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SELECTIVITY OF INTERPOLYMER SYSTEMS WITH RESPECT TO LANTHANUM IONS

Abstract. The paper deals with the sorption of lanthanum ions by an interpolymer system consisting of sulfonic cation exchanger KU2-8 and anion exchanger AV-17-8. To predict the sorption activity of the intergel system, the mutual activation of the KU2-8 sulfonic cationite with the AV-17-8 anionite in the aqueous medium was initially studied. Due to the mutual activation of hydrogels in the course of their remote interaction, the polymer macromolecules pass into a highly ionized state, which leads to a significant increase in the degree of extraction of lanthanum ions from polymer hydrogels in intergel vapors as compared to the initial polymers.

We calculated the degree of extraction of lanthanum ions by the interpolymer system KU2-8: AV-17-8, the degree of binding of the polymer chain (in relation to lanthanum ions) with the initial ion exchangers and the interpolymer system KU2-8: AV-17-8. Based on the data obtained, a comparative analysis of the sorption of lanthanum ions by individual sorbents and an interpolymer system was carried out within the limits of the ratio KU2-8: AV-17-8 = 5: 1–1: 5.

It has been established that the maximum degree of sorption of lanthanum ions by the KU2-8: AV-17-8 interpolymer system is observed within the ratio KU2-8: AV-17-8 = 2: 4 at 48 hours of remote interaction of the interpolymer system and is 54.73 mol. %, at which the degree of binding of the polymer chain is 6.15%.

Keywords: intergel systems, hydrogels, KU2-8 cation exchanger, AV-17-8 anion exchanger, remote interaction, La^{3+} ions, sorption, desorption.

Introduction. The growing scientific and technical interest in rare earth metals (REM) is due to their application in modern science-intensive fields of technology. The Republic of Kazakhstan has unique reserves of rare earth metals [1]. Rare earth metals are widely used in the modern world, as metals, alloys and chemical compounds, they are used in various fields of technology: in the chemical industry, ferrous and nonferrous metallurgy, electronics and electrical engineering, as well as magnets and phosphors.

Rare earth metals are characterized by an extremely low content in natural raw materials, which determines specific methods for their production. After acidic or alkaline opening of natural or technogenic raw materials in the course of the technological chain, a gradual concentration of rare earths occurs, for which I use various methods - extraction, ion exchange, precipitation. In the course of this process, a 60-70% concentrate is obtained, containing all the rare earth metals.

At present, technologies for the concentration and extraction of rare earth and other elements in hydrometallurium are based on the use of ion-exchange resins. Today, the market for ion-exchange resins is quite large and diverse, and despite the fact that sulfonic cation exchanger is a widespread and relatively cheap sorbent, the study of the sorption extraction of rare earth metals by other ion-exchange resins is of interest from the point of view of identifying selective sorbents.

EXPERIMENTAL PART

Equipment. The mass of sorbents was determined by weighing on a SHIMADZUAY220 electronic analytical balance (Japan). The determination of the optical density of lanthanum nitrate solutions for the subsequent calculation of the concentration of lanthanum ions was carried out on a KFK-3M spectrophotometer at 650 nm.

Materials. The studies were carried out in solutions of 6-aqueous lanthanum nitrate (concentration La^{3+} = 100 mg/l). Industrial ion exchangers were used: a strongly acidic cation exchanger KU2-8 - a sulfonated copolymer of styrene with 8% divinylbenzene (according to GOST 20298-74) and a strongly basic anion exchanger AB-17-8 based on a copolymer of styrene and divinylbenzene with benzyltrimethylammonium functional groups (according to GOST 20301-74).

For the research task, the interpolymer system KU2-8: AV-17-8 was made up of industrial ion exchangers.

Experiment. The experiments were carried out at room temperature. Ion-exchange resins KU2-8 and AV-17-8 were taken in a swollen state to study the sorption of lanthanum ions. Ion-exchange resins KU2-8 and AV-17-8 were previously left in distilled water for swelling (24 hours). Then polypropylene meshes with ion-exchange resins KU2-8 and AV-17-8 were placed in glasses with lanthanum nitrate solutions.

The study of the sorption properties of individual ion exchangers and interpolymer systems was carried out as follows:

1) The calculated amount of each ion-exchange resin (KU2-8, AV-17-8) in dry form was placed in polypropylene nets. The interpolymer system was composed of ion-exchange resins KU2-8 and AV-17-8: KU2-8: AV-17-8;

2) Sorption of lanthanum ions by individual ion-exchange resins KU2-8, AV-17-8 was carried out for 48 hours. During this time, aliquots were taken for subsequent determination of the concentration of lanthanum ions.

Method for the determination of lanthanum ions. Method for the determination of ions lanthanum in solution is based on the formation of a colored complex

compound of the organic analytical reagent Arsenazo III with rare earth metal ions (REM); the concentration of lanthanum ions was calculated on a KFK-3M spectrophotometer at 650 nm [4-8]. The degree of extraction (sorption) was calculated using the formula:

$$\eta = \frac{C_{init} - C_{resid}}{C_{init}} * 100\% ,$$

where C_{init} – is the initial concentration of metal in the solution, g / l; C_{resid} – is the residual concentration of metal in the solution, g / l.

RESULTS AND DISCUSSION

Our earlier studies [2-12] showed that almost all intergel systems based on acidic (polyacrylic and polymethacrylic acids) and basic (poly-4-vinylpyridine and poly-2-methyl-5-vinylpyridine) rare-crosslinked polymer hydrogels exhibit higher activity than their constituents. Moreover, it was found that the ratio of polymers, at which a high sorption of ions is manifested, differ significantly depending on the nature of acidic and basic hydrogels and the nature of rare earth metals.

Figure 1 shows the dependence of the pH of solutions with the KU2-8: AV-17-8 interpolymer system on time. As can be seen from the figure, their mutual activation occurs, leading to a significant change in their electrochemical and conformational properties. These results indicate the emergence of ionized structures with optimal conformation, providing an optimal ligand environment around lanthanum ions.

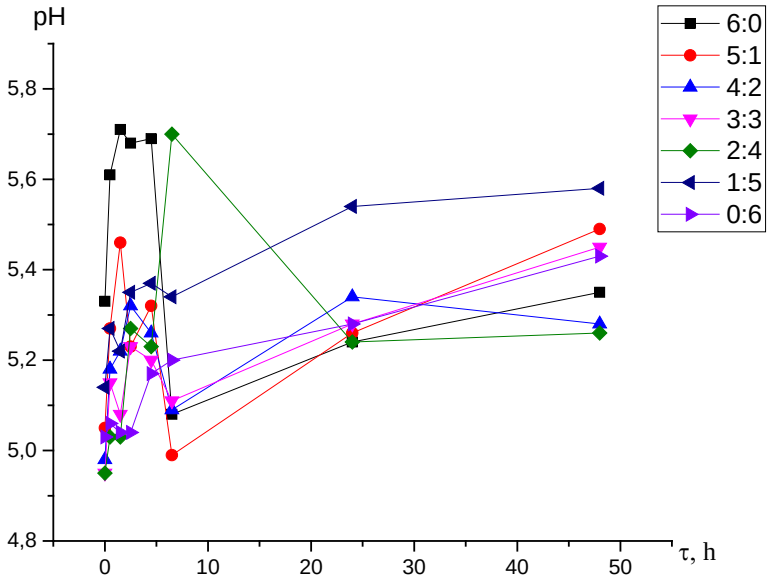

Figure 1 – Dependence of pH of solutions by an interpolymer system KU2-8: AV-17-8 from time to time

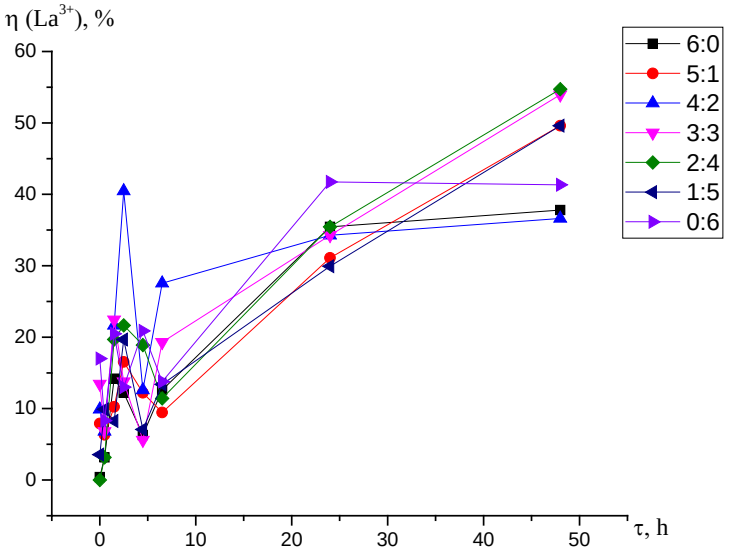

Figure 2 – Dependence of the degrees of extraction of lanthanum ions by the KU2-8: AV-17-8 interpolymer system on time

Figure 2 shows the dependence of the degrees of extraction of lanthanum ions by the KU2-8: AV-17-8 interpolymer system on time. It should be noted that the transition of polymer macromolecules to a highly ionized state due to the mutual activation of ion exchangers during their remote interaction leads to an increase in the degree of extraction of lanthanum ions from ion exchangers in interpolymer vapors compared to the initial ion exchangers. As can be seen from the figure, in the interpolymer system, the degree of extraction of lanthanum ions increases with time.

The main amount of lanthanum ions is sorbed by the KU2-8: AV-17-8 interpolymer systems during 48 hours of their interaction with salt solutions. The maximum degree of extraction of lanthanum ions is observed in the interpolymer system within the ratios KU2-8: AV-17-8 = 3: 3–2: 4 after 48 hours and is 53.94 and 54.73 mol.%, Respectively. The degree of extraction of lanthanum ions by individual ion exchangers KU2-8 and AV-17-8 is 37.8 mol.% and 41.34 mol.%.

Table shows the degree of binding of the polymer chain (with respect to lanthanum ions) by the initial ion exchangers and interpolymer systems KU2-8: AV-17-8 from time to time. The most intense binding of lanthanum ions by initial ion exchangers and interpolymer systems occurs within 48 hours. High values of the degree of binding of the polymer chain in relation to lanthanum ions are observed within the ratios KU2-8: AB-17-8 = 3: 3–2: 4, is 6.06% and 6.15%, respectively.This indicates a high degree of ionization of macromolecules as a result of mutual activation of ion exchangers KU2-8 and AV-17-8. The degree of binding of the polymer chain of individual ion exchangers KU2-8 and AV-17-8 in relation to lanthanum ions after 48 hours is 4.12% and 4.60%, respectively.

Degrees of binding of the polymer chain (with respect to lanthanum ions)
by the initial ion exchangers and the interpolymer system KU2-8: AV-17-8 on time, %

Ratio	0 h	0,5 h	1,5 h	2,5 h	4,5 h	6,5 h	24 h	48 h
6:0	0.043	0.33	1.54	1.33	0.68	1.37	3.86	4.12
5:1	0.86	0.68	1.11	1.8	1.32	1.02	3.38	5.49
4:2	1.09	0.75	2.42	4.48	1.39	3.05	3.79	4.05
3:3	1.51	0.76	2.52	1.55	0.63	2.17	3.85	6.06
2:4	0	0.35	2.21	2.43	2.12	1.28	3.75	6.15
1:5	0.40	1.12	0.94	2.24	0.80	1.52	3.41	5.66
0:6	1.94	0.94	2.33	1.47	2.38	1.57	4.60	4.60

Conclusions.

1. As a result of remote interaction within the limits of the ratio KU2-8: AV-17-8 = 5: 1–1: 5, mutual activation of ion exchangers occurs, which consists in the fact that inter-site chains acquire an additional charge without counterions.

2. The maximum degree of sorption of lanthanum ions by the interpolymer system KU2-8: AV-17-8 is observed within the ratios KU2-8: AV-17-8 = 2: 4 at 48 hours of remote interaction of the interpolymersystem and is 54.73 mol.%. An increase in the degree of sorption of lanthanum ions by interpolymer systems in comparison with individual ion exchangers is associated with a high degree of ionization of ion exchangers in the interpolymer system.

3. The results obtained indicate that it is possible to develop an interpolymer system selective to other ions, which can be used for a highly efficient sorption technology for the extraction of ions of rare earths and other elements from industrial solutions.

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Резюме

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ЛАНТАН ИОНДАРЫНА ҚАТЫСТЫ
ИНТЕРПОЛИМЕРЛІ ЖҮЙЕЛЕРДІҢ СЕЛЕКТИВТІЛІГІ

Жұмыста лантан иондарының КУ 2-8 сульфокатионитінен және АВ-17-8 анионитінен тұратын интерполимерлік жүйемен сорбциясы қарастырылады. Интергелдік жүйенің сорбциялық белсенділігін болжау үшін алдымен су ортасында АВ-17-8 анионитімен КУ 2-8 сульфокатионитінің өзара активтенуі зерттелді. Гидрогельдердің өзара әрекеттесуі нәтижесінде олардың қашықтықтан өзара әрекеттесуі кезінде полимерлі макромолекулалар жоғары иондалған күйге ауысады, бұл бастапқы полимерлермен салыстырғанда интергельді жұптардағы полимерлі гидрогельдердегі лантан иондарының шығарылу деңгейінің едәуір артуына әкеледі.

КУ2-8:АВ-17-8 интерполимерлік жүйесімен лантан иондарының сіңірілуінің ең жоғары дәрежесі КУ 2-8:АВ-17-8=2:4 ара қатынасында интерполимерлік жүйенің қашықтықтан өзара әрекеттесуінің 48 сағатында байқалады және 54,73 мольді құрайды.%, онда полимер тізбегінің байланыстыру дәрежесі 6,15% құрайды.

Түйін сөздер: интергелді жүйелер,La^{3+} ионы, гидрогель, катионит КУ 2-8, анионит АВ-17, сорбция, десорбция.

Резюме

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СЕЛЕКТИВНОСТЬ ИНТЕРПОЛИМЕРНЫХ СИСТЕМ ПО ОТНОШЕНИЮ К ИОНАМ ЛАНТАНА

В работе рассматривается сорбция ионов лантана интерполимерной системой, состоящей из сульфокатионита КУ 2-8 и анионита АВ-17-8. Для прогнозирования сорбционной активности интергелевой системы первоначально изучена взаимная активация сульфокатионита КУ 2-8 с анионитом АВ-17-8 в водной среде. Вследствие взаимной активации гидрогелей в ходе их дистанционного взаимодействия происходит переход полимерных макромолекул в высокоионизованное состояние, что приводит к существенному увеличению степени извлечения ионов лантана у полимерных гидрогелей в интергелевых парах по сравнению с исходными полимерами.

Были рассчитаны степень извлечения ионов лантана интерполимерной системой КУ 2-8:АВ-17-8, степень связывания полимерной цепи (по отношению к ионам лантана) исходными ионитами и интерполимерной системой КУ 2-8:АВ-17-8. На основе полученных данных был проведен сравнительный анализ сорбции ионов лантана индивидуальными сорбентами и интерполимерной системой в пределах соотношений КУ 2-8:АВ-17-8=5:1–1:5.

Ключевые слова: интергелевые системы, гидрогели, катионит КУ 2-8, анионит АВ-17-8, дистанционное взаимодействие, ионы La^{3+}, сорбция, десорбция.

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