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SELECTIVITY OF INTERGEL SYSTEM BASED ON HYDROGELS OF POLYMETHACRYLIC ACID AND POLY-4-VINYLPYRIDINE TO LANTHANUM AND CERIUM IONS

Abstract. Process of lanthanum and cerium ions sorption by intergel system hydrogel of polymethacrylic acid (hPMAA) – hydrogel of poly-4-vinylpyridine (hP4VP) is studied. Found that intergel system hPMAA-hP4VP has selectivity to lanthanum and cerium ions. PMAA hydrogel doesn't have high values of extraction degree in relation to lanthanum and cerium ions (66.28% and 60.33% respectively). P4VP hydrogel also has low values of La^{3+} and Ce^{3+} ions sorption degree (66.05% and 56.67% respectively). In intergel system hPMAA-hP4VP selectivity can be controlled by changing hydrogels ratio. Maximum extraction degree of lanthanum ions is observed at 17%hPMAA:83%hP4VP ratio, sorption degree is 90.34%. Maximum sorption degree of cerium ions is observed at 50%hPMAA:50%hP4VP ratio, extraction degree is 89.33%. Individual PMAA and P4VP hydrogels also do not have high polymer chain binding degree. Polymer chain binding degree (in relation to lanthanum ions) of hPMAA and hP4VP is 55.17% and 55.00% respectively. Binding degree (in relation to cerium ions) of hPMAA and hP4VP is 50.05% and 47.00%. Maximum values of polymer chain binding degree (in relation to lanthanum ions) in intergel system hPMAA-hP4VP are observed at 17%hPMAA:83%hP4VP ratio, binding degree is 75.33%. Maximum values of binding degree (in relation to cerium ions) are observed at 50%hPMAA:50hP4VP ratio, binding degree is 74.10%. At 17%hPMAA:83%hP4VP and 50%hPMAA:50hP4VP ratios effective dynamic exchange capacity (in relation to lanthanum and cerium ions) is higher almost on 30% comparatively with individual PMAA and P4VP hydrogels. Mutual activation of PMAA and P4VP hydrogels provides transition into highly ionized state and, as a result, significant increase of sorption properties in intergel pairs.

Keywords: intergel system, sorption, selectivity, La^{3+} ions, Ce^{3+} ions, polymethacrylic acid, poly-4-vinylpyridine.

Effect of mutual activation of polymer structures of different nature on electrochemical and volume-gravimetric properties is described in previous works [1-6]. It is found that remote interaction of hydrogels provides transition of initial polymers into highly ionized state and, as a result, significant changes in electrochemical and conformational properties. After that, it was found that mutual activation provides significant increase of sorption properties of initial hydrogels [7-11]. Levels of ionization in intergel systems are in dependence from hydrogels ratios. Consequently, changing hydrogels ratio in certain intergel system will provide opportunity to re-orientate intergel system to maximum sorption of another ion. In this regard, goal of this work is to study impact of hydrogels ratio on selectivity of intergel system hPMAA-hP4VP.

Experiment

Equipment. For measurement of optical density of solutions for further calculation of La^{3+} and Ce^{3+} ions concentration spectrophotometer Jenway-6305 was used.

Materials. Investigations was carried out in solutions of lanthanum and cerium nitrate solutions. Hydrogels of polymethacrylic acid were synthesized in presence of cross-linking agent N,N-methylene-bis-acrylamide and red-ox system $K_2S_2O_8$–$Na_2S_2O_3$. Hydrogel of poly-4-vinylpyridine (hP4VP) (2% of cross-linking agent) was synthesized by «Sigma Aldrich» company. Synthesized hydrogels in an aqueous medium were put to create intergel system polymethacrylic acid hydrogel – poly-4-vinylpyridine hydrogel (hPMAA-hP4VP). Swelling degrees of hydrogels are: $\alpha_{(hPMAA)}$=20.65 g/g; $\alpha_{(hP4VP)}$=2.65 g/g.

Experiment. Experiments were carried out at room temperature. Study of the intergel system was made as follows: calculated amount of each hydrogel in dry state was put in special glass filters, pores of which permeable for low-molecular ions and molecules, but non-permeable for hydrogels dispersion. Then the filters were put in glass in which salt solution presents. After that, aliquots were taken.

Methodology of lanthanum ions determination in solution is based on formation of colored complex compound of organic analytic reagent arsenazo III with La^{3+} ions [12].

Extraction (sorption) degree was calculated by equation:

$$\eta = \frac{C_{initial} - C_{residual}}{C_{initial}} * 100\%$$

where $C_{initial}$ – initial concentration of lanthanum in solution, g/L; $C_{residue}$ – residual concentration of lanthanum in solution, g/L.

Polymer chain binding degree was determined by calculations in accordance with equation:

$$\theta = \frac{\nu_{sorbed}}{\nu} * 100\%$$

where ν_{sorbed} – quantity of polymer links with sorbed lanthanum, mol; ν – total quantity of polymer links (if there are 2 hydrogels in solution, it is calculated as sum of each polymer hydrogel links), mol.

Effective dynamic exchange capacity was calculated by formula:

$$Q = \frac{\nu_{sorbed}}{m_{sorbent}}$$

where ν_{sorbed} – amount of sorbed metal, mol; $m_{sorbent}$ – sorbent mass (if there are 2 hydrogels in solution, it is calculated as sum of their masses), g.

Results and discussion

Lanthanum ions sorption. Dependence of lanthanum ions extraction degree of the intergel system hPMAA-hP4VP from hydrogels ratios is shown on figure 1. Obtained results point to the fact that mutual activation provides significant increase of sorption properties of the polymer hydrogels in the intergel system. Initial hydrogels of polymethacrylic acid and poly-4-vinylpyridine do not have high extraction degree of lanthanum ions. Extraction degree is 66.28% for polymethacrylic acid hydrogel and 66.05% for poly-4-vinylpyridine hydrogel.

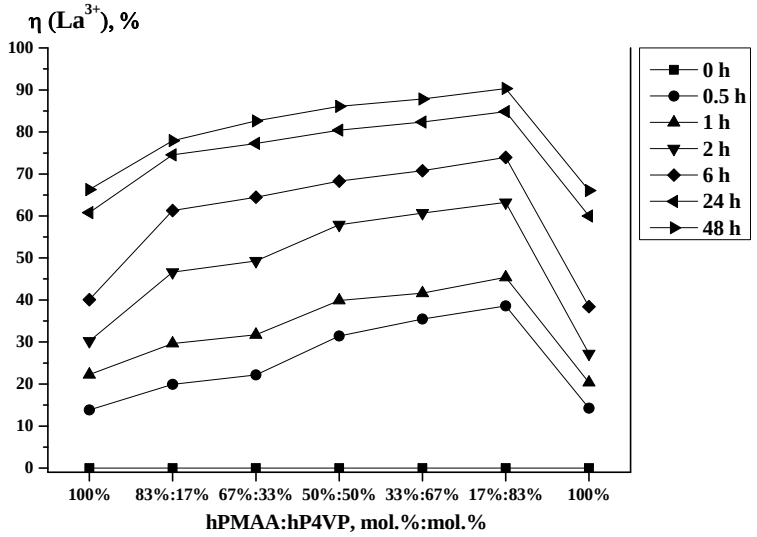

Figure 1 – Dependence of lanthanum ions extraction degree of intergel system hPMAA-hP4VP from hydrogels ratios

As seen from figure 1, maximum sorption of lanthanum ions occurs at 17%hPMAA:83%hP4VP ratio. Extraction degree of lanthanum ions at this ratio in the intergel system hPMAA-hP4VP is 90.34%. Main reason of such high sorption degree is high ionization of polymer structures due to their mutual activation.

Figure 2 shows dependence of polymer chain binding degree from time. Intergel pairs have higher values of binding degree comparatively with individual hydrogels. Polymer chain binding degree of individual hydrogels of polymethacrylic acid and poly-4-vinylpyridine is 55.17% and 55.00% respectively. Not very intensive sorption occurs at 83%hPMAA:17%hP4VP and 67%hPMAA:33%hP4VP ratios. Such binding degree indicates to not sufficient ionization degree of polymer structures at remote interaction in mentioned above intergel pairs. Maximum values of binding degree are observed at 17%hPMAA:83%hP4VP. As seen from the figure, at this ratio binding of lanthanum by the polymers is significantly higher, polymer chain binding degree is 75.33%.

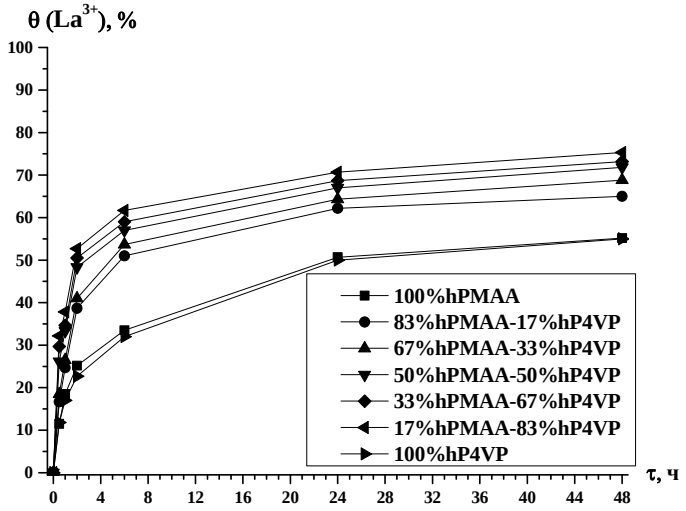

Figure 2 – Dependence of polymer chain binding degree
of intergel system hPMAA-hP4VP from hydrogels ratios

Dependence of effective dynamic exchange capacity of the intergel system based on hydrogels of PMAA and P4VP from hydrogels molar ratios is shown on figure 3. Remote interaction of hPMAA and hP4VP provides significant increase of exchange capacity of polymer structures. The highest values of exchange capacity are observed at 33%hPMAA:67%hP4VP and 17%hPMAA:83hP4VP

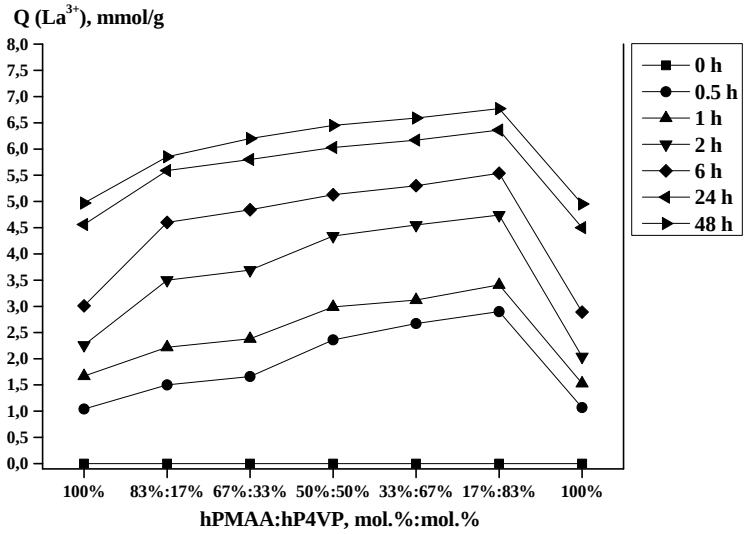

Figure 3 – Dependence of effective dynamic exchange capacity
of intergel system hPMAA-hP4VP from hydrogels ratios

ratios. Maximum values of exchange capacity is reached at 48 hours at 17%hPMAA:83hP4VP ratio, at this ratio exchange capacity is on 30% higher in comparison with individual hydrogels. Minimum values of capacity are seen in presence of polyacid or polybasis, wherein values of exchange capacity are almost the same.

Cerium ions sorption. As seen from figure 4, extraction degree of cerium ions of the intergel system hydrogel of polymethacrylic acid – hydrogel of poly-4-vinylpyridine increases with time. Values of sorption degree are higher in intergel pairs than in case with individual hydrogels. Cerium ions extraction degree reaches maximum values at 48 hours of remote interaction of hydrogels at 50%hPMAA:50%hP4VP ratio. Maximum values point to high ionization degree of polymer structures at their mutual activation. Extraction degree of cerium ions at this ratio is 89.33%. Individual hydrogels of polymethacrylic acid and poly-4-vinylpyridine have low values of extraction degree of cerium ions. Extraction degree of cerium ions by PMAA hydrogel is 60.33%, by P4VP hydrogel – 56.67%.

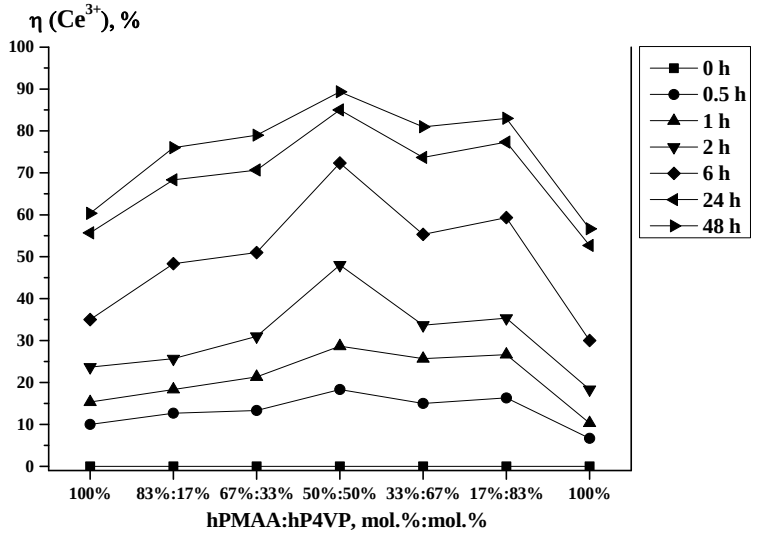

Figure 4 – Dependence of cerium ions extraction degree of intergel system hPMAA-hP4VP from hydrogels ratios

Figure 5 represents dependencies of polymer chain binding degree (in relation to cerium ions) of the intergel system hPMAA-hP4VP from time. The highest values of binding degree are observed at 50%hPMAA:50%hP4VP ratio, binding degree is 74.10%. Other intergel pairs also have high polymer chain binding degree values comparatively with individual hydrogels of polymethacrylic acid and poly-4-vinylpyridine. Initial hydrogels of PMAA and P4VP have the following values of polymer chain binding degree: 50.05% for hPMAA and 47.00% for hP4VP. Such significant difference of polymer chain binding degree values of

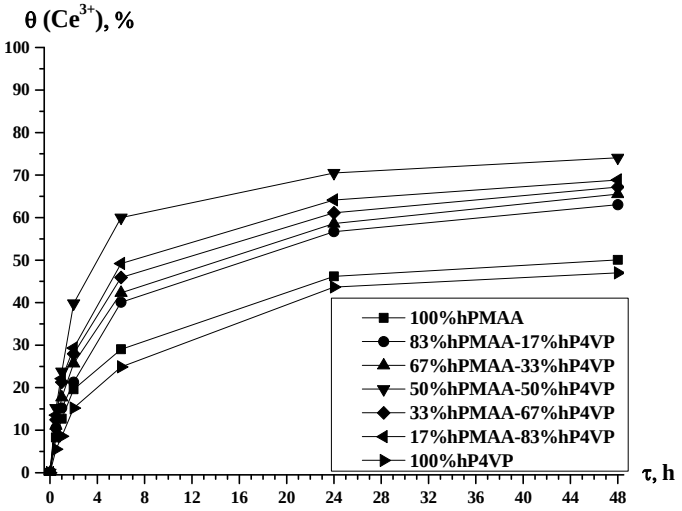

Figure 5 – Dependence of polymer chain binding degree of intergel system hPMAA-hP4VP from hydrogels ratios

intergel pairs and individual hydrogels is due to highly ionized state of hydrogels in intergel pairs due to their mutual activation at remote interaction in intergel system.

Figure 6 shows dependence of effective dynamic exchange capacity of the intergel system hPMAA-hP4VP from hydrogel ratios in time. Increase of exchange capacity occurs with time.

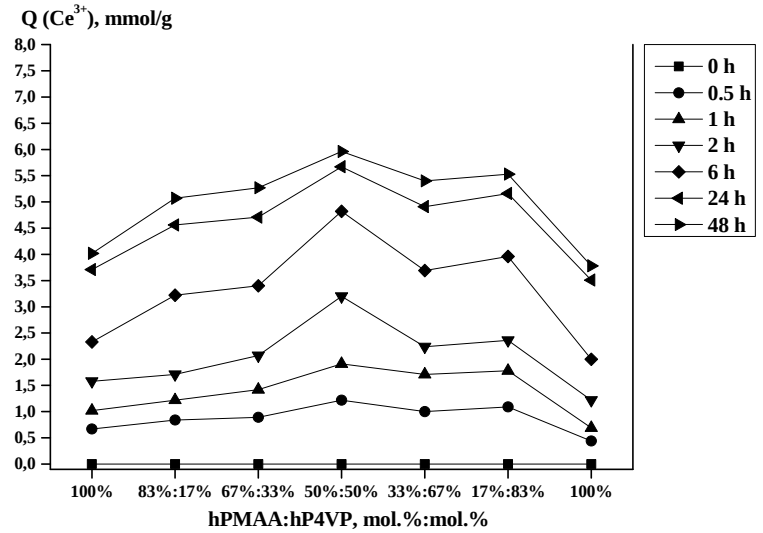

Figure 6 – Dependence of effective dynamic exchange capacity of intergel system hPMAA-hP4VP from hydrogels ratios

As seen from the figure, result of remote interaction of polymethacrylic acid and poly-4-vinylpyridine hydrogels is significant increase of effective dynamic exchange capacity of polymer hydrogels of PMAA and P4VP. Area of maximum values of effective dynamic exchange capacity is 50%hPMAA:50hP4VP ratio. At this ratio exchange capacity is over on 30% higher comparatively with individual PMAA and P4VP hydrogels.

Conclusion.

1. Intergel system based on rare-crosslinked polymer hydrogels of polymethacrylic acid and poly-4-vinylpyridine has selectivity to lanthanum and cerium ions.

2. Mutual activation of PMAA and P4VP hydrogels provides transition into highly ionized state and, as a result, significant increase of sorption properties in intergel pairs.

3. Polymethacrylic acid hydrogel doesn't have high values of extraction degree in relation to lanthanum and cerium ions (66.28% and 60.33% respectively). Poly-4-vinylpyridine hydrogel also has low values of sorption degree (66.05% and 56.67% respectively).

4. In intergel system hPMAA-hP4VP selectivity can be controlled by changing hydrogels ratio. Maximum extraction degree of lanthanum ions is observed at 17%hPMAA:83%hP4VP ratio, sorption degree is 90.34%. Maximum sorption degree of cerium ions is observed at 50%hPMAA:50%hP4VP ratio, extraction degree is 89.33%.

5. Individual PMAA and P4VP hydrogels also do not have high polymer chain binding degree. Polymer chain binding degree (in relation to lanthanum ions) of hPMAA and hP4VP is 55.17% and 55.00% respectively. Binding degree (in relation to cerium ions) of hPMAA and hP4VP is 50.05% and 47.00%.

6. Maximum values of polymer chain binding degree (in relation to lanthanum ions) in intergel system hPMAA-hP4VP are observed at 17%hPMAA:83%hP4VP ratio, binding degree is 75.33%. Maximum values of binding degree (in relation to cerium ions) are observed at 50%hPMAA:50hP4VP ratio, binding degree is 74.10%.

7. Transition into highly ionized state of PMAA and P4VP hydrogels due to mutual activation also provides significant increase of effective dynamic exchange capacity. At 17%hPMAA:83%hP4VP and 50%hPMAA:50hP4VP ratios exchange capacity (in relation to lanthanum and cerium ions) is higher almost on 30% comparatively with individual PMAA and P4VP hydrogels.

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Резюме

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ПОЛИМЕТАКРИЛ ҚЫШҚЫЛЫ ЖӘНЕ ПОЛИ-4-ВИНИЛПИРИДИН ГИДРОГЕЛДЕРІ НЕГІЗІНДЕГІ ИНТЕРГЕЛДІ ЖҮЙЕЛЕРДІҢ ЛАНТАН ЖӘНЕ ЦЕРИЙ ИОНДАРЫНА СҰРЫПТЫЛЫҒЫ

Полиметакрил қышқылы гидрогелімен (ПМАҚг) поли-4-винилпиридин (П4ВПг) гидрогелі негізінде алынған интергелді жүйемен лантан және церий иондарын сіңіру процесі зерттелді. ПМАҚг-П4ВП интергелді жүйесінің лантан мен церий иондарына сұрыптылық қасиет көрсететіні анықталды. ПМАҚ гидрогелінің лантан және церий иондарын шығару дәрежесі аса жоғары емес (сәйкесінше 66,28% және 60,33%). П4ВП гидрогелініңде La^{3+} және Ce^{3+} иондарын шығару дәрежесі төмен. (сәйкесінше 66,05% және 56,67%). Интергелді жүйеде гидрогелдердің қатынастарын өзгерту арқылы сұрыптылықты басқаруға болады. 17%ПМАҚг:83%П4ВПг қатынасында лантан иондарын шығару дәрежесі жоғары екені байқалады, сіңіру дәрежесі 90,34%-ке тең. 50%ПМАҚг:50%П4ВПг қатынасында церий иондарын шығару дәрежесі жоғары екені байқалады, сіңіру дәрежесі 89,33%-ке тең. Сонымен қатар ПМАҚ және П4ВП жекелеген гидрогелдерінде полимерлік тізбектерінің байланысу дәрежесі төмен болып келеді. ПМАҚг және П4ВПг полимерлік тізбектерінің байланысу дәрежесі (лантан иондарына қатысты) сәйкесінше 55,17% және 55,00%-ті, ал (церий иондарына қатысты) сәйкесінше 50,05% және 47,00%-ті құрайды. ПМАҚг-П4ВП интергелді жүйесінің 17%ПМАҚг:83%П4ВПг қатынасында полимерлік тізбектерінің байланысу дәрежесі (лантан иондарына қатысты) жоғары, байланысу дәрежесі 75,33%-ке тең. Ал 50%ПМАҚг:50%П4ВПг қатынасында (церий иондарына қатысты) байланысу дәрежесі жоғары, яғни 74,10%-ке тең. ПМАҚ мен П4ВП жекелеген гидрогелдерімен салыстырғанда 17%ПМАҚг:83%П4ВПг және 50%ПМАҚг:50%П4ВПг қатынастарында (лантан және церий иондарына қатысты) тиімді динамикалық алмасу сыйымдылығы шамамен 30%-ға жоғары. ПМАҚ мен П4ВП гидрогелдерінің өзара активтілігі олардың жоғары иондалған күйге көшуіне алып келеді, нәтижесінде интергелді жұптарда сіңіру қасиеттерінің анағұрлым өсуіне әсер етеді.

Түйін сөздер: интергелді жүйе, сіңіру, сұрыптылық, La^{3+} иондары, Ce^{3+} иондары, полиметакрил қышқылы, поли-4-винилпиридин.

Резюме

Т. К. Джумадилов, Р. Г. Кондауров

СЕЛЕКТИВНОСТЬ ИНТЕРГЕЛЕВОЙ СИСТЕМЫ НА ОСНОВЕ ГИДРОГЕЛЕЙ ПОЛИМЕТАКРИЛОВОЙ КИСЛОТЫ И ПОЛИ-4-ВИНИЛПИРИДИНА К ИОНАМ ЛАНТАНА И ЦЕРИЯ

Исследован процесс сорбции ионов лантана и церия интергелевой системой гидрогель полиметакриловой кислоты (гПМАК) – гидрогель поли-4-винилпиридина (гП4ВП). Установлено, что интергелевая система гПМАК-гП4ВП проявляет селективность к ионам лантана и церия. Гидрогель ПМАК не обладает высокой степенью

извлечения ионов лантана и церия (66,28 и 60,33% соответственно). Гидрогель П4ВП также имеет невысокие значения степени извлечения ионов La^{3+} и Ce^{3+} (66,05 и 56,67% соответственно). В интергелевой системе возможно управлять селективностью путем изменения соотношений гидрогелей. Максимальная степень извлечения ионов лантана наблюдается при соотношении 17%гПМАК:83%гП4ВП, степень сорбции равна 90,34%. Максимальная степень сорбции ионов церия наблюдается при соотношении 50%гПМАК:50%гП4ВП, степень извлечения равна 89,33%. Также индивидуальные гидрогели ПМАК и П4ВП не обладают высокими значениями степени связывания полимерной цепи. Степень связывания полимерной цепи (по отношению к ионам лантана) гПМАК и гП4ВП составляет 55,17 и 55,00% соответственно. Степень связывания (по отношению к ионам церия) гПМАК и гП4ВП равна 50,05 и 47,00%. Максимальные значения степени связывания полимерной цепи (по отношению к ионам лантана) в интергелевой системе гПМАК-гП4ВП наблюдаются при соотношении 17%гПМАК:83%гП4ВП, степень связывания равна 75,33%. Наибольшие значения степени связывания (по отношению к ионам церия) наблюдаются при соотношении 50%гПМАК:50%гП4ВП, степень связывания равна 74,10%. При соотношениях 17%гПМАК:83%гП4ВП и 50%гПМАК:50%гП4ВП эффективная динамическая обменная емкость (по отношению к ионам лантана и церия) практически на 30% выше по сравнению с индивидуальными гидрогелями ПМАК и П4ВП. Взаимная активация гидрогелей ПМАК и П4ВП приводит к переходу в высокоионизованное состояние и, как результат, к значительному росту сорбционных свойств в интергелевых парах.

Ключевые слова: интергелевая система, сорбция, селективность, ионы La^{3+}, ионы Ce^{3+}, полиметакриловая кислота, поли-4-винилпиридин.