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FEATURES OF SORPTION CALCIUM IONS BY INTERGEL HYDROGELS OF POLYMETHACRYLIC ACID - POLY-4-VINYLPYRIDINE AND POLYACRYLIC ACID –POLY-2-METHYL-5-VINYLPYRIDINE

Abstract. Process of sorptioncalcium ions by intergelhydrogelsystems of polymethacrylic acid – poly-4-vinylpyridine and polyacrylic acid –poly-2-methyl-5-vinylpyridine were studied by methods of conductometry, pH-metry, ion-metry. Calcium sorption process with individual rare-crosslinked hydrogels of PAA, PMAA, P4VP, P2M5VP and intergel systems hPMAA-hP4VP, hPAA-hP2M5VP were accompanied by significant changes of initial electrochemical properties of calcium chloride solution (specific electric conductivity and pH decreases with time of sorption of the metal ions). Individual hydrogels of PAA, PMAA, P4VP, P2M5VP relatively fast reach electrochemical equilibrium in salt solution, consequent slight increase after 24 hours is evidence of this phenomenon, sorption degree after 2 days of sorption of the metal ions reaches 70%. Formation optimal conformation of the polymers occurs in the intergel systems at ratios hPMAA:hP4VP=4:2 and hPAA:hP2M5VP=2:4, however, ionization process of macromolecules are complicated due to the fact, that structures of hPMAA and hP2M5VP have bulk methyl substituent, which interfere undfolding of polymer globe in process of its ionization. Sorption degree of calcium ions by the intergel systems hPMAA:hP4VP=4:2 and hPAA:hP2M5VP=2:4 is 93% and 92% respectively.

Key words: intergelsystem, mutualactivation, sorption, Ca^{2+}ions, hydrogels, polyacrylic acid, polymethacrylic acid, poly-4-vinylpyridine, poly-2-methyl-5-vinylpyridine.

Introduction. Water treatment is the process of water coming from a natural water source to bring its quality in line with the requirements of technological consumers.It can be produced on water treatment facilities or installations for the needs of the municipal economy, practically in all industries (for example, heat-generating enterprises). To evaluate the quality of drinking water, various methods are used, suggesting the study of hydrochemical, microbiological and other indicators [1].Water treatment consists in the release of water from coarsely dispersed and colloidal impurities and salts contained in it, thereby preventing deposition of scale, removal of salts by steam, corrosion of metals, as well as contamination of processed materials when water is used in technological processes.

As you know, the high content of calcium and magnesium ions makes water hard and unsuitable for drinking. Boiling of hard water promotes the appearance of scale on the walls of the vessel [2]. The peeling of the accumulated scale causes malfunctions in the operation of household appliances. American scientists carried out a study, thanks to which it was possible to establish that a layer of scale with a thickness of one and a half millimeter reduces the heat transfer about

15%, the thickness of the scale in three millimeters - about 25%, etc. In addition, such harmful impurities in water, like calcium and magnesium compounds, require for heating the liquid up to 25% more electricity.

Over 90% of heating devices become faulty of constantly contacting with hard water [3-4]. Dissolved in water, calcium and magnesium compounds adversely affect the quality of the laundry washed in it, reducing its "life" from 15 to 30%, while increasing by 30% the amount of consumable washing powder. If you use special cosmetic products during washing, their useful properties become ineffective at the contact with hard water.

With prolonged washing with hard water, the human skin also suffers. This leads to clogging of the pores, weakening of protective properties of the fatty film on the surface of the skin, which causes flaking, irritation and the appearance of various rashes [5]. In addition to skin itself, the hair also suffers, which is accompanied by symptoms such as itching, dandruff. The very hair becomes dry and tough to the touch, stop "obeying", visually acquire a neglected appearance.

Such harmful impurities in water, like calcium and magnesium, are able to accumulate in the body, leading eventually to the deposition of stones in the kidneys and obstruction of the vessels [6]. Do not drink hard water if you do not want serious health problems.

On the other hand, in many industrial solutions, there are problems of separation of alkaline-earth metals ions from the ions of target metal. In leaching solutions, after extraction of main ion (for example, uranyl, gold, zinc ions, etc.), calcium ions and other alkaline and alkaline earth metals remain.

At present, industrial water treatment plants assume the use of ion exchange resins [7]. The purpose of this work is study the features of sorption calcium ions withintergel systems based on the rare-crosslinked polymer hydrogels of acid and basic nature.

EXPERIMENTAL PART

Equipment. Specific electric conductivity was measured on conductometer MARK-603 (Russia), pH of the solutions was measured on pH-meter MetrohM 827 pH-Lab (Switzerland). Measurement of Ca^{2+} ions were made on ion-meter I-160MI (Russia).

*Materials.*Investigations the solution of calcium chloride containing 50 mg/Lwere made. Hydrogels of polyacrylic (PAA) and polymethacrylic (PMAA) acids were synthetized in presence of crosslinking agent N,N-methylene-bis-acrylamide and redox system $K_2S_2O_8$–$Na_2S_2O_3$. Hydrogel of poly-4-vinylpyridine (P4VP) was synthetized (2% of crosslinking agent) by “Sigma Aldrich” company. Hydrogel of poly-2-methyl-5-vinylpyridine (P2M5VP) was synthetized in medium of dimethylformamide in presence of crosslinking agent epichlorohydrine. Intergel pairs hydrogel of polymethacrylic acid – hydrogel of poly-4-vinylpyridine and hydrogel of polyacrylic acid – hydrogel of poly-2-methyl-5-vinylpyridinewere made from the synthetized hydrogels. Swelling degrees of the hydrogels are: $\alpha_{(hPAA)}$=29.13 g/g, $\alpha_{(hPMAA)}$=23.76 g/g; $\alpha_{(hP4VP)}$=2.65 g/g, $\alpha_{(hP2M5VP)}$=1.98 g/g.

Experiment. Experiments were made at room temperature. Studies were conducted as follows: calculated amount of each hydrogel in dry state was put in special glass filters, pores of which is permeable for low-molecular ions and molecules, but impermeable for hydrogels dispersion. After that the parameters (specific electric conductivity, pH, Ca^{2+} ions concentration) were measured during 48 hours. Measurements of above mentioned parameters were made in absence of the hydrogels in the solutions.

RESULTS AND DISCUSSION

Sorption of low-molecular ions (calcium ions) from solution is usually accompanied by significant changes of electrochemical properties of the salt. It should be noted that conformation of the macromolecules is also changed during their self-organization during interaction with the metal solution. Sorption process of calcium ions by functional groups of the polymer hydrogels of acid and basic nature can be described by the following chemical reactions:

$$\text{-COOH} + Ca^{2+} \rightarrow (\text{-COO})_2Ca + 2H^+ \quad (1)$$

$$N^+H + Ca^{2+} \rightarrow N^+{}_2Ca + 2H^+ \quad (2)$$

As seen from the reactions 1 and 2, sorption of calcium ions by the carboxyl group and heteroatom of pyridine ring occurs due to formation of coordination bonds.

Sorption of calcium by intergel system hPMAA-hP4VP. Figure 1 represents dependence on specific electric conductivity of calcium chloride from hPMAA:hP4VP molar ratios in time. Sorption of calcium provides decrease of the metal amount in the solution (in accordance with reaction 1), result of what is decrease of electric conductivity with time. It is seen from obtained data that maximum decrease of electric conductivity is observed at hPMAA:hP4VP=4:2 ratio, exact minimum is observed at 48 hours of remote interaction of the polymers. Also low values of electric conductivity are observed at hPMAA:hP4VP=3:3 ratio. In case with individual hydrogels of PMAA and P4VP electrochemical equilibrium is reached faster, after 24 hours electric conductivity decreases less intensive, what, in turn can be explained by absence of additional ionization of the macromolecules.

Sorption process of calcium ions by the intergel system hPMAA-hP4VP also impacts onconcentration of hydrogen ions in the solution (fig**ure** 2). Maximum release of protons is observed in presence of only acid hydrogel, what is due to absence of the polybasis which can associate protons in the process of ionization of the polymer hydrogels in intergel pairs. The lowest release of protons occur in presence of the basic hydrogel, what is due to low dissociation of water molecules. Decrease of pH with polyacid share in intergel pairs is due to predominance of carboxyl groups dissociation process over association process of hydrogen ions by nitrogen atom, also it should be noted that ionization of the polybasis at calcium sorption occurs also due to formation of coordination bonds between nitrogen atoms and the metal ion.

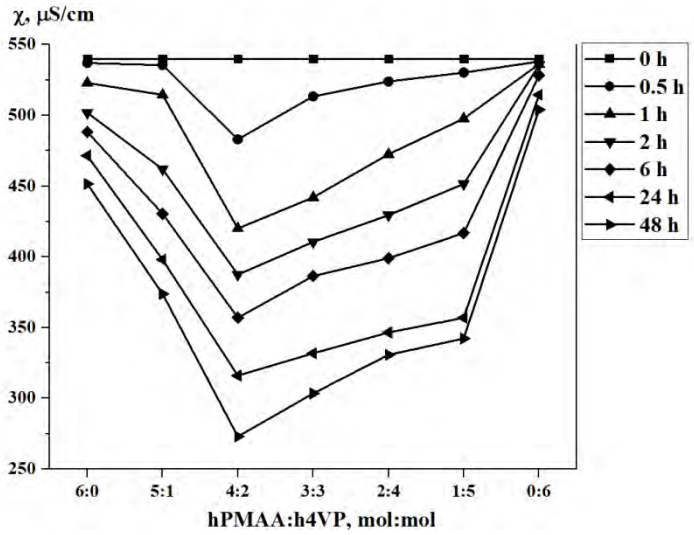

Figure1 – Dependence **on** specific electric conductivity
of calcium chloride versus of mole ratios of hPMAA:hP4VP

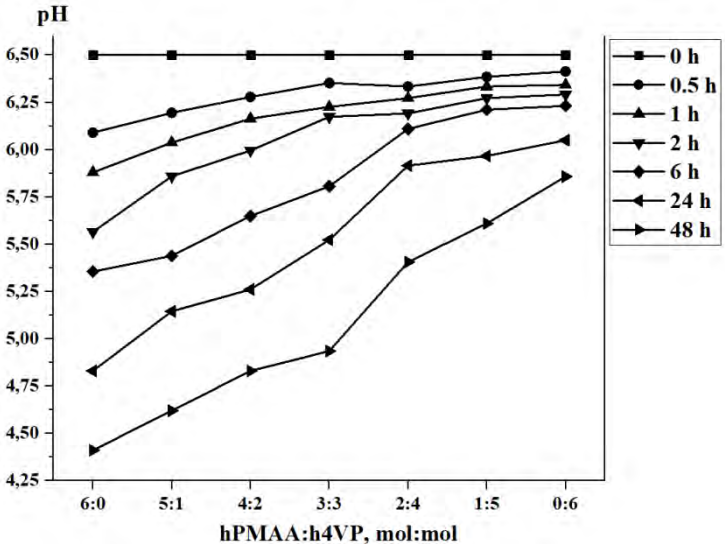

Figure 2 – Dependence on pH of calcium chloride versus of mole ratio hPMAA:hP4VP

Exact areas of maximum and minimum sorption of calcium ions by the intergel system are observed (figure 3). Calcium ions concentration decreases with time. High values of sorption degree of calcium ions are observed at ratios hPMAA:hP4VP=4:2 and 3:3, at that maximum amount of the metal is sorbed at ratio 4:2 (sorption degree is 93%), while individual hydrogels of PMAA and P4VP extract not more than 65% of calcium ions.

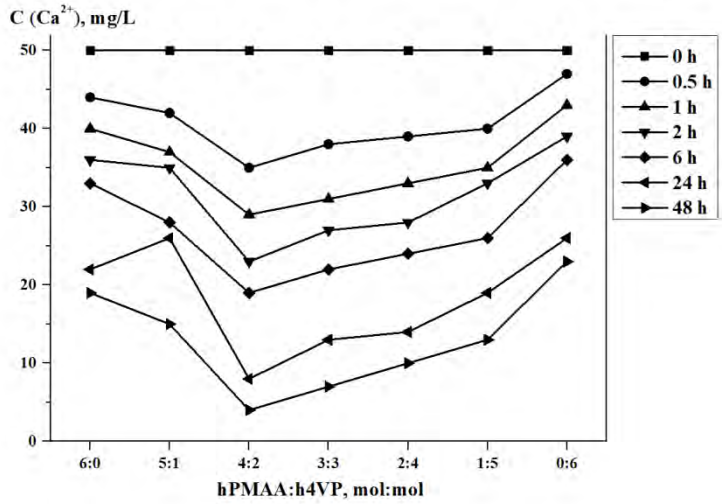

Figure3 – Dependence on Ca^{2+} ions concentration versus of mole ratios of hydrogels

Obtained results show that in all intergel pairs sorption occurs intensively in comparison with individual polymer hydrogels. This is due to formation of optimal conformation of the macromolecules for calcium ions sorption at hPMAA:hP4VP=4:2 ratio due to unfolding of polymer globes due to repulsion of same-charged groups on internode links in result of the polymers remote interaction.

*Sorption of calcium by intergel system hPAA-hP2M5VP***.** Sorption of calcium by intergel system hPAA-hP2M5VP (figure 4) is accompanied with decrease of

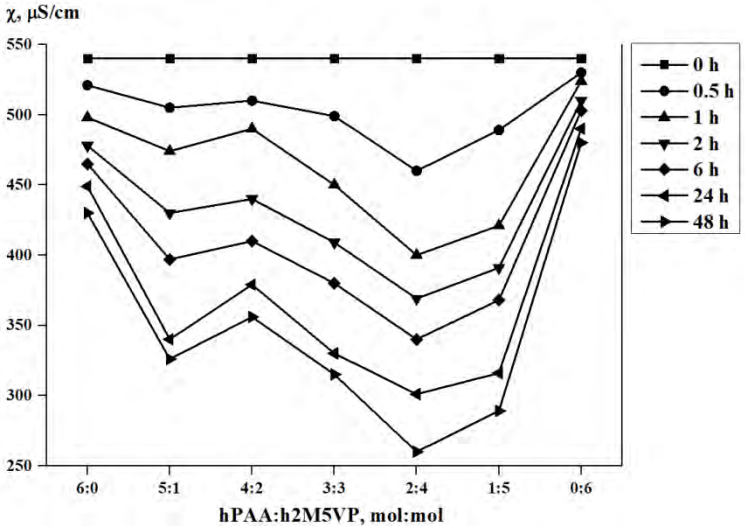

Figure 4 – Dependence on specific electric conductivity of calcium chloride versus of mole ratios of hPAA:hP2M5VP

specific electric conductivity with time similarly to intergel system hPMAA-hP4VP (figure 1). However, in this case minimums of electric conductivity are observed at another ratios of the hydrogels in intergel pairs. Exact minimum of electric conductivity is observed at ratio hPAA:hP2M5VP=2:4 at 48 hours of hydrogels interaction with calcium chloride solution. Also low values of electric conductivity are observed at ratio hPAA:hP2M5VP=1:5. Similarly to hydrogels of PMAA and P4VP hydrogels of PAA and P2M5VP rather fast reach electrochemical equilibrium, what is evidenced by absence of significant decrease of specific electric conductivity after 24 hours.

Sorption of calcium also provides changes of pH of the salt solution (figure 5). As seen from figure, with polyacid share increase in the intergel pairs pH decreases. However, at ratio hPAA:hP2M5VP=5:1 pH values are higherthat at ratios hPAA:hP2M5VP=4:2 and 3:3, what indicates to prevalence of proton binding by nitrogen atom in pyridine ring process over dissociation process of carboxyl groups. Change of self-organization of the polymer macromolecules in process of calcium ions sorption provides protons release in solution, and, in the end, decrease of pH.

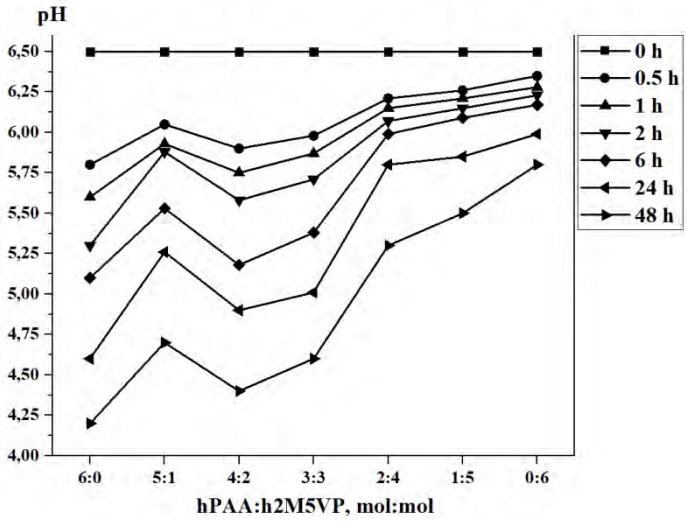

Figure 5 – Dependence of pH of calcium chloride from hPAA:hP2M5VP molar ratios in time

Dependence of calcium ions concentration from hydrogels molar ratios in presented on figure 6. Similarly to the case with PMAA and P4VP hydrogels (figure 6), hydrogels of PAA and P2M5VP do not have high values (not higher that 65%) of calcium ions sorption degree. High ionization of internode links of polymer chains of the polyacid and polybasis at hydrogels ratio hPAA:hP2M5VP=2:4 provides maximum sorption of calcium (92% of the metal is sorbed at 48 hours). More than 80% of calcium is extracted from the solution at ratios hPAA:hP2M5VP=3:3 and 1:5.

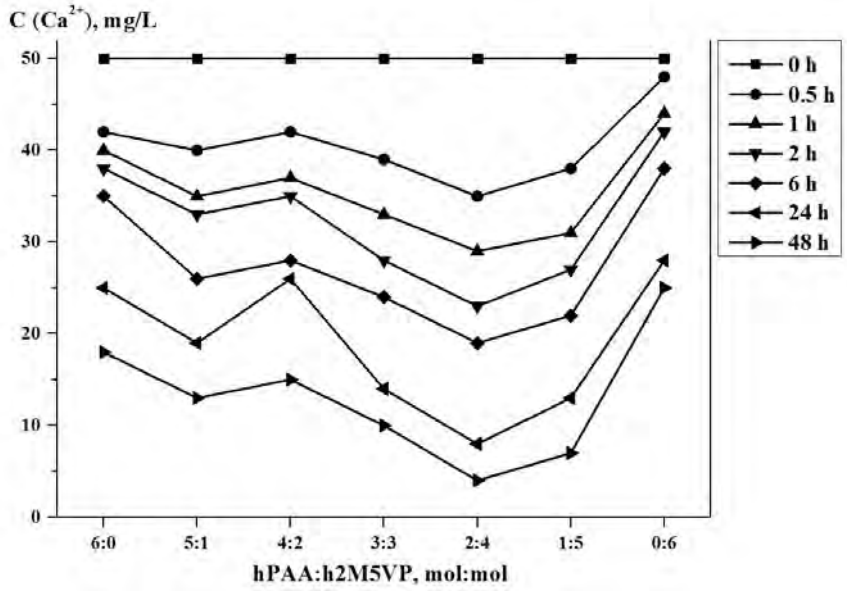

Figure 6 – Dependence of Ca^{2+} ions concentration from hydrogels molar ratios in time

Analysis of obtained results on specific electric conductivity, pH provides conclusion that highly ionized state of hPAA, hPMAA, hP4VP and hP2M5VP is a consequence of the polymers mutual activation at their remote interaction. Also it should be noted that transition into highly ionized state can be complicated if there is a bulk substituent (ex. methyl) in structure of polymer, what, in turn, interfeersunloding of polymer globe during mutual activation. By this phenomenon different degree of sorption of calcium ions in the intergel systems hPMAA:hP4VP=4:2 and hPAA:hP2M5VP=2:4 can be explained. Obtained data on specific electric conductivity also indicates to high ionization of the polymers at these ratios.

Conclusion.

1. Sorption of calcium ions by intergel system hPMAA-hP4VP and hPAA-hP2M5VP is accompanied with specific electric conductivity and pH decrease due to change of initial electrochemical equilibrium in salt solution.

2. Absence of phenomenon of mutual activation and further transition into highly ionized state, provides fast reach of electrochemical equilibrium of individual hydrogels of PAA, PMAA, P4VP, P2M5VP, consequence of what is very slight increase of sorption degree after 24 hours of interaction. Sorption degree of calcium ions by above mentioned hydrogels does not exceed 70%.

3. Optimal conformation of polymer macromolecules in intergel systems hPMAA-hP4VP and hPAA-hP2M5VP for maximum sorption of calcium ions appears during their self-organization at ratios hPMAA:hP4VP=4:2 and hPAA:hP2M5VP=2:4, sorption degree is 93% and 92% respectively.

4. Significant difference (over 25%) of sorption degree of individual hydrogels and intergel systems is due to the fact that remote interaction in intergel systems provides formation of high density of charged functional groups without counter ions on internode links of polymer chains.

5. Intergel systems based on rare-crosslinked hydrogels of PAA, PMAA, P4VP, P2M5VP can be used for development of innovative technologies in water purification and hydrometallurgy.

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Резюме

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ПОЛИМЕТАКРИЛ ҚЫШҚЫЛЫ – ПОЛИ-4-ВИНИЛПИРИДИН ЖӘНЕ ПОЛИАКРИЛҚЫШҚЫЛЫ – ПОЛИ-2-МЕТИЛ-5-ВИНИЛПИРИДИН ГИДРОГЕЛЬДЕРІНЕН ҚҰРАЛҒАН ИНТЕРГЕЛЬДЕРІМЕН КАЛЬЦИЙ ИОНДАРЫН СОРБЦИЯЛАУДАҒЫ ЕРЕКШЕЛІКТЕР

Полиметакрил қышқылы (ПМАКг) – поли-4-винилпиридин (П4ВПг) және полиакрил қышқылы (ПАКг) –поли-2-метил-5-винилпиридин (П2М5ВПг) гидрогельдері арқылы құрылған интергелді жүйелерімен Ca^{2+} ионын сорбциялау процессін кондуктометрия, рН-**м**етрия, ионометрия әдістерімен зерттелді. Анықталғаны, кальций иондарының сорбциялау процесі жеке сирек торланған полимерлік ПАК, ПМАК, П4ВП, П2М5ВП гидрогелдерімен, сондай-ақ ПМАКг-П4ВПг, ПАКг-П2М5ВПг интергелді жүйелерімен кальций хлориді ерітіндісінің бастапқы электрохимиялық қасиеттері айтарлықтай өзгерістерін байқауға болады (уақыт өте келе металл ионын сорбциялауда меншікті электрөткізгіштігінің және рН мәндері төмендейді). ЖекеПАК, ПМАК, П4ВП, П2М5ВП гидрогелінде тұз ерітіндісінің электрохимиялық тепе-теңдік жылдам теңеседі, соның салдарынан бір тәулік өткеннен кейін аз ғана өсуі байқалады. Кальций иондарының соңғы сорбциялау дәрежесі 70% дейін жетеді. Интергелді жүйелерде полимерлердің оңтайлы конформациясы гПМАК:гП4ВП=4:2 және гПАК:гП2М5ВП=2:4 қатынастарында түзіледі. Алайда, макромолекулалардың ауысу процесі қиындық туғызады, өйткені ПМАК және П2М5ВП құрылымдарда метилді корынбасарлар көптігінен иондану процесінде полимерлік түйіндердің айналуына кедергі келтіреді. гПМАК:гП4ВП=4:2 және

гПАК:гП2М5ВП=2:4 интергелді жүйелерімен сәйкесінше кальций иондарының сорбциялау дәрежесі 93% және 92% құрайды.

Түйін сөздер: интергелді жүйе, өзара белсендендіру, сорбция, Ca^{2+} иондары жағдай, гидрогельдер, полиакрилқышқылы, полиметакрилқышқылы, поли-4-винилпиридин, поли-2-метил-5-винилпиридин.

Резюме

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ОСОБЕННОСТИ СОРБЦИИ ИОНОВ КАЛЬЦИЯ ИНТЕРГЕЛЕВЫМИ ГИДРОГЕЛЯМИ ПОЛИМЕТАКРИЛОВОЙ КИСЛОТЫ – ПОЛИ-4-ВИНИЛПИРИДИНА И ПОЛИАКРИЛОВОЙ КИСЛОТЫ – ПОЛИ-2-МЕТИЛ-5-ВИНИЛПИРИДИНА

Методами кондуктометрии, pH-Метрии, ионометрии исследован процесс сорбции ионов Ca^{2+}интергелевыми системами гидрогель полиметакриловой кислоты (гПМАК) – гидрогель поли-4-винилпиридина (гП4ВП) и гидрогель полиакриловой кислоты (гПАК) – гидрогель поли-2-метил-5-винилпиридина (гП2М5ВП). Установлено, что процесс сорбции ионов кальция как индивидуальными редкосшитыми полимерными гидрогелями ПАК, ПМАК, П4ВП, П2М5ВП, так и интергелевыми системами гПМАК-гП4ВП, гПАК-гП2М5ВП, сопровождается существенными изменениями исходных электрохимических свойств раствора хлорида кальция (со временем сорбции ионов металла происходит снижение значений удельной электропроводности и pH). Индивидуальными гидрогелями ПАК, ПМАК, П4ВП, П2М5ВП достаточно быстро достигается электрохимическое равновесие с раствором соли, вследствие чего происходит незначительный рост по истечению 1 сут, конечная степень сорбции ионов кальция достигает 70%. Образование оптимальной конформации полимеров в интергелевых системах происходит при соотношениях гПМАК:гП4ВП=4:2 и гПАК:гП2М5ВП=2:4, однако процесс перехода макромолекул затрудняется тем, что в структурах ПМАК и П2М5ВП присутствует объемный метильный заместитель, мешающий разворачиванию полимерного клубка в процессе его ионизации. Степень сорбции ионов кальция интергелевыми системами гПМАК:гП4ВП=4:2 и гПАК:гП2М5ВП=2:4 составляет 93 и 92% соответственно.

Ключевые слова: интергелевая система, взаимная активация, сорбция, ионы Ca^{2+}, гидрогели, полиакриловая кислота, полиметакриловая кислота, поли-4-винилпиридин, поли-2-метил-5-винилпиридин.