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COMPARATIVE CHARACTERISTICS OF POLYMETHACRYLIC ACID HYDROGEL SORPTION ACTIVITY IN RELATION TO LANTHANUM IONS IN DIFFERENT INTERGEL SYSTEMS

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Abstract. Phenomena of remote interaction in intergel systems polymethacrylic acid hydrogel – poly-4-vinylpyridine hydrogel (hPMAA-hP4VP) and polymethacrylic acid hydrogel – poly-2-methyl-5-vinylpyridine hydrogel (hPMAA-hP2M5VP) have been studied. It was found that there is a decrease of specific electric conductivity, pH and swelling degree of PMAA, P4VP, P2M5VP hydrogels during lanthanum ions sorption by the intergel systems. Significant increase of sorption properties (up to 30 %) in intergel systems comparatively with individual hydrogels of PMAA, P4VP, P2M5VP points to the fact of high ionization during mutual activation of the polymers. Maximum sorption of lanthanum ions occurs at the ratios of 17%hPMAA:83%hP4VP and 50%hPMAA: 50%hP2M5VP. Data on obtained IR spectra evidence to the sorption of the rare-earth metal by these intergel systems. The obtained results show a significant importance of possible application of intregel systems based on rare-crosslinked polymer hydrogels of acid and basic nature for creation of new innovative sorption technologies in hydrometallurgy.

Keywords: intergel systems, sorption, La^{3+} ions, IR spectroscopy, desorption.

1. Introduction

Modern sorption technologies for rare-earth metals extraction in hydrometallurgy are mainly based on ion-exchangers. Wide use of ion-exchangers in hydrometallurgy, chemical technology and other fields began after creation of ion-exchange synthetic resins. Current ion-exchange resins, which have high capacity, chemical resistance and mechanical strength, have displaced other ion-exchange materials.[1-8] Ion-exchange resins are widely used in various separation, purification and disinfection processes. The most common example of this application of ion-exchangers is extraction of target metal ions from industrial solutions and water treatment.[9-15] The main drawback of the ion exchange resins is the absence of selectivity. In other words, each ion-exchanger can be successfully applied only to one metal. Also, it should be noted that regeneration of the ion exchangers is a very complicated process. The process of ion-exchangers regeneration is the treatment of resin with a solution (basic for anion exchangers and acid for cation exchangers). During regeneration, the regenerating agent passes through the resin, trapping negative or positive ions and washing them, updating the ion exchange capacity of the resin.[16,17]

Ion-exchange resins are also important components in uranium extraction by the underground leaching method.[18-20] The underground leaching involves extraction of uranium-bearing waters through boreholes. The leaching solution containing uranium is then passed through the resin. The resin beads extract uranium from the solution by the ion-exchange. The process of uranium extraction is based on IER ability to selectively absorb uranium from solutions and pulps after leaching. In sulfuric acid solutions, uranium can be present as a uranyl (UO_2^{2+}) cation and anionic sulfate complexes that are in a dynamic balance:

$$UO_2^{2+} + nSO_4^{2-} \leftrightarrow UO_2(SO_4)_n^{2-2n} \qquad (1)$$

where n=1, 2 and 3.

Resins containing uranium are transported to a processing plant, where UO_2 is separated from resin beads and a yellow cake is subsequently produced. After that, the resin, if it needs is regenerated and sent to re-

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extract uranium from a leaching solution. Usually after sorption of uranium the industrial solution is wasted despite it contains several valuable components.

In this regard a relevant issue in hydrometallurgy is the development of new sorption technologies for extraction of rare earth metals. Intergel systems based on rare-crosslinked hydrogels of acid and basic nature can be used for it. The main differences between hydrogels and ion-exchange resins are physico-mechanical properties, swelling and conformational transformations in a polymer structure. Most hydrogels are polyelectrolytes.[21] The conformational behavior of polyelectrolytes is significantly influenced by the ionization degree of macromolecular coils.[22-25]

As can be seen from the previous studies,[26-33] intergel systems are multicomponent systems consisting of two or more hydro- or organogels and a common solvent. A feature of ionization process in intergel systems is the absence of a counterion in ionized groups. This is a consequence of intergel interactions, the result of which is the mutual activation of hydrogels and formation of uncompensated charges along the polymer chain. The uncompensated charge is formed as a result of cleavage of the proton from a carboxyl group upon dissociation of acid hydrogel and association of this ion with a heteroatom of basic hydrogel in an aqueous medium. The charge density of basic hydrogel is limited by the degree of acid hydrogel dissociation. Because of this, both hydrogels are ionized and do not have counterions in the charged links. The result is an increased sorption capacity in the comparison with individual hydrogels.[34-36]

Intergel system is represented in Fig. 1. The most important moment here is the absence of direct interaction between the macromolecules.

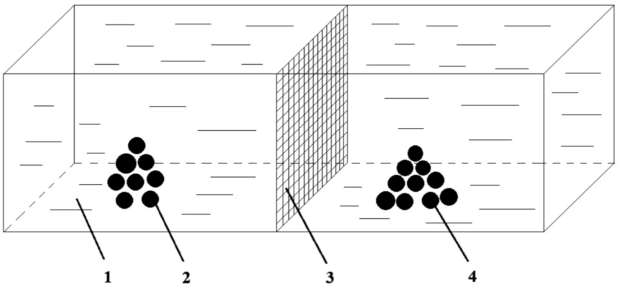

Fig. 1. Intergel system: solution (1); acid hydrogel (2); membrane (3) and basic hydrogel (4)

During remote interaction of hydrogels there is an occurrence of the following chemical reactions:

1) Dissociation of –COOH– groups of internode links:

$$-\mathrm{COOH} \rightarrow \mathrm{COO^{-}\cdots H^{+}} \rightarrow -\mathrm{COO^{-}} + \mathrm{H^{+}} \qquad (2)$$

It should be noted that ionization occurs first with the formation of ion pairs, then ion pairs are partially dissociated into separate ions.

2) Nitrogen atom in a pyridine ring is ionized and partially dissociated:

$$\equiv\mathrm{N} + \mathrm{H_2O} \rightarrow \equiv\mathrm{NH^{+}} \ldots \mathrm{OH^{-}} \rightarrow \equiv\mathrm{NH^{+}} + \mathrm{OH^{-}} \qquad (3)$$

As can be seen from the above processes, as a result of the "long-range effect" of polymer hydrogels, their mutual activation occurs. Mutual activation implies the transition of hydrogels into a highly ionized state. The result is significant changes in electrochemical properties (specific electric conductivity, pH) of solutions, as well as changes in conformational and sorption properties of macromolecules.

These interactions lead to the formation of uncompensated identical-charge functional groups on the inter-node links of both hydrogels (acid and base), which in turn repel each other according to the laws of electrostatics and lead to a macromolecular coil unfolding.

In this regard, the goal of the manuscript is to study sorption processes of lanthanum ions in two intergel systems: polymethacrylic acid hydrogel–poly-4-vinylpyridine hydrogel (hPMAA-hP4VP) and polymethacrylic acid hydrogel–poly-2-methyl-5-vinylpyridine hydrogel (hPMAA-hP2M5VP).

2. Experimental

2.1. Materials and Equipment

Studies were carried out in 0.005M lanthanum nitrate solution. Polymethacrylic acid hydrogel (hPMAA) was synthesized in the presence of crosslinking agent *N*,*N*-methylene-bis-acrylamide and $K_2S_2O_8$–$Na_2S_2O_3$ redox system in an aqueous medium. Synthesized hydrogels were crushed into small dispersions and washed with distilled water until a constant conductivity value of aqueous solutions was reached. Poly-4-vinylpyridine hydrogel (hP4VP) of Sigma-Aldrich company (linear polymer crosslinked by divinylbenzene) was used as a polybasis. Linear hydrogel of poly-2-methyl-5-vinylpyridine (hP2M5VP) was crosslinked by divinylbenzene. All polymer hydrogels were crushed into dispersions (the size of the hydrogels does not exceed 1 μm), which were sifted through a sieve with a diameter of 1 μm.

For investigations the intergel pairs: polymethacrylic acid hydrogel – poly-4-vinylpyridine hydrogel (hPAA-hP4VP) and polymethacrylic acid hydrogel – poly-2-methyl-5-vinylpyridine hydrogel (hPAA-hP2M5VP) were created. Swelling degrees of the hydrogels are: $\alpha_{(hPMAA)}$ = 20.41 g/g; $\alpha_{(hP4VP)}$ = = 3.19 g/g; $\alpha_{(hP2M5VP)}$ = 3.03 g/g. The concentration of hPMAA in the intergel system hPMAA-hP4VP decreased from 6.72 to 1.10 mmol/L along with the increase of hP4VP concentration from 1.12 to 6.74 mmol/L. The concentration of hPMAA in the intergel system hPMAA-hP2M5VP decreased from 6.74 to 1.07 mmol/L along with the increase of hP2M5VP concentration from 1.11 to 6.89 mmol/L.

For measurement of solutions specific electric conductivity a conductometer "MARK-603" (Russia) was used, hydrogen ions concentration was measured by a Metrohm 827 pH-meter (Switzerland). Samples weight was measured by analytic electronic scales Shimadzu AY120 (Japan). Measurement of optical density of lanthanum nitrate solutions for further calculation of La^{3+} ions concentration was carried out by a spectrophotometer Jenway-6305 (UK). IR-spectra of polymer complexes with lanthanum ions and IR-spectra of individual hydrogel were obtained using an IR-spectrometer Thermo Fischer Nicolet 5700 (USA).

2.2. Methodology

Electrochemical investigations. Experiments were carried out at room temperature (296.5 K). Studies of the intergel systems were made in the following order: each hydrogel was put in separate glass filters, pores of which are permeable for low molecular ions (lanthanum ions and protons) and molecules, but impermeable for hydrogels dispersion. The distance between 2 filters in each intergel pair (hPAA-hP4VP and hPAA-hP2M5VP) was 2 cm. After that the filters with hydrogels were put in glasses with a lanthanum nitrate solution without any stirring. Electric conductivity and pH of a lanthanum nitrate were measured in the presence of hydrogels in solutions.

Determination of hydrogels swelling degrees. Swelling degrees were calculated in accordance with Eq. (4):

$$\alpha = \frac{m_2 - m_1}{m_1} \qquad (4)$$

where m_1 and m_2 are weights of dry and swollen hydrogel, respectively, g.

Lanthanum ions desorption. After sorption each hydrogel separately from another was subjected to lanthanum ions desorption in 96% ethanol solution and 2M nitric acid.[37]

Desorption degree was calculated according to Eq. (5):

$$R_{des} = \frac{m_{des}}{m_{sorb}} \cdot 100\,\% \qquad (5)$$

where m_{des} and m_{sorb} are weights of desorbed and sorbed lanthanum, respectively, g.

Methodology of lanthanum ions determination. Determination of the rare-earth metal ions is based on a colorimetric determination with a complex forming agent arsenazo III.[38]

Extraction (sorption) degree was calculated by the equation:

$$\eta = \frac{C_{initial} - C_{residual}}{C_{initial}} \cdot 100\,\% \qquad (6)$$

where $C_{initial}$ and $C_{residual}$ are initial and residual concentrations of lanthanum in the solution, respectively, g/l.

Binding degree of polymer chain was calculated by the formula:

$$\theta = \frac{v_{sorbed}}{v} \cdot 100\,\% \qquad (7)$$

where v_{sorbed} is a quantity of polymer links with a sorbed lanthanum, mol; v is a total quantity of polymer links (if there are two hydrogels in the solution, it is calculated as the sum of each polymer hydrogel links), mol.

Effective dynamic exchange capacity was calculated by Eq. (8):

$$Q = \frac{v_{sorbed}}{m_{sorbent}} \cdot 100\,\% \qquad (8)$$

where v_{sorbed} is a quantity of sorbed lanthanum, mol; $m_{sorbent}$ is a sorbent mass (if there are two hydrogels in the solution it is calculated as the sum of their masses).

3. Results and Discussion

Lanthanum nitrate is the solution presented in a dissociated state. Lanthanum nitrate dissociation occurs in 3 stages:

$$La(NO_3)_3{\cdot}6H_2O \leftrightarrow La(NO_3)_2^{+}{\cdot}6H_2O + NO_3^{-}$$
$$La(NO_3)_2^{+}{\cdot}6H_2O \leftrightarrow LaNO_3^{2+}{*}{\cdot}H_2O + 2NO_3^{-}$$
$$LaNO_3^{2+}{\cdot}6H_2O \leftrightarrow La^{3+} + 3NO_3^{-} + 6H_2O$$

wherein the third stage dissociation constant is higher than this parameter in the second and third stage. In this regard there are different mechanisms of dissociated ions binding. Lanthanum nitrate formed at the third stage of dissociation interacts with polymer hydrogels by the ionic mechanism. At the first and second stages dissociation products sorption occurs as a result of coordination.

The following ions are present in the solution: H^+, La^{3+} and NO_3^-. Also–COO^- group of the polyacrylic acid hydrogel is present. Following chemical reactions occur in the solution:

1) Dissociation of lanthanum nitrate along with carboxyl groups dissociation and nitrogen atom ionization:

$$La(NO_3)_3{\cdot}6H_2O \leftrightarrow La^{3+} + 3NO_3^{-} + 6H_2O$$
$$\sim COOH \leftrightarrow \sim COO^{-} + H^{+}$$

$$\equiv N + H^+ \leftrightarrow \equiv NH^+$$

2) Sorption of lanthanum ions by polymer hydrogels:

$$3{\sim}COO^- + La^{3+} \rightarrow {\sim}COO_3La$$

$$3\equiv N + La^{3+} \rightarrow \equiv N^+{}_3La$$

Electrochemical equilibrium in the solution depends on these reactions and there could be changes of electrical conductivity values depending on dominance of any of them.

3.1. Sorption of Lanthanum Ions by Intergel System hPMAA-hP4VP

Fig. 1 shows the dependence of specific electric conductivity of the lanthanum nitrate solution in the presence of hPMAA-hP4VP. As seen from Fig. 1, there is the decrease of electric conductivity with time.

Main reason of the decrease of specific electric conductivity values is the sorption of lanthanum ions, along with a partial binding of the protons. After 30 min of the beginning of the interaction between the intergel system with the salt solution there is a sharp decrease of electric conductivity. Further remote interaction of the polyacid and the polybasis in the lanthanum nitrate provide the decrease of electric conductivity. Minimum values of the electric conductivity are observed for 48 h of interaction at the ratio of 17%hPMAA:83%hP4VP.

Dependence of lanthanum nitrate solution pH on time in the presence of the intergel system hPMAA-hP4VP is shown in Fig. 2. As seen from the obtained data there is an increase of hydrogen ions in the solution, that is evidenced by pH values. This is due to the fact that the ionization of poly-4-vinylpyridine hydrogel occurs owing to the association of protons by the heteroatom and formation of coordination bonds with the products of lanthanum nitrate dissociation. Lanthanum ions are bound by carboxylate anions and, as a result, their amount in the solution decreases. Due to this phenomenon, there is an occurrence of additional dissociation of carboxyl groups, that, in turn, provides a significant increase of acid hydrogel in the intergel system.

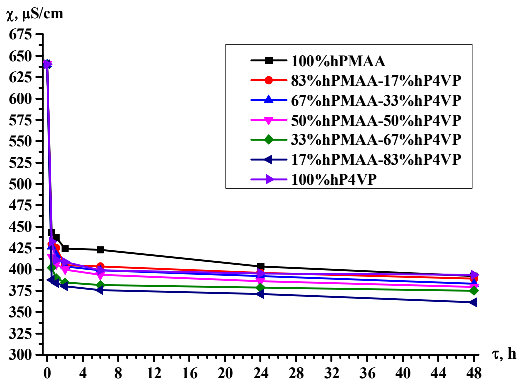

Fig. 1. Dependence of specific electric conductivity of the lanthanum nitrate solution on time in the presence of intergel system hPMAA-hP4VP

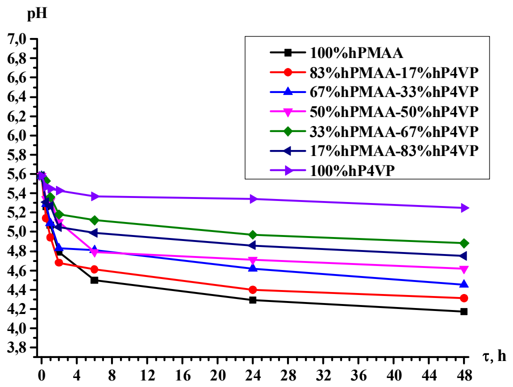

Fig. 2. Dependence of the lanthanum nitrate solution pH on time in the presence of intergel system hPMAA-hP4VP

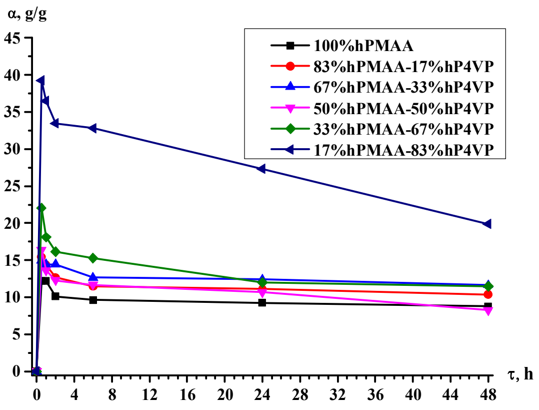

Fig. 3. Dependence of hPMAA swelling degree on time in the presence of hP4VP

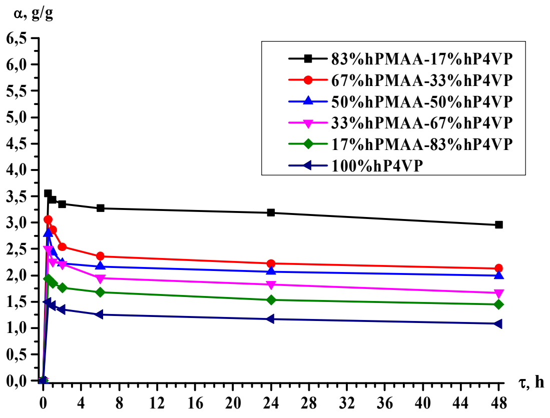

Fig. 4. Dependence of hP4VP swelling degree on time in the presence of hPMAA

Dependence of swelling degree of the polymethacrylic acid hydrogel on time in the presence of poly-4-vinylpyridine hydrogel is presented in Fig. 3. Maximum swelling of the polyacid is observed during the first 30 min of remote interaction of the polymers at the ratio of 17%hPMAA:83%hP4VP. Consequent remote interaction of the PMAA hydrogel with P4VP hydrogel provides a decrease of swelling degree of the polyacid due to the sorption of lanthanum ions. Sorption of lanthanum ions provides folding of the macromolecular globe, that is the main reason of swelling decrease of PMAA hydrogel.

Fig. 4 represents the dependence of poly-4-vinylpyridine hydrogel swelling degree on time in the presence of polymethacrylic acid in the lanthanum nitrate solution. Similarly to the polyacid (Fig. 3), maximum values of the swelling degree of the vinylpyridine are observed for 30 min of hydrogels interatcion at the ratio of 83%hPMAA:17%hP4VP in the intergel system. Absence of the mutual activation phenomenon when there is only polybasis in the solution provides minimum values of the swelling degree. The result of the lanthanum ions sorption is folding of the macromolecule and decrease of the swelling degree of the poly-4-vinylpyridine hydrogel with time.

Dependence of lanthanum ions extraction degree of the intergel system hPMAA-hP4VP on hydrogels molar ratios with time is shown in Fig. 5. Obtained results show that mutual activation of the initial polymers provides significant increase of sorption properties of polymer hydrogels. Initial hydrogels of polymethacrylic acid and poly-4-vinylpyridine do not have high values of lanthanum ions sorption degree. Extraction degree of the metal ions is 66.28 % for hPMAA and 66.05 % for hP4VP. Maximum sorption of lanthanum ions occurs at the ratio of 17%hPMAA:83%hP4VP. Sorption degree at this ratio is 90.34 %. Significant increase of sorption degree occurs due to the high ionization of polymer structures in result of their mutual activation.

Fig. 6 shows the dependence of polymer chain binding degree (in relation to lanthanum ions) of the intergel system hPMAA-hP4VP on time. Intergel pairs have higher values of binding degree comparatively with individual hydrogels. Polymer chain binding degree of individual hydrogels of PMAA and P4VP is 55.17 % and 55.00 %, respectively. Among intergel pairs a binding of lanthanum occurs not intensive at ratios of 83%hPMAA:17%hP4VP and 67%hPMAA:33%hP4VP. Not very high binding degree points to the insufficient ionization degree in mentioned above intergel pairs during their remote interaction. Maximum values of binding degree are observed at the ratio of 17%hPMAA:83%hP4VP for 48 h of interaction. Polymer chain binding degree at this ratio is 75.33 %.

Effective dynamic exchange capacity (in relation to lanthanum ions) of the intergel system is presented in Fig. 7. Remote interaction of hPMAA and hP4VP provides significant increase (up to 30 %) of exchange capacity of the polymer structures. The highest values of exchange capacity are observed in the intergel system at ratios of 33%hPMAA:67%hP4VP and 17%hPMAA:3%hP4VP. Wherein, maximum values of effective dynamic exchange capacity are reached for 48 h at the ratio of 17%hPMAA:83%hP4VP. Minimum values of exchange capacity are observed in the presence of only polyacid and polybasis.

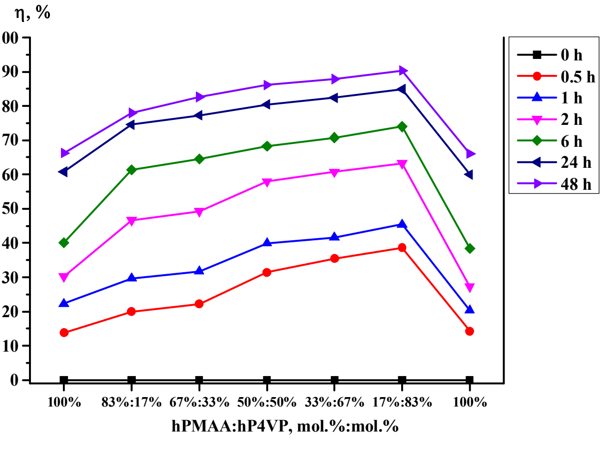

Fig. 5. Dependence of lanthanum ions extraction degree of intergel system hPMAA-hP4VP on hydrogels molar ratios with time

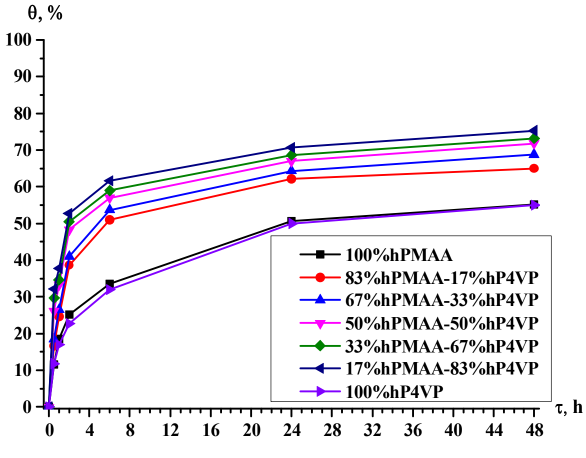

Fig. 6. Dependence of polymer chain binding degree (in relation to lanthanum ions) of intergel system hPMAA-hP4VP on time

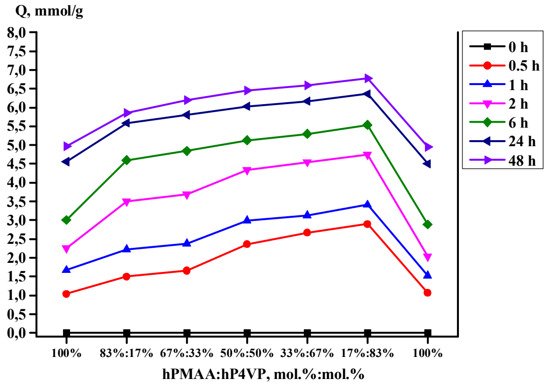

Fig. 7. Dependence of effective dynamic exchange capacity (in relation to lanthanum ions) of intergel system hPMAA-hP4VP on hydrogels molar ratios with time

3.2. Sorption of Lanthanum Ions by Intergel System hPMAA-hP2M5VP

Sorption of lanthanum ions by intergel system hPMAA-hP2M5VP is accompanied by the decrease of specific electric conductivity with time (Fig. 8). Significant decrease of electric conductivity occurs during 30 min after start of the intergel system interction with the lanthanum nitrate solution. Character of the electric conductivity decrease at various ratios is different. The decrease of conductivity at the ratio of 83%hPMAA:17%hP2M5VP is not intensive. This fact points to not very high ionization degree of the polymer structures during their remote interaction. Minimum values of electric conductivity of lanthanum nitrate soluion are observed at the ratio of 50%hPMAA: 0%hP2M5VP for 48 h of remote interaction. There is release of protons in the solution during mutual activation of the macromolecules, however, electric conductivity decreases, that evidences about sorption of the metal by the polymers.

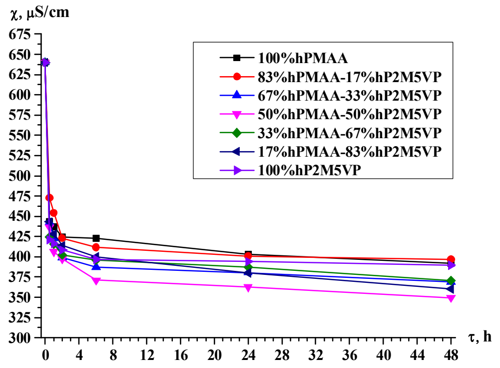

Fig. 8. Dependence of specific electric conductivity of the lanthanum nitrate solution on time in the presence of intergel system hPMAA-hP2M5VP

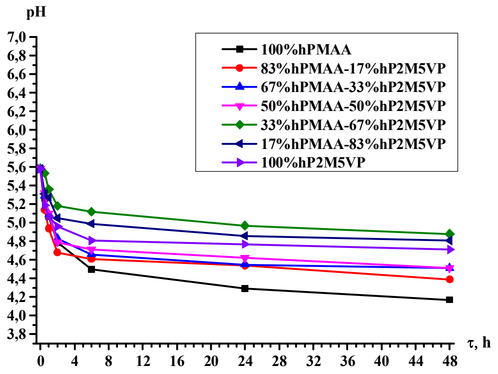

Fig. 9. Dependence of the lanthanum nitrate solution pH on time in the presence of intergel system hPMAA-hP2M5VP

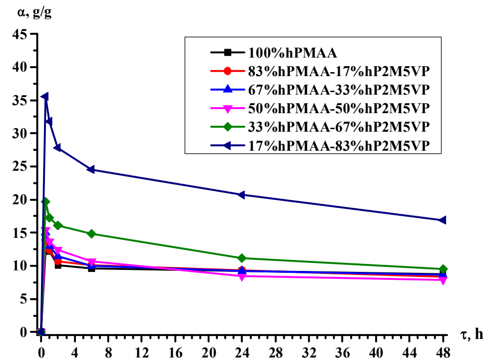

Fig. 10. Dependence of hPMAA swelling degree on time in the presence of hP2M5VP

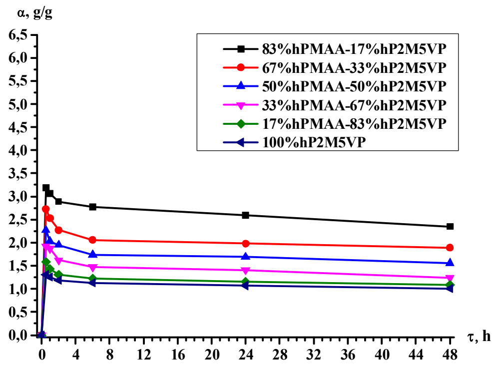

Fig. 11. Dependence of hP2M5VP swelling degree on time in the presence of hPMAA

Dependence of lanthanum nitrate solution pH on time in the presence of intergel system hPMAA-hP2M5VP is presented in Fig. 9. As seen from the obtained results, minimum values of pH are observed in the presence of polyacid only. This fact provides conclusion about the release of protons in the solution due to the decrease of their amount as a result of electrochemical equilibrium shift to the right (formation of H^+).

Fig. 10 shows the change of swelling degree of hPMAA acid hydrogel on time in the presence of hP2M5VP basic hydrogel. Maximum swelling of the polyacid occurs during the first 30 min of the intergel system interaction with the solution at the ratio of 17%hPMAA:83%hP2M5VP. Sorption of lanthanum ions provides folding of the macromolecular globe due to the absence of charged groups on internode links.

Dependence of swelling degree of poly-2-methyl-5-vinylpyridine basic hydrogel on time is shown in Fig. 11. Change of swelling degree of the polybasis occurs similar to polyacid (Fig. 10) – the swelling degree of hP2M5VP increases with the increase of the second hydrogel (hPMAA) concentration. Maximum values of swelling degree are achieved during 30 min of remote interaction in the salt solution at the ratio of 50%hPMAA:50%hP2M5VP. Impossibility of transition into highly ionized state of the polybasis in case when there is only polybasis in the solution, provides the absence of additional activation of links, that, in turn, provides unfolding of macromolecular globe. The result of this phenomenon is the minimum values of hP2M5VP swelling degree.

Fig. 12 presents dependence of extraction degree of lanthanum ions by the intergel system hPMAA-hP2M5VP on hydrogels molar ratios with time. Lanthanum ions sorption degree increases with time. Extraction degree of lanthanum ions by individual hydrogels of PMAA and P2M5VP is not high due to the absence of mutual activation phenomenon. Lanthanum ions sorption degree is 66.28 % for hPMAA and 63.65 % for hP2M5VP. As seen from the obtained data, the sorption of lanthanum in the intergel system occurs more intensive in comparison with individual hydrogels, that is a result of transition of the intergel system initial components into highly ionized state during mutual activation. Result of such transition is a significant increase of sorption properties. High values of sorption degree are observed at ratios of 67%hPMAA: 3%hP2M5VP and 50%hPMAA:50%hP2M5VP. Area of lanthanum ions maximum sorption is the ratio of 50%hPMAA:50%hP2M5VP, the sorption degree is 89.65 %.

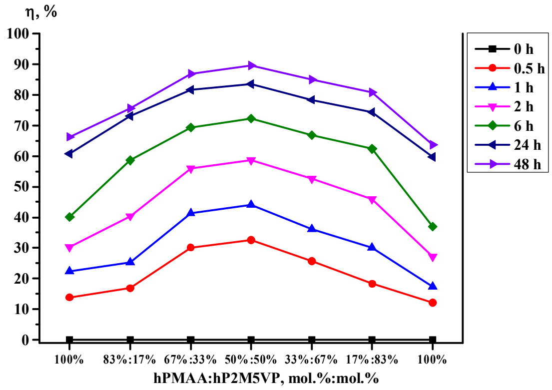

Fig. 12. Dependence of lanthanum ions extraction degree of intergel system hPMAA-hP2M5VP on hydrogels molar ratios with time

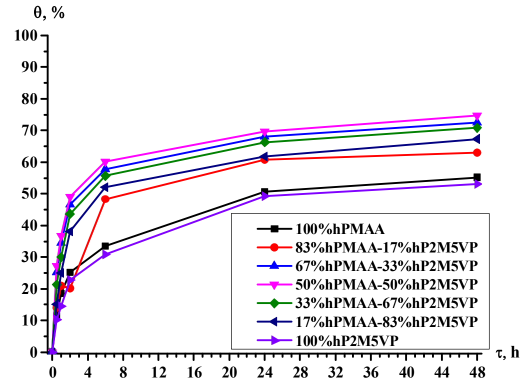

Fig. 13. Dependence of polymer chain binding degree (in relation to lanthanum ions) of intergel system hPMAA-hP2M5VP on time

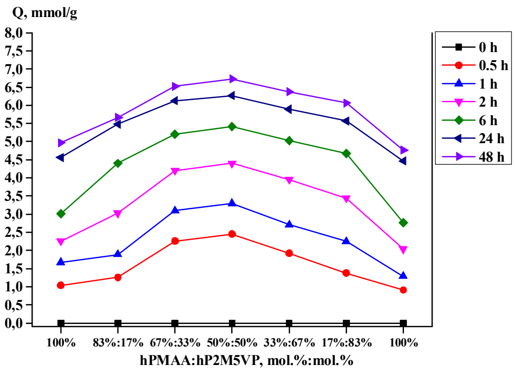

Fig. 14. Dependence of effective dynamic exchange capacity (in relation to lanthanum ions) of intergel system hPMAA-hP2M5VP on hydrogels molar ratios with time

Polymer chain binding degree (in relation to lanthanum ions) of the polymer system hPMAA-hP2M5VP is shown in Fig. 13. Binding degree of individual hydrogels of PMAA and P2M5VP is not very high: 55.17 % and 53.00 %, respectively. High ionization of the polymers in intergel pairs provides significant increase (more than 20 %). Maximum values of the parameter are observed at the ratio of 50%hPMAA:50%hP2M5VP, polymer chain binding degree is 74.67 %.

Fig. 14 presents the dependence of effective dynamic exchange capacity of the intergel system hPMAA-hP2M5VP on hydrogels molar ratios with time. Obtained results show that the intergel system based on rare-crosslinked hydrogels of PMAA and P2M5VP has higher values of exchange capacity comparatively with individual hydrogels. It should be noted that due to the fact that P2M5VP hydrogel has a bulky methyl substituent, its ionization occurs slowly in comparison with polybasis in the intergel system hPMAA-hP4VP. Highest values of exchange capacity in the intergel system hPMAA-hP2M5VP are observed at ratios 67%hPMAA:33%hP2M5VP and 50%hPMAA:50%hP2M5VP. The highest values of the effective dynamic exchange capacity are shown at ratio 50%hPMAA:50%hP2M5VP for 48 h of remote interaction. Obtained results show that the transition of initial polymers into highly ionized state is accompanied with the significant increase (up to 30 %) of exchange capacity comparatively with individual hydrogels.

Sorption properties (in relation to lanthanum ions) of the intergel systems hPMAA-hP4VP and hPMAA-hP2M5VP and individual hydrogels of PMAA, P4VP and P2M5VP are presented in Tables 1 and 2.

Table 1. Sorption properties of the intergel system hPMAA-hP4VP and individual hydrogels of PMAA and P4VP

	hPMAA	hPMAA:hP4VP					hP4VP
		83 %:17 %	67 %:33 %	50 %:50 %	33 %:67 %	17 %:83 %	
η, %	66.28	77.92	82.63	86.10	87.85	90.35	66.05
θ, %	55.17	65.00	68.83	71.83	73.17	75.33	55.00
Q, mmol/g	4.97	5.85	6.20	6.45	6.59	6.77	4.95

Table 2. Sorption properties of the intergel system hPMAA-hP2M5VP and individual hydrogels of PMAA and P2M5VP

	hPMAA	hPMAA:hP2M5VP					hP2M5VP
		83 %:17 %	67 %:33 %	50 %:50 %	33 %:67 %	17 %:83 %	
η, %	66.28	75.57	86.93	89.65	84.94	80.83	63.65
θ, %	55.17	63.00	72.50	74.67	70.83	67.33	53.00
Q, mmol/g	4.97	5.67	6.52	6.72	6.37	6.06	4.77

As can be seen from the tables, the values of sorption properties of the intergel system hPMAA-hP4VP are higher than those in the intergel system hPMAA-hP2M5VP. Such difference in sorption properties is due to the presence of bulky methyl substituent in the structure of P2M5VP hydrogel. Presence of the substituent makes the process of macromolecular globe unfolding slower than in the intergel system hPMAA-hP4VP.

3.3. Desoprtion of Lanthanum Ions from the Polymer Matrix

Desorption of the rare-earth elements, which were extracted as hydrophobic complexes, can be conducted by strong mineral acids or by organic solvents. For desorption the following hydrogels ratios were taken: 17%hPMAA:83%hP4VP and 50%hPMAA: 0%P2M5VP. These ratios were selected for desorption process due to the fact that maximum sorption of lanthanum ions occurs in these intergel pairs in the intergel systems.

3.3.1. Desorption of lanthanum ions by ethyl alcohol

Fig. 15 presents dependence of desorption degree of lanthanum ions by ethyl alcohol from matrixes of hPMAA and hP4VP on time. Significant increase of lanthanum desorption has been observed for 6 h. Further desorption occurs less intensively for both hydrogels. Total desorption degree from matrixes of both hydrogel for 48 h is 82.26 %. Obtained data show that overwhelming majority of lanthanum ions was firstly sorbed by the polyacid.

Comparison of sorption degrees of lanthanum ions by ethyl alcohol is presented in Table 3. Relatively not high values of desorption degree are due to the desorption agent nature and structure of initial polymers.

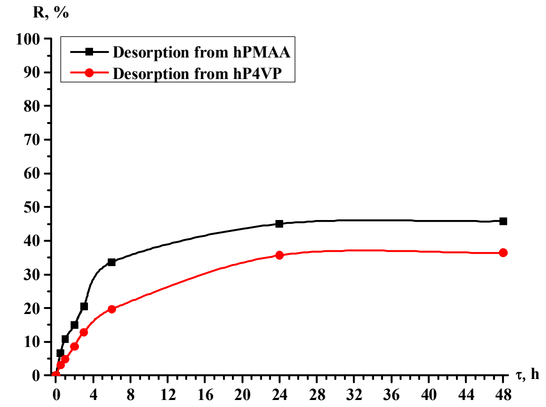

Fig. 15. Dependence of lanthanum ions desorption degree by ethyl alcohol from matrixes hPMAA and hP4VP on time

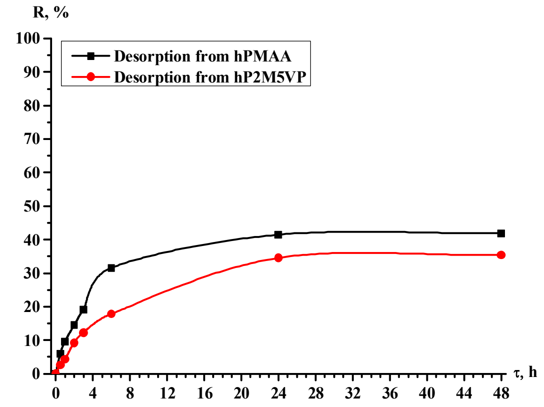

Fig. 16. Dependence of lanthanum ions desorption degree by ethyl alcohol from matrixes hPMAA and hP2M5VP on time

Table 3. Desorption degree of lanthanum ions from hPMAA and hP4VP by ethyl alcohol

Time, h	0	0.5	1	2	3	6	24	48
R (from hPMAA), %	0	6.65	10.79	14.98	20.40	33.64	44.99	45.81
R (from hP4VP), %	0	3.07	4.86	8.59	12.83	19.68	35.69	36.45
R total	0	9.72	15.65	23.57	33.23	53.32	80.68	82.26

Table 4. Desorption degree of lanthanum ions from hPMAA and hP2M5VP by ethyl alcohol

Time, h	0	0.5	1	2	3	6	24	48
R (from hPMAA), %	0	5.92	9.58	14.48	19.17	31.58	41.47	41.89
R (from hP4VP), %	0	2.63	4.33	9.17	12.21	17.83	34.57	35.39
R total	0	8.55	13.91	23.65	31.38	49.41	76.04	77.28

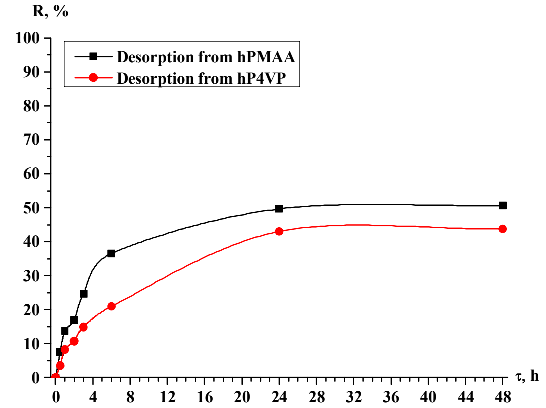

Fig. 17. Dependence of desorption degree of lanthanum ions by nitric acid from matrixes hPMAA and hP4VP on time

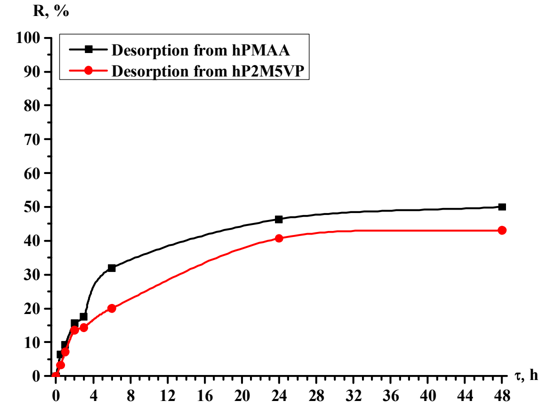

Fig. 18. Dependence of desorption degree of lanthanum ions by nitric acid from matrixes hPMAA and hP2M5VP on time

Dependence of desorption degree of lanthanum ions by ethyl alcohol is shown in Fig. 16. Similarly to previous case (Fig. 15), the most intense desorption occurs for 6 h, 31.58 % of lanthanum is desorbed from hPMAA and 17.83 % – from hP2M5VP. Total desorption degree of lanthanum ions from matrixes of hPMAA and hP2M5VP for 48 h is 77.28 %.

Table 4 presents values of desorption degree of lanthanum ions from matrixes of polymer hydrogels of PMAA and P2M5VP. As seen from the obtained results, relatively not high (~77–83 %) desorption degree is directly impacted by nature of desorbent (as known, ethyl alcohol is the polar solvent). Due to this phenomenon there is an occurrence of not full desorption of lanthanum ions from matrixes of the polymer hydrogels.

3.3.2. Desorption of lanthanum ions by nitric acid

Fig. 17 represents desorption process of lanthaum ions from polymer hydrogels of PMAA and P4VP by nitric acid. More than half of sorbed lanthanum is desorbed during 6 h of interaction between the desorbent and macromolecules. At this time 36.55 % of lanthanum is desorbed from hPMAA and 20.96 % – from hP4VP. The total desorption degree is 94.43 % for 48 h of interaction. Values of desorption degree from matrixes of hydrogels of PMAA and P4VP by nitric acid are presented in Table 5.

As seen from Fig. 18, the most intensive desorption of the rare-earth metal occurs during 6 h – 31.94 % of lanthanum is desorbed from hPMAA and 20.04 % – from hP2M5VP. Total desorption degree is 93.09 % for 48 h of interaction. Comparative analysis of desorption degree of lanthanum ions from hPMAA and hP2M5VP is presented in Table 6.

Obtained results point to the fact, that nitric acid, being a strong mineral acid, interacts quite intensively with the polymer hydrogels that is evidenced by the higher desorption degree (~ 93–95 %) comparatively with ethyl alcohol.

Table 5. Desorption degree of lanthanum ions from hPMAA and hP4VP by nitric acid

Time, h	0	0.5	1	2	3	6	24	48
R (from hPMAA), %	0	7.41	13.65	16.87	24.54	36.55	49.64	50.66
R (from hP4VP), %	0	3.48	8.18	10.74	14.83	20.96	43.00	43.76
R total	0	10.89	21.83	27.61	39.37	57.51	92.64	94.42

Table 6. Desorption degree of lanthanum ions from hPMAA and hP2M5VP by nitric acid

Time, h	0	0.5	1	2	3	6	24	48
R (from hPMAA), %	0	6.34	9.27	15.71	17.52	31.94	46.37	49.97
R (from hP4VP), %	0	3.25	7.21	13.60	14.32	20.04	40.70	43.12
R total	0	9.59	16.48	29.31	31.84	51.98	87.07	93.09

3.4. IR Spectra of PMAA and P4VP Hydrogels

For IR analysis the following hydrogels ratios were taken: 17%hPMAA:83%hP4VP and 50%hPMAA: 0%hP2M5VP. These ratios were selected for desorption process due to the fact that maximum sorption of lanthanum ions occurs in these intergel pairs in the intergel systems. Also, initial hydrogels of hPMAA and hP4VP were taken for the comparative analysis.

3.4.1. Characteristics of IR spectra of hPMAA and hP4VP hydrogels before and after sorption of lanthanum ions

Fig. 19 presents IR spectra of hPMAA before and after sorption of lanthanum ions. Based on this figure, one can observe that the spectrum of polymethacrylic acid hydrogel obtained after the sorption process of lanthanum ions practically repeats the contour of the spectrum of the original hydrogel, but with a noticeable reduction in the intensity of the absorption bands (approximately by 2.5–3 times). This fact of reduction indicates a process of lanthanum ions sorption occurring in a hydrogel. Hydrogel of PMAA has a characteristic mechanism for the sorption of heavy metal ions by the carboxyl group, as evidenced by a decrease in the intensity of the –COOH absorption band in the 1700 cm^{-1} region. Strong decrease of the intensity can be explained by the effect of the methyl substituent on the valent vibrations in the polymethacrylic acid chain. The effect of the $-CH_3$ substituent on the formation of hydrogen bonds between the –OH fragments of the carboxyl group of the PMAA chain can be also observed. From the figure it can be seen that the intensity of the broad absorption band in the region of 3600–2800 cm^{-1}, which is responsible for the stretching vibrations of intra- and intermolecular bonds, decreases quite strongly. It can be concluded that the process of sorption of lanthanum ions by the PMAA hydrogel is accompanied by the destruction of large amount of hydrogen bonds between hydroxyl groups in the polymer chain.

Further, IR spectra of the initial poly-4-vinylpyridine hydrogel and poly-4-vinylpyridine hydrogel after sorption of lanthanum ions by the hPMAA-hP4VP intergel system were obtained, which are presented in Fig. 20. As seen from the figure, there is a decrease in the intensity of some absorption bands down to the noise level, as well as the formation of new characteristic frequencies. On the spectrum of a hydrobasis hydrogel after sorption one can observe the absorption band, which corresponds to the C=N group, which indicates an increase in the electron donor effect. In addition, a shift of the absorption band of $R_2C=NH^+$ groups from 2500–2350 to 2400–2300 cm^{-1} can be observed. It is also worth noting that after sorption of lanthanum ions on the infrared spectrum of poly-4-vinylpyridine, the intensity of the absorption band of vibrations of intra- and intermolecular bonds increased. These facts confirm the above-described proposed mechanism of sorption of lanthanum ions by P4VP hydrogel. The initial polymer in the solution is in a charged state. In the process of sorption, the polybasis is deionized, the electrical donor effect on the heteroatom in the pyridine ring is enhanced. Due to this, intramolecular and intermolecular bonds are formed, including the coordination complex of nitrogen atom with lanthanum ions.

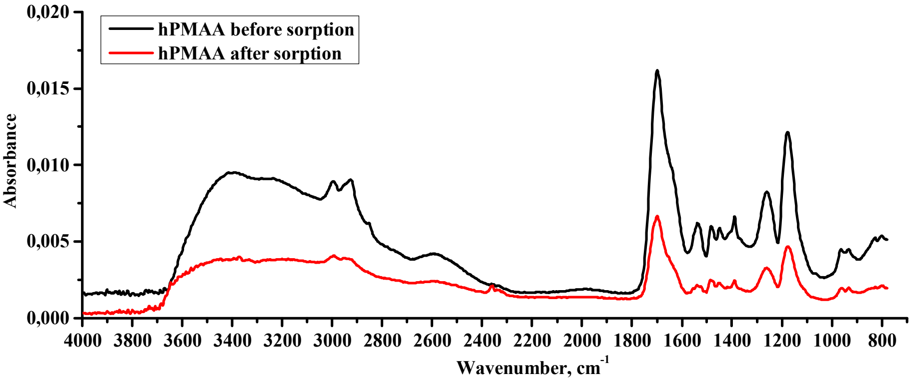

Fig. 19. IR spectra of hydrogel of polymethacrylic acid before and after sorption of lanthanum ions by the intergel system hPMAA-hP4VP

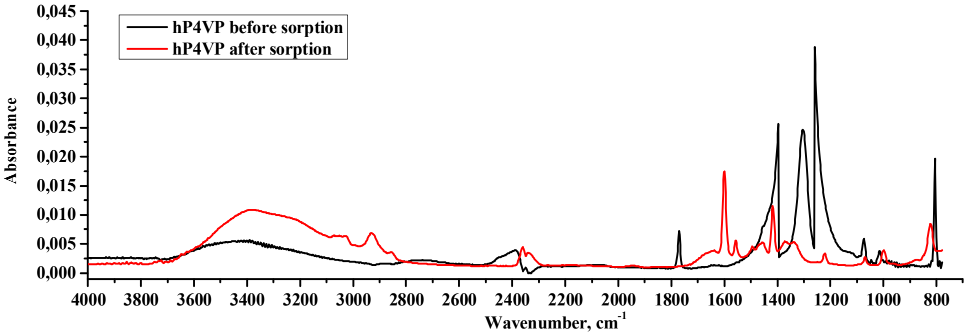

Fig. 20. IR spectra of hydrogel of poly-4-vinylpyridine before and after sorption of lanthanum ions by the intergel system hPMAA-hP4VP

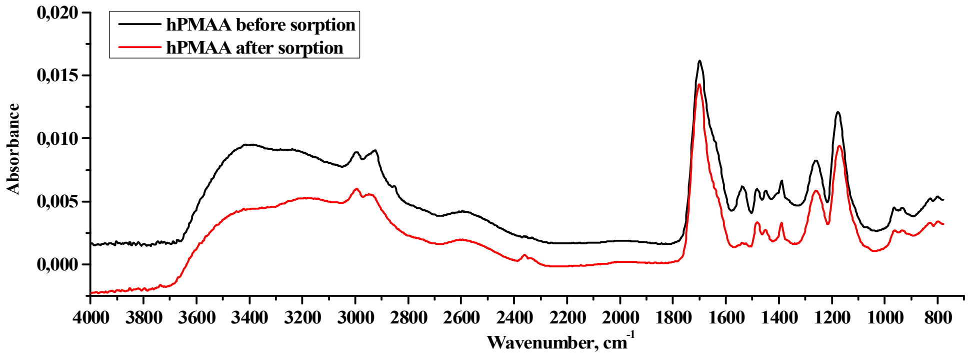

Fig. 21. IR spectra of hydrogel of polymethacrylic acid before and after sorption of lanthanum ions by the intergel system hPMAA-hP2M5VP

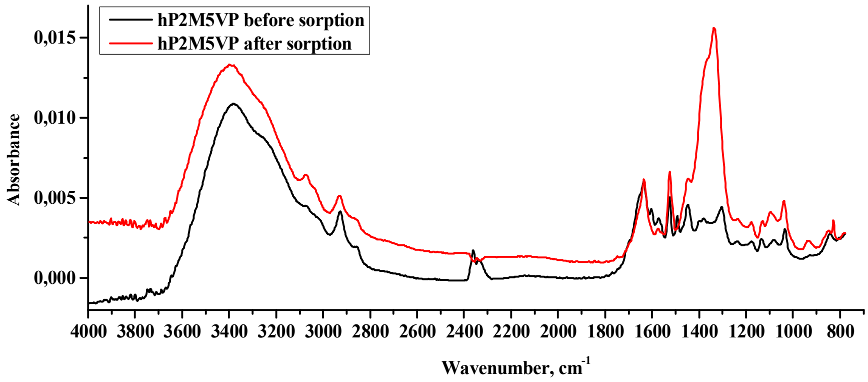

Fig. 22. IR spectra of hydrogel of poly-2-methyl-5-vinylpyridine before and after sorption of lanthanum ions by the intergel system hPMAA-hP4VP

3.4.2. Characteristics of IR spectra of hPMAA and hP2M5VP hydrogels before and after sorption of lanthanum ions

Fig. 21 shows the IR spectra of the initial hydrogel of polymethacrylic acid and the hydrogel of polymethacrylic acid after sorption of lanthanum ions by the hPMAA-hP2M5VP intergel system.

As can be seen from the obtained results, in this figure, after sorption of lanthanum ions, the contour of the spectrum of polymethacrylic acid remained unchanged in comparison with the initial hydrogel. However, it is worth noting that the intensity of the characteristic peaks decreased by approximately 1.5–2 times, which nevertheless confirms the process of sorption of heavy metal ions in the hydrogel. As was already described above, in the case of analogues of high molecular weight acrylic acids, PMAA is characterized by the mechanism of sorption of lanthanum ions through their electrostatic attraction to the carboxyl group, as evidenced by a decrease in the intensity of the –COOH absorption band in the 1700 cm^{-1} region. This decrease points to the high sorption ability of PMAA. Clear decrease in the intensity of the broad absorption band in the region of 3600–2800 cm^{-1} is due to the stretching vibrations of intra- and intermolecular bonds. When comparing the spectra of polymethacrylic acid in two intergel systems hPMAA-hP4VP and hPMAA-hP2M5VP, it can be noted that the degree of decrease in the intensity of the characteristic absorption bands in the presence of P4VP is higher, which affects the higher sorption ability of the hPMAA-hP4VP system.

Further, IR spectra of the initial poly-2-methyl-5-vinylpyridine hydrogel and the poly-2-methyl-5-vinylpyridine hydrogel after sorption of lanthanum by the hPMAA-hP2M5VP intergel system were obtained, which are shown in Fig. 22. This figure shows that the sorption process is characterized by an increase in the intensity of the absorption bands in the spectrum of poly-2-methyl-5-vinylpyridine. Such changes are especially noticeable in such areas as 3400–3100 cm^{-1}, corresponding to intra- and intermolecular bonds, in particular, to associated NH groups, and 1170–1050 cm^{-1}, characteristic only for pyridines. In the process of sorption, there is a loss of charge on the polymer chain, as evidenced by a decrease in the intensity of the absorption band in the region of 2390–2290 cm^{-1}, which corresponds to the $R_2C{=}NH^+$ group, and a sharp increase in the intensity of the characteristic peak in the region of 1310 cm^{-1}, which is responsible for C–N bond. The absorption bands of 1700–1480 cm^{-1}, which determine the vibrations of the pyridine ring, and the 1560–1480 cm^{-1} band, which is responsible for the C=N bond, remained practically unchanged in terms of the intensity after sorption of lanthanum ions. Separately, it is worth noting the effect of $-CH_3$ substituent in the pyridine ring on the spectrum and, accordingly, on the structure and sorption properties of the polybasis, which can be seen on the IR spectrum of P2M5VP in the region of 2930–2920 cm^{-1}. In this spectrometric analysis, there is also a tendency of a very strong difference in the hP4VP and hP2M5VP spectra, which was described above (Figs. 20 and 22), due to the influence of the location of the heteroatom and the double bond in the pyridine ring relative to the main polymer chain.

Thus, it can be concluded that the polymer structure affects the sorption ability, including the mehanism of sorption of heavy metal ions by polylectrolyte hydrogels, which is confirmed by the results of IR spectrometric analysis of the studied hydrogels before and after the sorption of lanthanum ions.

4. Conclusions

Obtained results on electrochemical (specific electric conductivity, pH) and conformational (swelling degree) properties indicate the fact of lanthanum ions sorption by the intergel systems hPMAA-hP4VP and hPMAA-hP2M5VP. During lanthanum ions sorption there is the decrease of conductivity and pH. Swelling degree also decreases with time.

Individual polymer hydrogels of PMAA, P4VP, P2M5VP do not have the high values of sorption properties. Extraction degree of lanthanum ions is 66.28, 66.05 and 63.65 %, respectively; polymer chain binding degree is 55.17, 55.00 and 53.00 %, respectively; effective dynamic exchange capacity is 4.97, 4.95 and 4.77 mmol/g, respectively.

"Long-range" provides macromolecules transfer into the highly ionized state during their remote interaction. Due to the mutual activation phenomenon, there is a significant increase (more than 25 %) of the sorption properties in the intergel systems. Maximum sorption of lanthanum ions by the intergel system hPMAA-hP4VP occurs at the ratio of 17%hPMAA: 3%hP4VP. Sorption degree is 90.35 %, polymer chain binding degree is 75.33 %, effective dynamic exchange capacity is 6.77 mmol/g. Area of lanthanum ions maximum sorption in the intergel system hPMAA-hP2M5VP is the ratio of 50%hPMAA:50%hP2M5VP. Extraction degree is 89.65 %, polymer chain binding degree is 74.67 %, effective dynamic exchange capacity is 6.72 mmol/g.

Strong mineral acids are more effective than polar solvents for desorption of lanthanum ions from matrix of polyacids and polybases. Desorption degree of lanthanum ions by ethyl alcohol is 82.26 % (desorption from intergel pair 17%hPMAA:83%hP4VP) and 77.28 % (desorption from intergel pair 50%hPMAA: 0%hP2M5VP). Desorption degree of lanthanum ions by ethyl alcohol is 94.42 % (desorption from intergel pair 17%hPMAA:83%hP4VP) and 93.09 % (desorption from intergel pair 50%hPMAA:50%hP2M5VP).

Data on IR spectra of PMAA, P4VP, P2M5VP hydrogels before and after sorption point to the sorption of lanthanum ions.

Obtained data show possibilities for application of the intergel systems in the development of modern sorption technologies for rare-earth metals extraction.

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ПОРІВНЯЛЬНА ХАРАКТЕРИСТИКА СОРБЦІЙНОЇ АКТИВНОСТІ ГІДРОГЕЛІВ ПОЛІМЕТАКРИЛОВОЇ КИСЛОТИ СТОСОВНО ЙОНІВ ЛАНТАНУ В ДЕЯКИХ МІЖГЕЛЕВИХ СИСТЕМАХ

Анотація. *Вивчено явища віддаленої взаємодії в міжгелевих системах гідрогель поліметакрилової кислоти – гідрогель полі-4-вінілпіридину (hPMAA-hP4VP) та гідрогель поліметакрилової кислоти – гідрогель полі-2-метил-5-вінілпіридину (hPMAA-hP2M5VP). Встановлено, що питома електропровідність, pH та ступінь набухання гідрогелів PMAA, P4VP та P2M5VP зменшуються під час сорбції йонів лантану за участю міжгелевих систем. Визначено, що сорбційні властивості міжгелевих систем значно збільшуються (до 30 %) у порівнянні з окремими гідрогелями PMAA, P4VP та P2M5VP, що вказує на факт високої йонізації під час взаємної активації полімерів. Максимальна сорбція йонів лантану відбувається за співвідношень 17% hPMAA:83% hP4VP та 50% hPMAA:50% hP2M5VP. За допомогою ІЧ спектроскопії встановлено сорбцію рідкісноземельного металу міжгелевими системами. Показана важливість можливого застосування міжгелевих систем на основі рідкоземельних зшитих полімерних гідрогелів кислотної та основної природи для створення нових інноваційних сорбційних технологій у гідрометалургії.*

Ключові слова: *міжгелеві системи, сорбція, йони* La^{3+}, *ІЧ-спектроскопія, десорбція.*