. Yarusova, Yu.A. Azarova, S.N. Somova, A.V. Perfilev, 2017, published in Khimicheskaya Tekhnologiya, 2017, Vol. 18, No. 1, pp. 2–8.

Study of the Composition, Structure, and Sorption Properties of Nanostructured Aluminosilicates

P. S. Gordienko[a, b], I. A. Shabalin[a], S. B. Yarusova[a, b, *],
Yu. A. Azarova[a, b], S. N. Somova[a], and A. V. Perfilev[a, c]
[a] *Institute of Chemistry, Far Eastern Branch, Russian Academy of Sciences, Vladivostok, 690022 Russia*
[b] *Vladivostok State University of Economics and Service, Vladivostok, 690014 Russia*
[c] *Pacific National University, Khabarovsk, 680035 Russia*
**e-mail: yarusova_10@mail.ru*

Received March 14, 2016

Abstract—Sorption properties of synthetic nanostructured potassium aluminosilicates with Si/Al ratios from 1 to 5 fabricated in a multicomponent system $KOH–Al_2(SO_4)_3 \cdot 18H_2O–SiO_2 \cdot nH_2O–H_2O$ under static sorption conditions at various temperatures and nitrate salt background have been investigated; the activation energy of cesium ions sorption has been evaluated.

Keywords: nanoscaled structures, synthetic aluminosilicates, sorption, cesium ions, sorption kinetics, activation energy

DOI: 10.1134/S0040579518040127

INTRODUCTION

Earlier, the authors provided data on the synthesis of nanostructured potassium aluminosilicates (PAS) fabricated in a multicomponent system $KOH—Al_2(SO_4)_3 \cdot 18H_2O—SiO_2 \cdot nH_2O—H_2O$; the IR and NMR spectra were examined. According to the NMR spectra data, aluminum was located in different structural positions in aluminosilicates depending on the Si/Al ratio with tetrahedral and octahedral coordination with respect to oxygen.

The objective of the present study was to investigate sorption properties and the effect of salt background on the sorption capacity of a series of potassium aluminosilicates with varied Si/Al ratios (from 1 to 5) towards Cs^+ ions, to examine sorption kinetics parameters of Cs^+ ions, and to determine the activation energy of the sorption process.

EXPERIMENTAL

Sorption of Cs^+ ions was performed from aqueous solutions of cesium chloride under static conditions at a solid to liquid phase ratio S : L of 1 : 400 at 20°C for 3 hours. Cesium chloride solutions were prepared from aqueous solutions by dissolving CsCl sample weights of analytically pure grade in distilled water. A series of initial aqueous solutions were prepared by dilution with Cs^+ ions concentration ranging from 0.24 to 43.9 mmol/L. Sorbent sample weights were placed in a series of test tubes that were then filled with cesium chloride aqueous solutions of various initial concentrations within the indicated range and then stirred by means of a *RT* 15 *power* magnetic mixer (*IKA WERKE*, Germany). As a control experiment, a sorbent sample was placed in a tube with distilled water alongside the investigated samples. Then, the solutions were separated from the sorbent by filtering, and Cs^+ and K^+ ions concentrations in filtrates were estimated. To determine sorption kinetics parameters at 20, 40, and 70°C, 20 mL of solutions with a Cs^+ ion concentration of 7.67 mmol/L was poured into a series of tubes with 0.5-g sorbent samples and stirred for 1, 5, 10, 30, 60, 120, and 240 min. Sorbent was separated from the solution after every preset period of time, and the Cs^+ ion concentration in the filtrates was estimated.

The effect of alkali metals (sodium, potassium) and ammonium (chemically pure) nitrates on the cesium ion extraction rate α (%) by nanostructured potassium aluminosilicates was examined at S : L ratio = 1 : 1000 at 20°C. The stirring time the sorbent with the saline solution was 3 hours. The sorption capacity (A_s, mmol/g) of the investigated samples was calculated according to the formula:

$$A_s = \frac{(C_{init} - C_{eq})}{m} V, \tag{1}$$

where C_{init} is the initial concentration of Cs^+ ions in the solution, mmol/L; C_{eq}, the equilibrium concentration of Cs^+ ions in the solution, mmol/L; V, the solution volume, L; and m, the sorbent weight, g.

The Cs^+ ion extraction rate α (%) was calculated according to the formula:

$$\alpha = \frac{C_{\text{init}} - C_{\text{eq}}}{C_{\text{init}}} \times 100\%. \tag{2}$$

Sorption isotherms were described by the Langmuir equation:

$$A_{\text{s}} = K_{\text{L(I)}} C_{\text{init}} A_{\text{m}} \left(1/\left(1 + K_{\text{L}} C_{\text{init}}\right)\right), \tag{3}$$

where A_{m} is the maximum sorption capacity, mmol/g; and $K_{\text{L(I)}}$, the Langmuir constant, L/mmol.

The Langmuir constant $K_{\text{L(Eq)}}$ was determined based on the dependence of the sorbent sorption capacity on the initial sorbate concentration in the solution via the technique described in [1] considering the maximum sorption capacity A_{m} according to the equation:

$$K_{\text{L(Eq)}} = 1/\left(C^*_{\text{init}} - (1/2)\, A_{\text{m}} \left(m/V\right)\right), \tag{4}$$

where C^*_{init} is the initial sorbate concentration at which the sorption capacity of the sorbent is half the maximum sorption capacity.

The data on Cs^+ ions sorption kinetics were analyzed using pseudofirst- and pseudosecond-order kinetic models for chemical reactions [2, 3]. A pseudofirst-order kinetic model for chemical reaction rate (Lagergren model) was described by an equation:

$$\left(dA_t/dt\right) = k_1(A_e - A_t), \tag{5}$$

where k_1 is the pseudofirst-order apparent rate constant; A_e, A_t the sorption values at the equilibrium state and at a specific time t, respectively.

Equation (5) takes the following shape in a linear integral form under the initial conditions: $A_t = 0$, at $t = 0$ and $A_t = A_t$ at specific time t:

$$\log(A_e - A_t) = \log A_e - (k_1 t)/2.303. \tag{6}$$

The pseudosecond-order kinetic model was described by the equation:

$$\left(dA_t/dt\right) = k_2(A_e - A_t)^2, \tag{7}$$

where k_2 is the pseudosecond-order model rate constant.

Equation (7) was transformed as follows:

$$\left(1/A_t\right) = \left(1/A_{\text{m}}\right) - 1/\left(t k_2 A_{\text{m}}^2\right), \tag{8}$$

where A_{m} is the maximum sorption capacity of the sorbent, mmol/g.

Time dependences of the sorption process were analyzed and, taking into account the Kolmogorov–Erofeev equation for topochemical reactions, the following dependence was obtained:

$$\alpha = 1 - \exp\left(-kt^n\right), \tag{9}$$

where α is the rate of extraction of Cs^+ ions from the solution; t, the sorption time; k, the coefficient determining the sorption process rate constant; and n, the order of the reaction (k and n were defined by diagram).

To analyze the experimental kinetic data, Eq. (9) was written in the form of a linear regression equation:

$$\ln(-\ln(1 - \alpha)) = \ln k + n \ln t. \tag{10}$$

Kinetic dependences in coordinates $\ln(-\ln(1-\alpha)) = f(\ln t)$ had the form of straight lines, while the slope angle determined the value of the reaction order: at $n < 1$ the sorption process was described as a process controlled by diffusion phenomena and at $n > 1$, as a kinetic process. At $\ln t = 0$, the section proportional to the $\ln k$ value was an intercept on the ordinate axis.

The temperature dependence of the sorption rate constant was described by the Arrhenius equation:

$$k = A \exp\left(E_{\text{a}}/RT\right), \tag{11}$$

where A is the preexponential factor expressed in units of the sorption process rate constant k; E_{a}, the activation energy of the sorption process, kJ/mol; T, the absolute temperature, K; and R, the gas constant, kJ/mol.

The Arrhenius equation in a logarithmic form was written as follows:

$$\ln k = \ln A - \left(E_{\text{a}}/RT\right). \tag{12}$$

The activation energy of the Cs^+ ion sorption process by the nanostructured aluminosilicates from aqueous solution was determined from the dependence of $\ln k$ on $1/T$.

ANALYTICAL METHODS

The hydrogen ion concentration in aqueous solution was estimated by means of a pH-meter/ion meter, a Multitest IPL-102 with glass electrode ESK-10601/7 normalized by reference to buffer solutions.

The concentration of Cs^+ and K^+ ions in the solutions was determined via atomic absorption spectrometry using a *Solaar* 6 M spectrometer by reference to analytical lines at 852.1 and 766.5 nm, respectively. The detection limit for cesium ions in the aqueous solutions was 0.01 μg/mL and for potassium ions, 0.002 μg/mL.

Table 1. Sorption capacity and rates of extraction of Cs^+ ions by aluminosilicates (S : L = 1 : 400 at $T = 20°C$)

$KAlSiO_4 \cdot H_2O$ ($K_{L(I)} = 1.053$ L/mmol, $K_{L(I)} = 0.2244$ L/mmol)				$KAlSi_2O_6 \cdot 1.5H_2O$ ($K_{L(Eq)} = 0.1$ L/mmol, $K_{L(I)} = 0.0651$ L/mmol)			
C_{init}, mmol/L	C_{eq}, mmol/L	A_s, mmol/g	α, %	C_{init}, mmol/L	C_{eq}, mmol/L	A_s, mmol/g	α, %
0.24	0.003	0.095	98.8	0.24	0.006	0.0936	97.5
0.35	0.01	0.136	97.1	1.09	0.18	0.364	83.5
0.86	0.135	0.29	84.3	1.11	0.21	0.36	81.1
1.11	0.11	0.4	90.1	3.43	1.37	0.824	60.1
4.01	1.67	0.936	58.4	7.72	5.0	1.088	35.2
6.34	0.36	2.4	94.3	26.6	17.9	3.48	32.7
18.0	11.16	2.736	38.0	43.9	33.3	4.24	24.1
$KAlSi_4O_{10} \cdot 2.4H_2O$ ($K_{L(Eq)} = 1.067$ L/mmol, $K_{L(I)} = 0.2831$ L/mmol)				$KAlSi_5O_{12} \cdot 2.7H_2O$ ($K_{L(Eq)} = 0.926$ L/mmol, $K_{L(I)} = 0.3075$ L/mmol)			
C_{init}, mmol/L	C_{eq}, mmol/L	A_s, mmol/g	α, %	C_{init}, mmol/L	C_{eq}, mmol/L	A_s, mmol/g	α, %
0.24	0.007	0.09	97.1	0.24	0.006	0.0936	97.5
0.29	0.006	0.114	97.9	0.29	0.06	0.092	79.3
1.6	0.02	0.632	98.8	1.6	0.18	0.57	88.8
3.43	0.41	1.208	88.1	3.43	1.33	0.84	61.2
11.5	6.18	2.13	46.3	11.5	8.0	1.4	30.4
19.0	14.0	2.0	26.3	19.0	15.14	1.54	20.3
37.9	31.91	2.4	15.8	37.9	33.7	1.68	11.1

RESULTS AND DISCUSSION

Sorption Isotherms

Table 1 shows the data on sorption capacity and extraction rate of Cs^+ ions from aqueous solutions at 20°C at S : L = 1 : 400.

Figure 1 demonstrates the dependences of the sorption capacity on the initial concentration of cesium ions in the solution (C_{init}) according to the data obtained experimentally and described by Eq. (1), formally reminiscent of the Langmuir equation for the equilibrium concentration of cesium ions in the solution with coefficients $K_{L(I)}$ $\left(K_{L(I)} = 1/C^*_{init}\right)$ provided in Table 1.

The presented sorption isotherms dependences, both experimental and built according to the Langmuir equation (1), complied within the accepted measurement error. The calculation of Langmuir constants $K_{L(Eq)}$ was performed by Eq. (2), the values are provided in Table 1.

The maximum sorption capacities of aluminosilicates with the Si/Al ratio equal to 1 and 3 were similar [1]. Note that the investigated series of aluminosilicates exhibited high rates of extraction of Cs^+ ions from aqueous solutions, up to 98%. Taking into account the potassium ion molar ratio in the prepared aluminosilicates, the Cs^+ maximum sorption capacity values (see Table 1), measurement errors for sorbate concentration values, the sorbent weight, and the solution volume, the ratio of exchange of K^+ ions by Cs^+ ions was >80%.

The experimental data on the salt metal and ammonium nitrates background effect on the Cs^+ ion extraction by aluminosilicates are provided in Fig. 2.

As seen from Fig. 2, the Cs^+ ion extraction rate decreased rapidly when the salt background concentration increased and depended greatly on the salt cation nature.

High rates of extraction of Cs^+ ions from sodium nitrate solution of a concentration of 0.01 mol/L (up to 78%) was established for all the aluminosilicates except aluminosilicate with the Si/Al ratio of 2, for

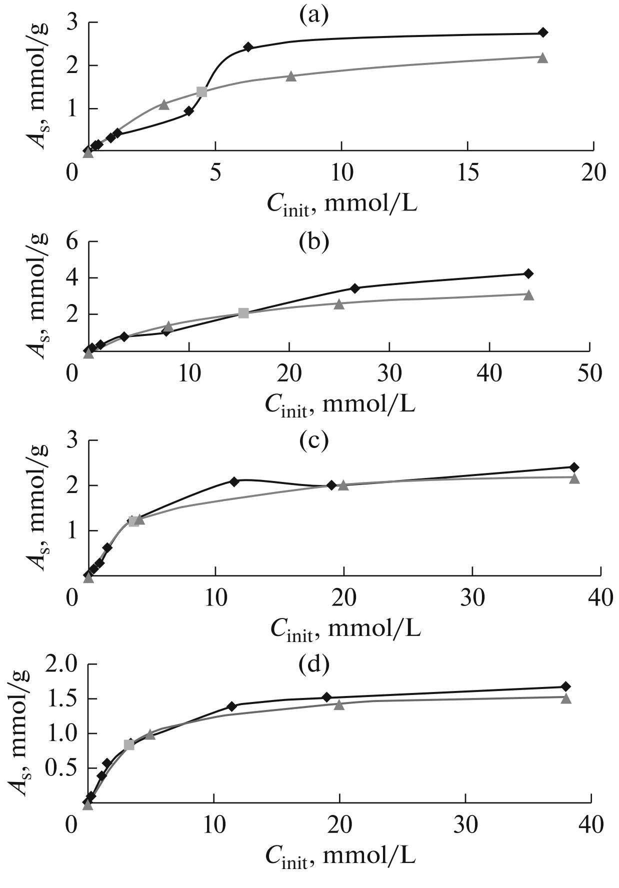

Fig. 1. Dependence of sorption capacity of the aluminosilicates with the Si/Al ratio of 1 (a), 2 (b), 4 (c), 5 (d) on cesium ions concentration in the solution (◆—experimental points, ▲—points plotted according to equation (3).

which this parameter is lower. Further investigation is necessary to determine the reasons for this dependence. As established earlier, this particular aluminosilicate typically exhibited a large amount of aluminum with octahedral oxygen coordination in the structure.

Potassium and ammonium salts had the greatest influence on the rate of extraction of Cs^+ ions by aluminosilicates (see Fig. 2). One should consider that this could be due to the magnitude of the chemical affinities of the indicated elements, and to different solubility products of cesium, sodium, potassium, and ammonium aluminosilicates in the investigated solutions.

Table 2 demonstrates the experimental data on the sorption kinetics of Cs^+ ions obtained for aluminosilicates with the Si/Al ratio equal to 1 and 5 at various temperatures (20, 40, and 70°C).

One should mention the high cation exchange rate between the sorbent and the solution. The sorption capacity of $KAlSiO_4 \cdot H_2O$ and $KAlSi_5O_{12} \cdot 2.7H_2O$ was 95% of the equilibrium capacity as early as within 1 minute (disregarding the filtration time) (see Table 2). This dependence was obtained earlier for $KAlSi_3O_8 \cdot 1.5H_2O$ as well [1].

Temperature changes influenced the process kinetics insignificantly. The data on sorption kinetics for $KAlSiO_4 \cdot H_2O$ and $KAlSi_5O_{12} \cdot 2.7H_2O$ at various temperatures were processed in accordance with the pseudosecond-order kinetic model by Eq. (7) and shown in Fig. 3 and were described by linear equations (Table 3) with high correlation coefficients (R^2).

$KAlSi_5O_{12} \cdot 2.7H_2O$ demonstrated much higher correlation coefficients, i.e., the cation exchange process kinetics for Cs^+ ion sorption for this compound was described by the pseudosecond-order kinetic model the most accurately. This was presumably related to the structure of this aluminosilicate, which contained an elevated amount of SiO_2 and, therefore, a decreased concentration of structural groups of the Si—O—Al type.

The k_2, g min^{-1} mmol^{-1} constants were calculated from linear equations provided in Table 3 and according to the Eq. (7) of the pseudosecond-order model of

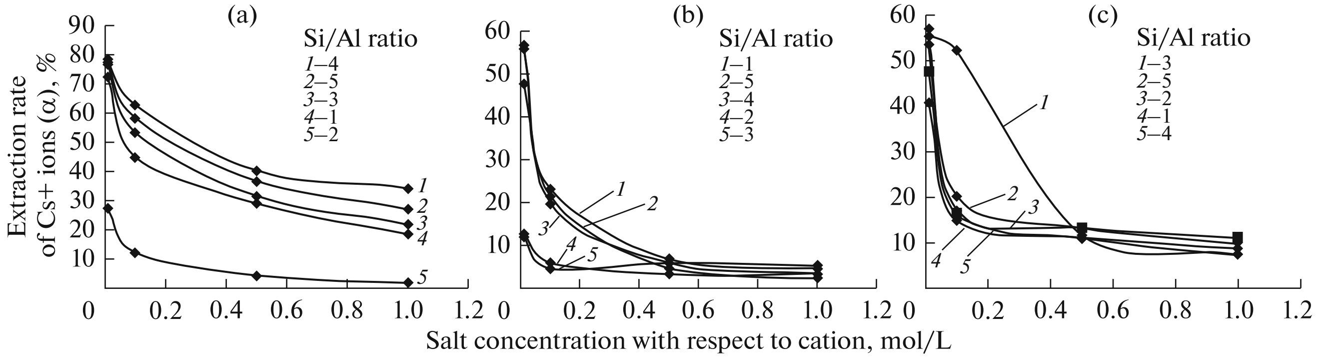

Fig. 2. Dependence of the rate of extraction of Cs^+ ions by aluminosilicates on the nitrates concentration: (a) $NaNO_3$, (b) KNO_3, (c) NH_4NO_3.

Table 2. Dependence of the sorption capacity on time at varied temperature at Cs^+ ions sorption by aluminosilicates $KAlSiO_4 \cdot H_2O$ and $KAlSi_5O_{12} \cdot 2.7H_2O$

Temperature, °C	Time, min	Sorbent			
		$KAlSiO_4 \cdot H_2O$		$KAlSi_5O_{12} \cdot 2.7H_2O$	
		C_{eq}, mmol/L	$A_s(t)$, mmol/g	C_{eq}, mmol/L	$A_s(t)$, mmol/g
20	1	1.0981	0.2626	0.8320	0.2732
	5	1.0830	0.2634	0.5946	0.2832
	10	1.0009	0.2668	0.5766	0.2836
	30	0.9995	0.2667	0.5819	0.2837
	60	0.9961	0.2667	0.5712	0.2841
	120	0.9970	0.2666	0.5692	0.2842
	240	0.9840	0.2674	0.5680	0.2840
40	1	1.0505	0.2650	0.5864	0.2829
	5	1.0099	0.2663	0.4973	0.2869
	10	1.0014	0.2666	0.4634	0.2878
	30	1.0036	0.2664	0.4540	0.2886
	60	0.8903	0.2712	0.4730	0.2878
	120	0.9073	0.2703	0.4870	0.2872
	240	0.8773	0.2719	0.4680	0.2880
70	1	1.3657	0.2588	0.6119	0.2818
	5	1.0587	0.2711	0.4987	0.2870
	10	1.2235	0.2645	0.5118	0.2864
	30	1.0391	0.2718	0.4651	0.2883
	60	1.0429	0.2717	0.4532	0.2885
	120	0.9722	0.2745	0.4470	0.2891
	240	0.8841	0.2780	0.5043	0.2868

the sorption process at 20, 40, and 70°C and were equal to, respectively, for $KAlSiO_4 \cdot H_2O$, 225.5, 205.4, 65.3 and for $KAlSi_5O_{12} \cdot 2.7H_2O$, 86.53, 191.3, 156.7.

Sorption of Cs^+ ions by aluminosilicates should be considered as a topochemical reaction and, on that basis, the kinetics data were analyzed by means of the Kolmogorov—Erofeev equation (9) with a representation of the experimental data in a form of graphic dependence (Fig. 4).

Table 3. Linear equations of the pseudosecond-order kinetic model

T, °C/sorbent	$KAlSiO_4 \cdot H_2O$, (R^2)	$KAlSi_5O_{12} \cdot 2.7H_2O$, ($R^2$)
20	$y = 3.7512 - 0.0624x$ (0.8300)	$y = 3.5151 - 0.1428x$ (0.9925)
40	$y = 3.7152 - 0.0672x$ (0.6283)	$y = 3.4719 - 0.06302x$ (0.9706)
70	$y = 3.6647 - 0.2058x$ (0.8300)	$y = 3.4715 - 0.0769x$ (0.9366)

Analysis of dependences provided in Fig. 4 demonstrated that the sorption process reaction order was significantly less than 1 (around 0.03) according to the Kolmogorov—Erofeev model, which was typical for the processes controlled by diffusion phenomena. The same dependence curves allowed us to obtain the logarithm values of the sorption process rate constant, and, according to the Arrhenius law (11), the activation energy of the sorption process was determined from dependences (Fig. 5) and appeared to be 1 kJ/mol for the aluminosilicate with Si/Al = 1 and to 1.5 kJ, for Si/Al = 5.

In this case of such low activation energy of the sorption process reaction, the temperature dependence is insignificant, which was corroborated experimentally. Note that in any case the activation energy was 1.5-fold higher for the aluminosilicate with a high concentration of SiO_2. This was presumably determined by the higher energy of the silicate crystal lat-

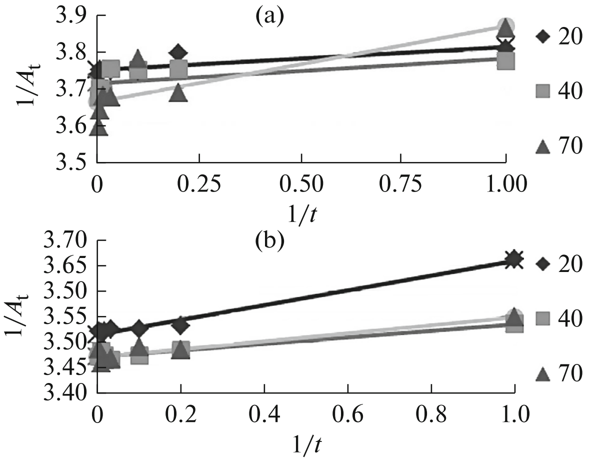

Fig. 3. Pseudosecond-order kinetic model upon Cs^+ ions sorption by aluminosilicates with Si/Al ratio of 1 (a) and 5 (b).

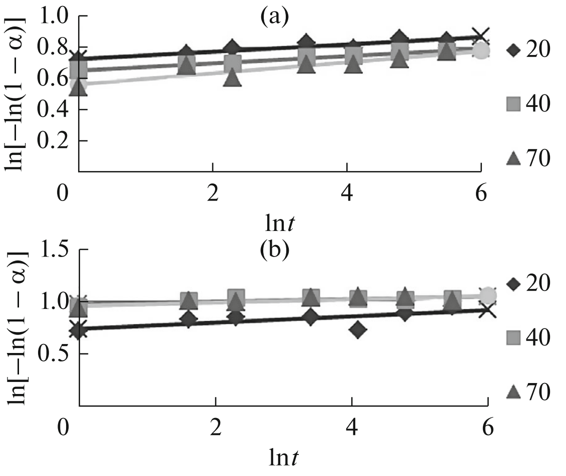

Fig. 4. Logarithmic dependences according to the Kolmogorov–Erofeev equation for aluminosilicates with Si/Al ratio of 1 (a) and 5 (b).

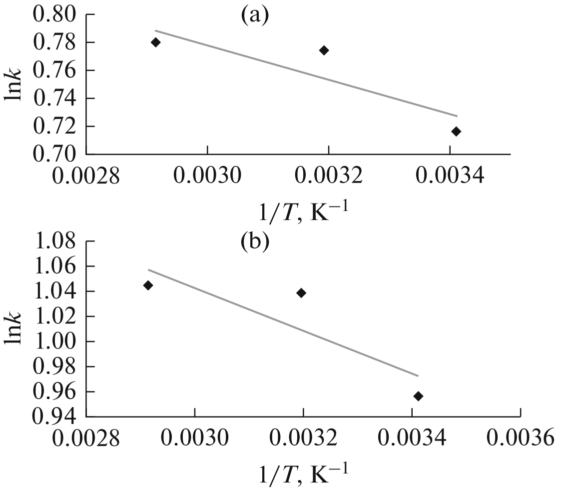

Fig. 5. Logarithmic dependences of Cs^+ ion sorption rate constant on the inverse temperature for aluminosilicates with Si/Al ratio of 1 (a) and 5 (b) in the temperature range 20–70°C.

tice, which increased as the Si/Al ratio increased [4]. This fact was also corroborated by the frequency shift of the peak maxima to the high-frequency range in the previously examined IR spectra upon an increase in the Si/Al ratio.

CONCLUSIONS

The processes of sorption of Cs^+ ions from chloride solutions under static conditions have been studied. The largest sorption capacity value (>4.0 mmol/g) among the studied aluminosilicates series was observed for the aluminosilicate with the Si/Al ratio of 2. With a study of the nitrate influence on Cs^+ ion sorption, it has been established that the greatest influence on the Cs^+ ion extraction rate is provided by potassium and ammonium salts. A high rate of extraction of Cs^+ ions from the solution with a sodium nitrate concentration of 0.01 mol/L (up to 78%) has been established for all the investigated aluminosilicates, except one with a Si/Al ratio of 2. The sorption kinetics parameters have been determined. It has been found that the time necessary to achieve equilibrium values was a few minutes. The obtained nanostructured aluminosilicates are suitable for removing Cs^+ ions from solutions with low salinity and, due to their nontoxicity, for removing cesium from animal bodies.

ACKLOWLEDGMENTS

The present study was performed with a support of the Russian Science Foundation (project no. 15-17-10016).

REFERENCES

1. Gordienko, P.S., Yarusova, S.B., Bulanova, S.B., Shabalin, I.A., and Kuryavyi, V.G., The use of synthetic aluminosilicate for cesium ion sorption, *Khim. Tekhnol.*, 2013, vol. 14, no. 3, pp. 185–192.
2. Coleman, N.J., Brassington, D.S., Raza, A., and Mendham, A.P., Sorption of Co^{2+} and Sr^{2+} by waste-derived 11 Å tobermorite, *Waste Manage.*, 2006, vol. 26, no. 3, pp. 260–267. https://doi.org/10.1016/j.wasman.2005.01.019.
3. Ho, Y.S. and McKay, G., Pseudo-second order model for sorption processes, *Process Biochem.*, 1999, vol. 34, no. 5, pp. 451–465. https://doi.org/10.1016/S0032-9592(98)00112-5.
4. Kostov, I., *Mineralogy,* Edinburgh: Oliver & Boyd, 1971.

Translated by D. Marinin