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Adsorption of Lanthanide(III) Cations on Cross-Linked Ionic Polymer, Composition and Thermal Analysis of the Formed Composites

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Abstract—The adsorption of lanthanide(III) cations by a strongly basic cross-linked polymer containing R_4N^+ groups was studied at 21 and 50°C. At both temperatures the sorption is best described with the Langmuir model. The maximum adsorption at both 21 and at 50°C increases in the series: $La^{3+} < Eu^{3+} < Nd^{3+} < Er^{3+}$. The results show that polymers containing strongly basic groups can, under certain conditions, be used to separate lanthanide(III) cations in solutions containing mono- and bivalent cations. SEM EDX studies show that La^{3+}, Nd^{3+}, Eu^{3+} and Er^{3+} form composites in the polymer phase. The elemental composition of structural units of the composites is $La_1Cl_{13.7}S_{64.3}O_{287.7}N_{122.6}C_{2869}$, $Nd_1Cl_{27.4}S_{50.7}O_{391.6}N_{169.3}C_{2896}$, $Eu_1Cl_{8.5}S_{50.8}O_{285}N_{130}C_{2118}$ and $Er_1Cl_{36.8}S_{263.9}O_{1106}N_{447}C_{8657}$. The thermodynamic parameters of the sorption process are calculated: free energy, enthalpy, and entropy. Thermogravimetric analysis made it possible to determine the stability of the formed composites, the stages of their decomposition and the corresponding kinetic parameters.

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1. INTRODUCTION

It is known that many lanthanide compounds are widely used in science and technology. Their fluorescent properties are being intensively studied [1, 2]. Lanthanide luminescent compounds immobilized on polystyrene polymers are used to detect certain pesticides [3]. Significant amounts of lanthanide compounds, including lanthanide(III) cations, are used as catalysts [4, 5]. The separation of lanthanides in solutions from other metals is a complex process. Ion exchangers are often used in lanthanide separation technologies. The use of strongly acidic cation exchangers is not effective because the interaction of the cations with the polymer is caused by Coulomb's electrostatic forces. This means that sorption is not a selective process. Polymers containing carboxylic groups have a higher selectivity in sorption processes. But they are not effective in the separation of lanthanide cations from other mono- or trivalent cations capable of forming complexes with carboxyl groups [6]. In addition, the sorption of cations by such polymers is highly dependent on solution pH.

It is known that cross-linked polymers containing quaternary ammonium nitrogen can interact with lanthanides being only in the form of anionic complexes [7]. The strongly basic gel and macroporous polyacrylate polymers Amberlite IRA 458 and Amberlite IRA 958 were used to separate lanthanide complexes [8]. However, sorption of anionic complexes by these polymers is not selective, because it is also caused by the electrostatic forces.

It is believed that strongly basic polymers cannot adsorb metal cations from solutions, since they do not contain negatively charged or electron-donating atoms in their matrix. And yet, although it seems incredible, under certain conditions such polymers are able to retain some cations in solutions. They can adsorb trivalent cations of some metals in the presence of the sulfate anions [9]. The absorption of cations by strongly basic polymers is a chemical process, that is, chemisorption. The chemisorption process consists in the formation in the polymer phase of some composites of the jarosite mineral-type: $R_4N[M_3(OH)_6(SO_4)_2]$, where R_4N^+ is a functional group of the polymer, M^{3+} is a metal cation. The cations of mono- and bivalent metals cannot form jarosite mineral-type compounds and therefore cannot be adsorbed by polymers with strongly basic functional groups. Thus, strongly basic polymers could be used for the selective separation of lanthanide(III) cations from cations of other metals. On the other hand, polymers that contain jarosite mineral-type

compounds radically change their properties, which extend their field of use. They become sorbents and catalysts with selective properties. The composites in the polymer phase can be mono- or polynuclear (contain cations of different metals), i.e., contain various and multiple active centers [10], which is important in heterogeneous catalysis.

The purpose of this article is to determine the maximum capacity of a polymer with R_4N^+ groups upon the sorption of lanthanide(III) cations. In addition, the elemental composition of compounds containing lanthanide(III) cations and their thermal behavior were also determined.

2. MATERIALS AND METHODS

A commercial cross-linked, gel-type polymer Purolite A-400 in Cl-form was used. The polymer contains quaternary ammonium nitrogen (R_4N^+), and its exchange capacity is about 4 meq/g [11]. For the study, we used solutions of $La_2(SO_4)_3$, $Nd_2(SO_4)_3$, $Eu_2(SO_4)_3$ and $Er_2(SO_4)_3$. In the all experiments, samples of 0.1 g of polymer were in contact with 50 mL of a solution with a different concentration of lanthanide(III) cations. NaOH and H_2SO_4 solutions were used to maintain a constant pH of 6 ± 0.05. The concentration of lanthanide(III) cations in the solution was determined photocolorimetrycally [12].

The morphology of the solid samples was examined by using a Quanta 200 scanning electron microscope (FEI), operating at 20 kV with secondary electrons in low vacuum mode. The SEM studies were performed on uncoated samples fixed on aluminum supports using a carbon based adhesive. The Quanta 200 microscope is equipped with an Energy Dispersive X-ray system (EDX) for qualitative analysis which permits the identification of the elements in the samples.

The thermal behaviour of the lanthanide(III)–Purolite A-400 composites was analysed using Mettler Toledo 851^e equipment. Thermogravimetric curves were recorded in the air, with a flow rate of 20 mL/min in the temperature range 25–900°C. The mass of the samples which were subjected to thermogravimetric analysis ranges between 2 and 3.8 mg. The heating rate was 10°C/min, and the thermogravimetric curves were processed with the help of STAR^e software.

3. RESUITS AND DISCUSSION

3.1. Sorption Isotherms

Purolite A-400, the polymer that was used, does not contain negatively charged or electron donate atoms in its matrix. Sorption of lanthanide(III) cations on polymers of this type containing quaternary ammonium nitrogen takes place due to the formation in their phases of the jarosite-type compounds: $NH_4[La_3(OH)_6(SO_4)_2]$. To determine the maximum polymer capacity during sorption of lanthanide(III) cations, sorption isotherms were obtained at 21 and 50°C. The amount of the lanthanide cations adsorbed at equilibrium was calculated with equation (1):

$$S = \frac{(C_0 - C_e)V}{m}, \quad (1)$$

where S is the lanthanide(III) cation sorption at the equilibrium (mmol M^{3+}/g), C_0 and C_e are the initial and equilibrium concentration of cations in the solution (mmol M^{3+}/L), respectively, V is the volume of the solution in contact with sorbent (L), m is the mass of the air dried polymer (g).

The isotherms, obtained experimentally, were calculated using the Langmuir and Freundlich adsorption models. When calculating isotherms and their constants according to the Langmuir model, Eqs. (2) and (3) were used [13]:

$$S = \frac{S_L k_L C_e}{1 + S_L C_e}, \quad (2)$$

$$\frac{C_e}{S} = \frac{1}{S_L k_L} + \frac{C_e}{S_L}, \quad (3)$$

where S is the cation sorption value at equilibrium (mmol M^{3+}/g); S_L is the monolayer capacity of the sorbent (mmol M^{3+}/g); k_L is the Langmuir isotherm constant (L/mmol), C_e is the cation concentration at sorption equilibrium (mmol M^{3+}/L).

The linear and nonlinear Freundlich isotherms were calculated using equations (4) and (5) [14]:

$$S = k_F C_e^{1/n}, \quad (4)$$

$$\ln S = \ln k_F + \left(\frac{1}{n}\right)\ln C_e, \quad (5)$$

where S is the same as in Eq. (2), k_F is the Freundlich isotherm constant, which predicts the quantity of the sorbate per gram of adsorbent at the equilibrium. $1/n$ is a measure of the nature and strength of the sorption process and of the distribution of active centers. If $1/n > 1$, bond energy increases with the surface density; if $1/n < 1$, bond energy decreases with the surface density; and when $1/n = 1$, all surface sites are equivalent. The constants $1/n$ and k_F were calculated by the graph of the linear Freundlich isotherm (Eq. (5)).

The sorption isotherms obtained experimentally and calculated using the Langmuir and Freundlich models are presented in Figs. 1–4.

Figures 1–3 suggest that the sorption isotherms of the cations of the lanthanides(III), which have a higher molar mass, will be similar. The data in Fig. 4 confirm this assumption. But, obviously, the characteristics of the isotherms will be different.

The experimentally obtained isotherms are described by the Langmuir adsorption model slightly better than by the Freundlich model (Table 1). The

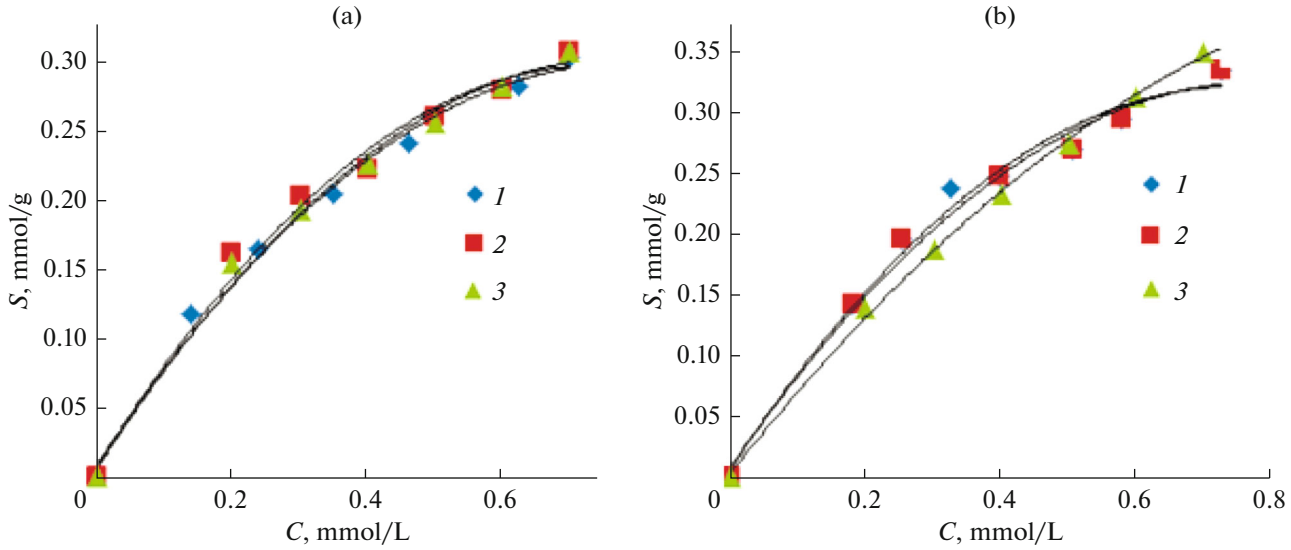

Fig. 1. Equilibrium sorption isotherms of La^{3+} at 21 (a) and 50°C (b) on Purolite A-400: obtained experimentally (*1*) and calculated by Langmuir (*2*) and Freundlich (*3*) adsorption models.

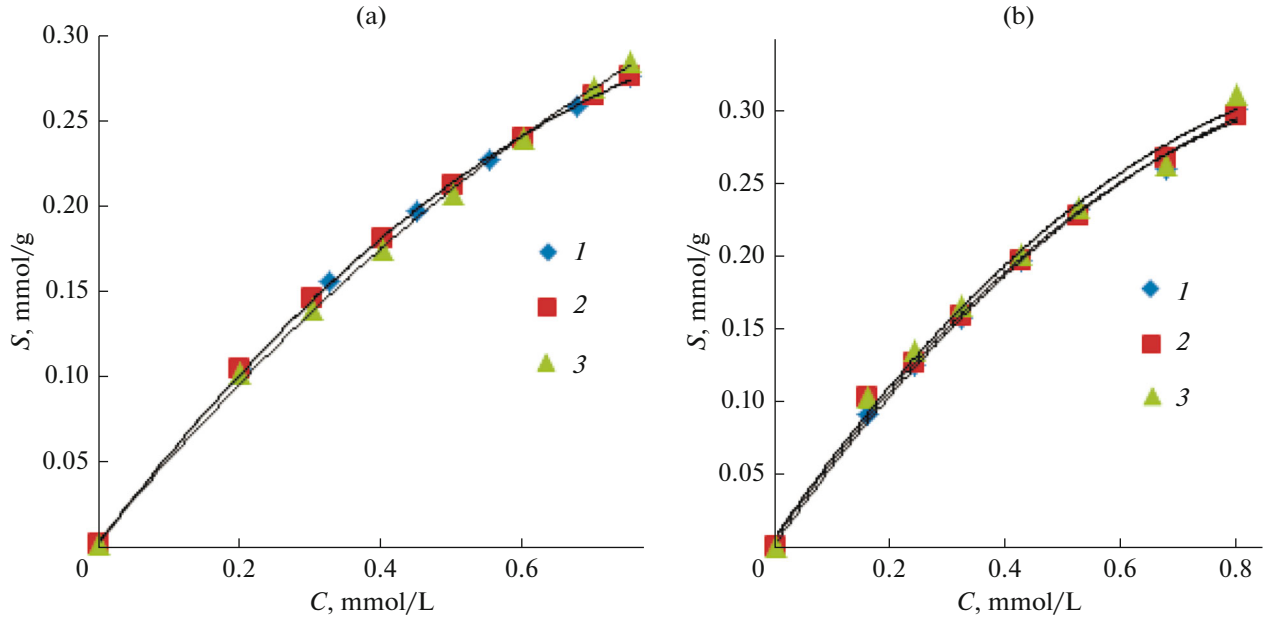

Fig. 2. Equilibrium sorption isotherms of Nd^{3+} at 21 (a) and 50°C (b) on Purolite A-400: obtained experimentally (*1*) and calculated by Langmuir (*2*) and Freundlich (*3*) adsorption models.

fact that k_L increases, but $1/n$ decreases with temperature increasing, additionally shows that the sorption of lanthanide(III) cations on Purolite A-400 is a chemical process. In the case of physical sorption, the temperature dependence of the Freundlich isotherm constants is inverse.

The feasibility of adsorption in a certain concentration range can be expressed in terms of a dimensionless constant (R_L), called constant separation factor or equilibrium parameter, was calculated using equation (6) [15]:

$$R_L = \frac{1}{1 + k_L C_0}, \quad (6)$$

where k_L is the Langmuir adsorption constant (L/mmol), and C_0 is the initial concentration of metal ions (mmol/L).

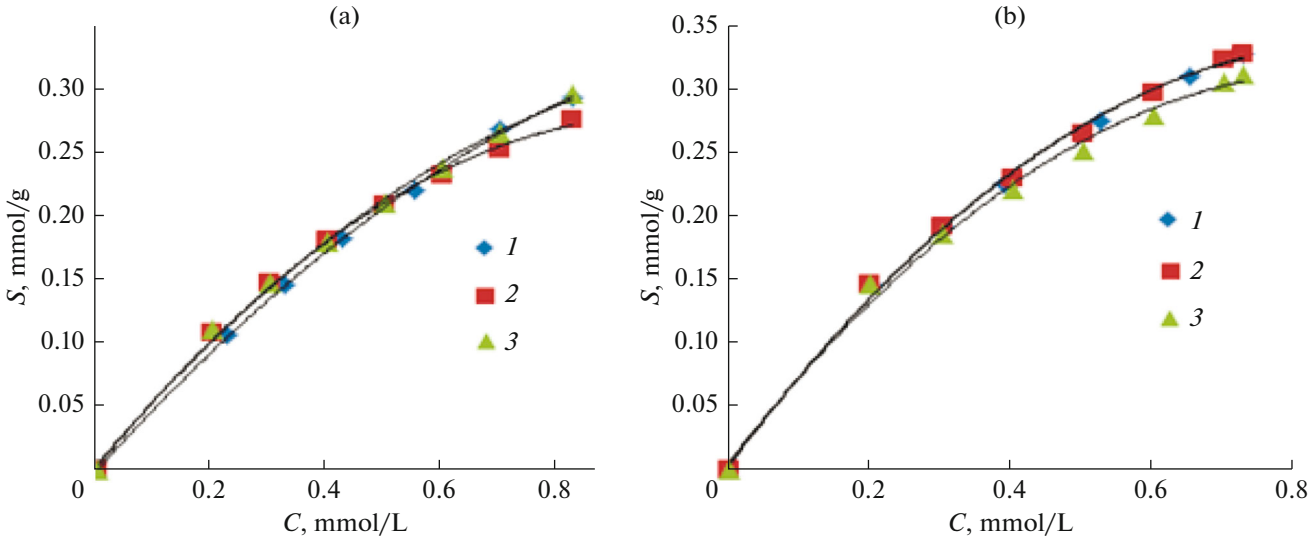

Fig. 3. Equilibrium sorption isotherms of Eu^{3+} at 21 (a) and 50°C (b) on Purolite A-400: obtained experimentally (*1*) and calculated by Langmuir (*2*) and Freundlich (*3*) adsorption models.

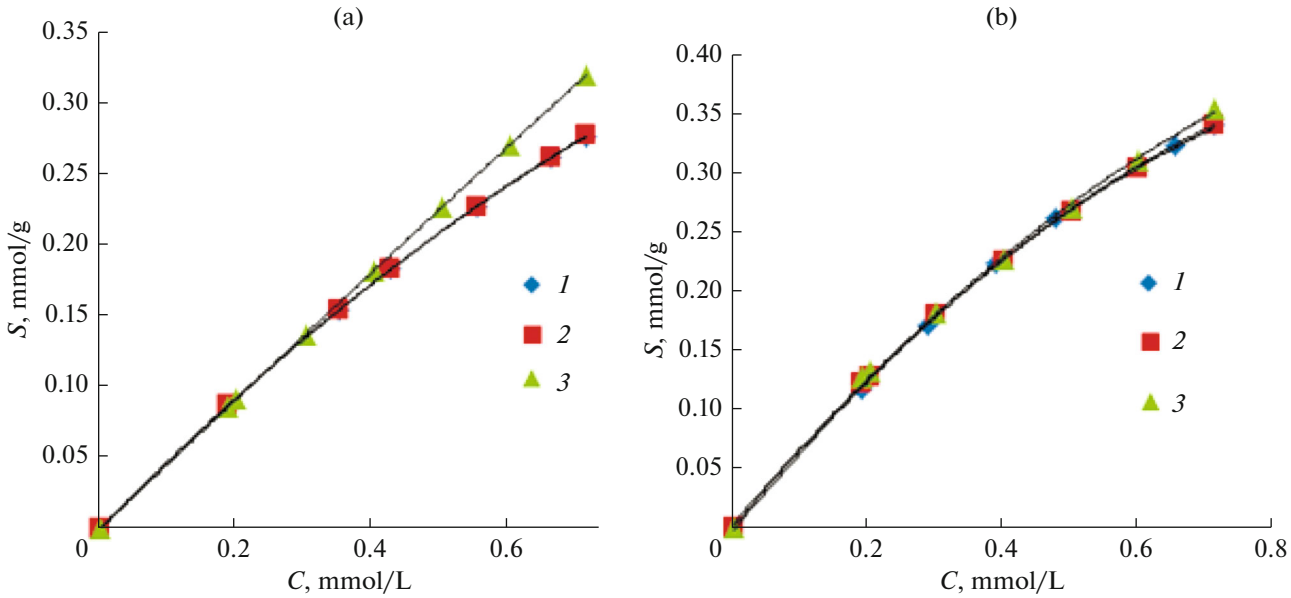

Fig. 4. Equilibrium sorption isotherms of Er^{3+} at 21 (a) and 50°C (b) on Purolite A-400: obtained experimentally (*1*) and calculated by Langmuir (*2*) and Freundlich (*3*) adsorption models.

According to the values of R_L, the sorption is: unfavorable when $R_L > 1$; linear when $R_L = 1$; favorable when $0 < R_L < 1$; irreversible when $R_L = 0$.

Beside the correlation coefficient of determination (R^2), the statistical analysis of errors was performed by the nonlinear Chi-square test (χ^2) using Eq. (7) [16]:

$$\chi^2 = \sum \frac{(S_{exp} - S_{calc})^2}{S_{calc}}. \quad (7)$$

The values of R_L, R^2 and χ^2 are also shown in Table 1.

From the data in Table 1 it can be seen that the maximum sorption of cations on Purolite A-400 at 50°C is higher than at 21°C. The maximum sorption both at 21 and 50°C is quite high, which is an important factor in the technology of cation separation and increases in the following order: $La^{3+} < Eu^{3+} < Nd^{3+} < Er^{3+}$.

The data in Table 1 also show that the sorption of Er^{3+} is significantly higher than that of other cations. To explain this, we must remember that compounds like the jarosite mineral-type are in the form of

Table 1. Parameters of sorption isotherms of lanthanide(III) cations on Purolite A-400 calculated using the Langmuir and Freundlich adsorption models

Cation	Langmuir model		Freundlich model	
	21°C	50°C	21°C	50°C
La^{3+}	$S_L = 0.425$ mmol/g $S_L = 59.04$ mg/g $K_L = 1.8292$ L/mmol $R^2 = 0.9866$ $R_L = 0.4385$ $\chi^2 = 0.0066$	$S_L = 0.539$ mmol/g $S_L = 74.87$ mg/g $K_L = 2.125$ L/mmol $R^2 = 0.9967$ $R_L = 0.3936$ $\chi^2 = 0.0017$	$K_F = 0.3716$ $1/n = 0.55$ $R^2 = 0.9924$ $\chi^2 = 0.006$	$K_F = 0.4535$ $1/n = 0.453$ $R^2 = 0.9984$ $\chi^2 = 0.0013$
Nd^{3+}	$S_L = 0.691$ mmol/g $S_L = 99.67$ mg/g $K_L = 0.8754$ L/mmol $R^2 = 0.9996$ $R_L = 0.6036$ $\chi^2 = 0.0017$	$S_L = 0.702$ mmol/g $S_L = 101.2$ mg/g $K_L = 0.905$ L/mmol $R^2 = 0.9962$ $R_L = 0.58$ $\chi^2 = 0.0014$	$K_F = 0.3548$ $1/n = 0.7869$ $R^2 = 0.9991$ $\chi^2 = 0.0018$	$K_F = 0.3621$ $1/n = 0.6914$ $R^2 = 0.9923$ $\chi^2 = 0.0027$
Eu^{3+}	$S_L = 0.542$ mmol/g $S_L = 82.6$ mg/g $K_L = 1.2563$ L/mmol $R^2 = 0.9985$ $R_L = 0.49$ $\chi^2 = 0.0017$	$S_L = 0.681$ mmol/g $S_L = 103.48$ mg/g $K_L = 1.2847$ L/mmol $R^2 = 0.9971$ $R_L = 0.52$ $\chi^2 = 0.0028$	$K_F = 0.3246$ $1/n = 0.6393$ $R^2 = 0.9967$ $\chi^2 = 0.0011$	$K_F = 0.3753$ $1/n = 0.5833$ $R^2 = 0.9941$ $\chi^2 = 0.0044$
Er^{3+}	$S_L = 1.219$ mmol/g $S_L = 203.89$ mg/g $K_L = 0.4168$ L/mmol $R^2 = 1.000$ $R_L = 0.4356$ $\chi^2 = 0.0167$	$S_L = 0.963$ mmol/g $S_L = 161.07$ mg/g $K_L = 0.7673$ L/mmol $R^2 = 0.9997$ $R_L = 0.6465$ $\chi^2 = 0.0005$	$K_F = 0.4493$ $1/n = 0.9825$ $R^2 = 9948$ $\chi^2 = 0.0132$	$K_F = 0.463$ $1/n = 0.7765$ $R^2 = 0.9986$ $\chi^2 = 0.0017$

pseudo-layers of 3 and/or 6 octahedral cycles [17]. In jarosites $4OH^-$ groups are located in the equatorial plane, forming a bridge between metal ions, and $2SO_4^{2-}$ groups are located in the axial position, each of them being coordinated by three metal ions of three octahedra. Between the layers are R_4N^+ groups of the polymer, held electrostatically.

According to [18, 19], the enthalpy of hydration of Er^{3+} cations is higher than that of other studied cations. The M^{3+}–O distance and diffusion coefficient in water decreases in the series $La^{3+} > Nd^{3+} > Eu^{3+} > Er^{3+}$ [19]. Thus, the interactions of Er^{3+} cations with 4 O atoms of OH^- and 2 O atoms of SO_4^{2-} groups in compounds of the jarosite mineral-type are stronger than those of other studied cations. In addition, the coordination number of the Er^{3+} cation (less than 9) differs from that of the other 3 cations, which is equal to 9.

This means that the composition and structure of the Er^{3+} compounds in the polymer phase may differ slightly from the compounds of other cations. That would be the reason why the adsorption of Er^{3+} cations is greater than the other cations. It should be noted that in the solutions used there are ions of various types: aqua and hydroxy cations with different compositions, which depend on pH, temperature and concentration [20]. But not all cation species participate in the formation of jarosite mineral-type compounds in the polymer phase. Most likely, $[MOH(H_2O)_5]^{2+}$ cations are involved in the formation of jarosite mineral-type compounds. In solutions with a pH lower than 1.5, in which there are only aqua cations

Table 2. The values of the thermodynamic functions for the sorption of lanthanide(III) cations on Purolite A-400

Cation	T, °C	$\Delta G°$, kJ mol^{-1}	$\Delta H°$, kJ mol^{-1}	$\Delta S°$, J K^{-1}
La^{3+}	21	−18.36	4.081	76.33
	50	−20.57		76.32
Nd^{3+}	21	−16.56	0.905	59.40
	50	−18.28		59.40
Eu^{3+}	21	−17.44	0.609	61.39
	50	−19.223		61.40
Er^{3+}	21	−14.75	16.61	106.67
	50	−17.84		106.67

$[M(H_2O)_6]^{3+}$, the sorption on polymers with strongly basic groups does not take place.

On the other hand, as is it known, polynuclear cations cannot be easily restructured to form new units [21]. Therefore, they also cannot participate in the formation of mineral-type jarosite compounds.

Another factor that could to some extent affect the sorption process is the nature and concentration of anions in the system. For the study, polymer Purolite A-400 in the form of chloride (R_4NCl) and sulfate solutions ($M_2(SO_4)_3$) were used. So in the system, besides the process of forming the jarosite mineral-type compounds, the process expressed by Eq. (8) also takes place:

$$2R_4NCl + SO_4^{2-} \rightleftarrows (R_4N)_2SO_4 + 2Cl^-. \quad (8)$$

But the influence of process (8) is insignificant, since the affinity, and especially the concentration of SO_4^{2-} anions in the system, is much higher than the concentration of Cl^- ions. Thus the equilibrium (8) is shifted to the right.

Considering the factors mentioned above and the fact that the pH in the polymer phase is different from the pH of solution, it can be explained why the sorption of Er^{3+} cations is higher at 21°C than at 50°C.

The R_L values calculated using Eq. (6) are greater than zero and less than one (Table 1) for the sorption of all investigated lanthanide(III) cations. This indicates that the sorption process is favorable and reversible. An increase in temperature favors the formation of composites by La^{3+} and Nd^{3+} cations. In the case of Eu^{3+} and Er^{3+} cations, an increase in temperature in the range of 21–50°C less favors this process. The values of R^2 and χ^2 are almost identical for the processes described using the Langmuir and Freundlich models. However, the Langmuir adsorption model gives us more information. Using the data obtained according to the Langmuir model, the thermodynamic parameters of the sorption process were calculated: free energy $\Delta G°$), enthalpy ($\Delta H°$), and entropy ($\Delta S°$).

The values of $\Delta G°$ were calculated with Eq. (9):

$$\Delta G° = -RT\ln k_L. \quad (9)$$

For calculation of the $\Delta H°$, in the assumption that in the range of temperature 21–50°C it is constant, the Eq. (10) has been used:

$$\Delta H° = R\frac{T_1T_2(\ln k_{L2}/\ln k_{L1})}{T_2 - T_1}, \quad (10)$$

where $T_1 = 294$ K, $T_2 = 320$ K, k_{L1} is Langmuir constant at 21°C, k_{L2}—at 50°C and $R = 8.314$ J/(mol K).

The values of $\Delta S°$ were calculated using Eq. (11):

$$\Delta S° = \frac{\Delta H° - \Delta G°}{T}, \quad (11)$$

The values of the thermodynamic functions for lanthanide(III) cations sorption on Purolite A-400 at 21 and 50°C are presented in Table 2. The data in Table 2 show that the lanthanide(III) cations adsorption on Purolite A-400 is a spontaneous process and thermodynamically favorable. Negative values of $\Delta G°$ show that as the temperature rises from 21 to 50°C, the affinity of cations for Purolite A-400 also increases. Positive values of $\Delta H°$ indicate that the sorption process is endothermic. The temperature dependence of adsorption is weak, being more pronounced for Er^{3+} cations.

The change in the entropy (Table 2) of the sorption process depends on the nature of the cation, but does not depend on temperature. The temperature independence of $\Delta S°$ can be explained by the assumption that the change in the heat capacity of the formation of metal compounds in the polymer phase is about zero ($\Delta C_p = 0$).

3.2. SEM EDX Investigation of Lanthanide(III)–Polymer Composites

The idea mentioned above about composites formation on the Purolite A-400 during sorption of lanthanide(III) cations is confirmed by the SEM EDX investigation (Figs. 5 and 6). The sorption values of the lanthanide(III) cations on Purolite A-400 are of the same order as that of the In^{3+} or Ga^{3+} cations [22] and are much lower than that of Fe^{3+} or Cr^{3+}. It is not excluded that redox processes will occur in a system containing a strongly basic polymer and a solution of lanthanide(III) sulfate, as in the case of systems containing Fe- or Ga-jarosite [22].

The elemental composition of the lanthanide (III)-containing structural unit on the polymer granules was obtained using the SEM EDX technique. The empirical formulas of the La(III)-, Nd(III)- , Eu(III)- and Er(III)-containing structural unites of composites on a polymer granule were calculated and they turned out to be as follows: $La_1Cl_{13.7}S_{64.3}O_{287.7}N_{122.6}C_{2869}$,

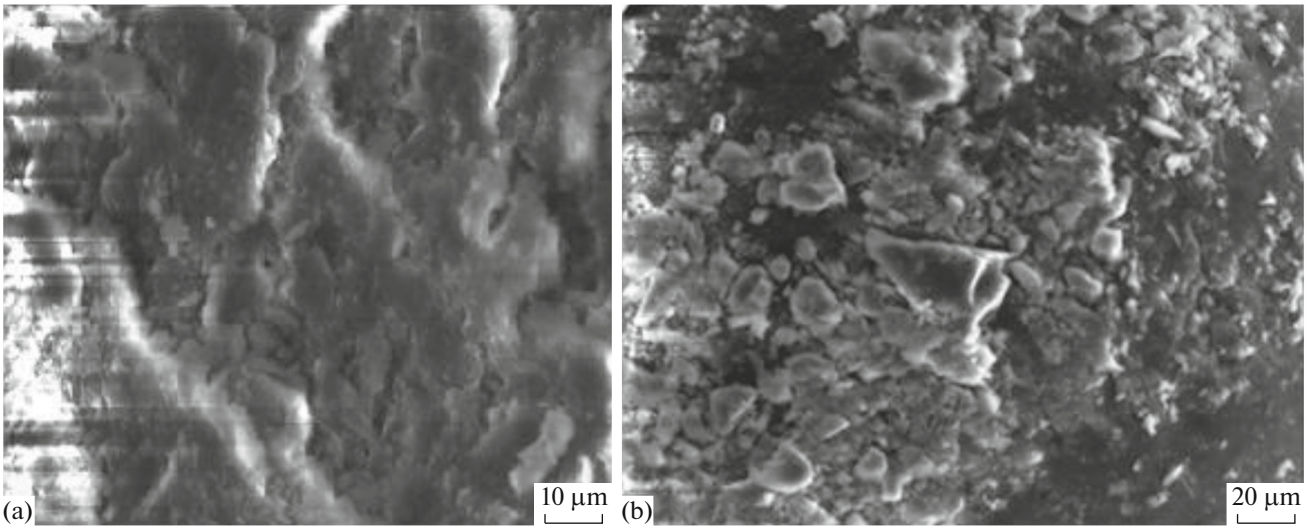

Fig. 5. SEM images of La^{3+} (a) and Nd^{3+} (b) compounds on a polymer granule.

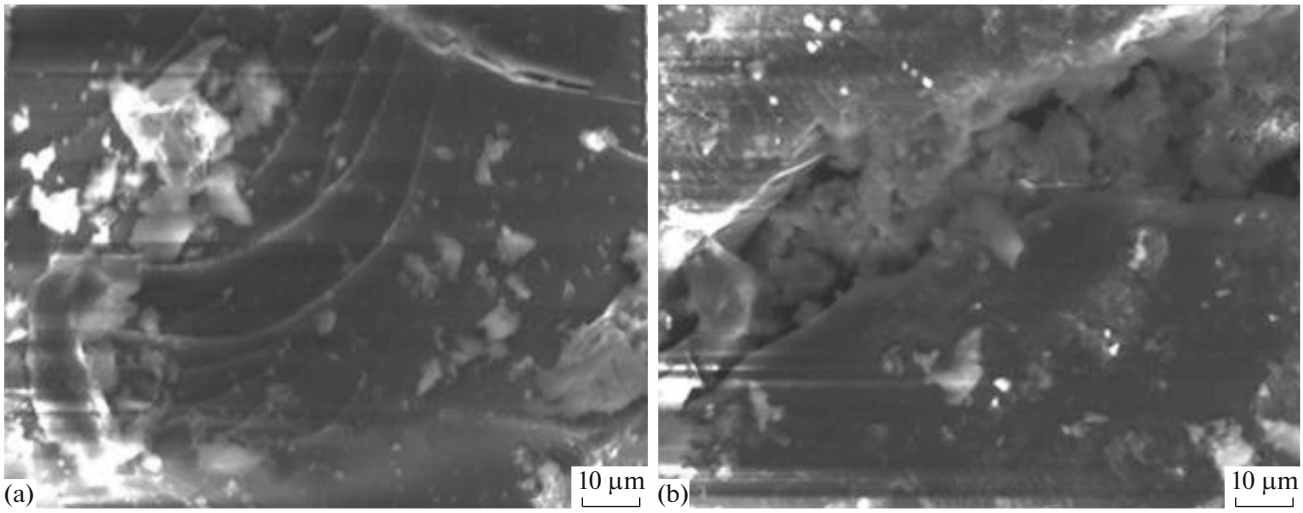

Fig. 6. SEM images of Eu^{3+} (a) and Er^{3+} (b) compounds on a polymer granule.

$Nd_1Cl_{27.4}S_{50.7}O_{391.6}N_{169.3}C_{2896}$, $Eu_1C_{18.5}S_{50.8}O_{285}N_{130}C_{2118}$ and $Er_1C_{136.8}S_{263.9}O_{1106}N_{447}C_{8657}$, respectively.

Compounds such as jarosite mineral-type do not contain Cl, N or C atoms. The high content of Cl, O, S, N and especially C atoms in the empirical formulas confirms that lanthanide(III) compounds are located on the $[-N(CH_3)_3]_2SO_4$, $-N(CH_3)_3Cl$ groups, and on a part of $-CH_2-$ polymer chain.

The obtained composites can be used as sorbents and catalysts with selective properties.

3.3. Thermogravimetric Study of Composites

The TG and DTG curves presented comparatively in Fig. 7 revealed a complex degradation mechanism involving six or seven stages with different mass loss percentages. With the exception of Nd^{3+} sample, according to the thermogravimetric data presented in Table 3 and to the thermogravimetric curves in Fig. 7, there was a tendency of the separation of two processes with T_{peak} in the temperature range 282–292°C at approximately 200, 218 and 247°C, respectively. This different behavior was also observed in the Eu^{3+} and Er^{3+} samples, in the temperature range 489–589°C, when two decomposition stages were separated comparatively to one in the case of the other two compounds—La^{3+} and Nd^{3+}. The mass percentage loss had approximately the same value in this temperature range for all the samples subjected to analysis, namely about 30%. Both hydrated and free water are lost in the first stage [23].

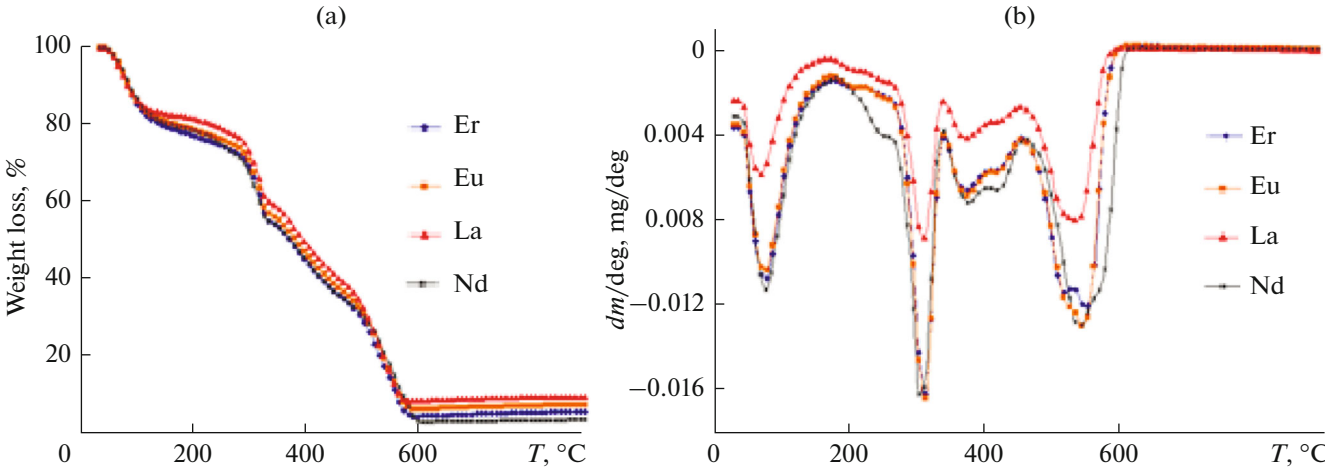

Fig. 7. TG (a) and DTG (b) curves of the Purolite A-400 samples containing lanthanide(III) compounds.

We assumed that the intermediates formed in the previous step were decomposed in the temperature range 282–292°C. Moreover, according to previous studies to which the TG/MS/FTIR technique was applied for strongly basic anion exchanger modified with Cr^{3+}, the following fragments could result: $m/z =$ 30 ($C_2H_6^+$), $m/z = 59$ ($N(CH_3)_3^+$), $m/z = 64$ (SO_+^2) and $m/z = 16$ (O^+) [23]. At temperatures ranging between 292 and 325°C, we assumed the onset of thermal decomposition of the raw polymer structure containing polystyrene–divinylbenzene, which also continues at temperatures higher than 489°C with the thermal oxidation process, occurred [24]. The third stage of decomposition highlighted approximately the same mass loss percentage (16%), as well as the temperature at which the degradation rate is maximum, $T_{peak} \cong$ 310°C. In the case of all the samples subjected to analysis, the decomposition was not complete, but resulted in a residual amount comprised between 3.6 and 8.8%.

The research was completed through the kinetic interpretation of the thermogravimetric curves with the help of the Freeman–Carroll method [25]. The *n*-th order kinetics allows calculating the activation energy (E_a, J mol^{-1}), pre-exponential factor (A) and order of reaction (n) from a single TG curve and the Eq. (12):

$$\frac{d\alpha}{dt} = Ae^{\frac{E_a}{RT}}(1-\alpha)^n, \qquad (12)$$

were $d\alpha/dt$ – rate of reaction in s^{-1}, $R = 8.31$ J mol^{-1} K^{-1}, T—sample temperature in K and α—conversion of reaction [25].

The kinetic parameters obtained for the stages for which the experimental data were sufficient for both the TG and DTG curves are presented in Table 3. For the first stage, the value of the apparent activation energy was approximately 52 kJ/mol. For the third stage, in which we assumed that the onset of the thermal decomposition of the raw polymer structure containing polystyrene–divinylbenzene took place, the activation energy was approximately 135 kJ/mol.

And finally, we can conclude that the composites formed by the polymer Purolite A-400 and the jarosite mineral-type compounds of lanthanides(III) are thermostable at temperatures up to almost 200°C.

4. CONCLUSIONS

The sorption of lanthanide(III) cations on a polymer containing strongly basic groups (quaternary ammonium nitrogen) is a chemical process. The sorption capacity (from 0.54 mmol of La^{3+}/g to 0.96 mmol of Er^{3+}/g) of Purolite A-400, a commercial cross-linked polymer, for lanthanide(III) cations is quite large and can be used in metal separation technologies. Chemisorption at 50°C is higher (with the exception of Er^{3+} cations) than at 21°C. The sorption isotherms of lanthanide(III) cations on the Purolite A-400 polymer are slightly better described by the Langmuir model than by the Freundlich model. The values of the thermodynamic functions $\Delta G°$, $\Delta H°$ and $\Delta S°$ show that the sorption of lanthanide(III) cations on the Purolite A-400 polymer is an endothermic and spontaneous process. In the Purolite A-400 phase, as a result of absorption, the La^{3+}, Nd^{3+}, Eu^{3+} and Er^{3+} cations form composites of the $R_4N[La_3(OH)_6(SO_4)_2]$ type (where R_4N^+ is the sorption center of the polymer and La^{3+} is the metal cation), which are located on the functional groups of the polymer. The elemental composition of structural units of the composites is $La_1Cl_{13.7}S_{64.3}O_{287.7}N_{122.6}C_{2869}$, $Nd_1Cl_{27.4}S_{50.7}O_{391.6}N_{169.3}C_{2896}$, $Eu_1C_{18.5}S_{50.8}O_{285}N_{130}C_{2118}$ and $Er_1Cl_{36.8}S_{263.9}O_{1106}N_{447}C_{8657}$. Thermogravimetric and kinetic characteristics of the Purolite A-400 containing lanthanide (III) compounds show that composites are stable to heating up to a temperature of at least 185°C. The total destruction of the

Table 3. Thermogravimetric and kinetic characteristics of the Purolite A-400 containing lanthanide(III) compounds

Sample	Stage	T_{onset}[a], °C	T_{peak}[b], °C	T_{end}[c], °C	W, %[d]	Residue at 900°C, %	E_a[f], kJ/mol	n[g]	ln$A$[h]
La^{3+}	I	46	69	109	16.67	8.79	56.13 ± 1.24	1.50 ± 0.003	14.89 ± 0.46
	II	194	204/248[e]	289	8.04		–	–	–
	III	289	310	323	16.38		125.46 ± 1.49	0.27 ± 0.008	20.98 ± 0.31
	IV	360	373	395	10.03		65.76 ± 3.48	0.43 ± 0.009	6.98 ± 0.66
	V	395	423	439	10.45		–	–	–
	VI	490	539	567	29.64		151.64 ± 2.82	0.27 ± 0.009	17.76 ± 0.45
Nd^{3+}	I	55	77	109	21.45	3.65	48.80 ± 0.52	1.07 ± 0.009	11.78 ± 0.18
	II	228	249	289	9.12		–	–	–
	III	289	308	321	15.35		136.27 ± 0.72	0.31 ± 0.003	23.38 ± 0.15
	IV	354	376	398	12.08		–	–	–
	V	398	426	442	7.08		–	–	–
	VI	510	541	592	31.27		90.23 ± 5.10	0.64 ± 0.009	7.54 ± 0.77
Eu^{3+}	I	54	75	115	17.98	6.32	50.50 ± 0.64	1.32 ± 0.009	12.47 ± 0.23
	II	194	200/218[e]	292	10.18		–	–	–
	III	292	311	325	16.26		145.42 ± 0.68	0.29 ± 0.003	25.10 ± 0.14
	IV	354	375	394	8.75		81.93 ± 3.22	0.40 ± 0.009	10.10 ± 0.61
	V	394	422	451	10.83		–	–	–
	VI	499	523	541	21.72		172.61 ± 2.57	0.26 ± 0.008	21.26 ± 0.40
	VII	541	548	577	7.96		–	–	–
Er^{3+}	I	52	75	119	18.47	4.77	55.41 ± 0.55	1.49 ± 0.009	14.23 ± 0.20
	II	184	198/246[e]	291	11.37		–	–	–
	III	291	312	323	15.80		138.84 ± 1.12	0.18 ± 0.006	23.69 ± 0.24
	IV	352	372	394	9.10		97.94 ± 4.49	0.44 ± 0.009	13.24 ± 0.86
	V	394	422	446	11.65		–	–	–
	VI	489	520	543	17.00		223.75 ± 2.91	0.90 ± 0.009	29.02 ± 0.45
	VII	543	552	573	11.84		–	–	–

[a]The temperature at which the thermal decomposition begins; [b]the temperature at which the degradation rate is maximum; [c]the temperature at which the thermal decomposition process ends; [d]mass losses percentage in each stage; [e]temperature at which the degradation rate reaches its maximum, corresponding to the two processes that are separated in the second stage; [f]activation energy; [g]reaction order; [h]pre-exponential factor.

composites takes place at a temperature of about 600°C in 6 stages (composite containing La^{3+}) and 7 stages (composite containing Nd^{3+}, Eu^{3+} or Er^{3+}).

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CONFLICT OF INTEREST

The authors declare that they have no conflicts of interest.

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