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«Ә. Б. БЕКТҰРОВ АТЫНДАҒЫ  
ХИМИЯ ҒЫЛЫМДАРЫ ИНСТИТУТЫ»  
АКЦИОНЕРЛІК ҚОҒАМЫ

# ҚАЗАҚСТАННЫҢ ХИМИЯ ЖУРНАЛЫ

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## ХИМИЧЕСКИЙ ЖУРНАЛ КАЗАХСТАНА

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### CHEMICAL JOURNAL of KAZAKHSTAN

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## SELF-ORGANIZATION OF POLYMER HYDROGELS OF POLYACRYLIC ACID IN INTERGEL SYSTEMS IN CERIUM IONS SORPTION PROCESS

**Abstract.** Sorption process of cerium ions by intergel systems hydrogel of polyacrylic acid (hPAA) – hydrogel of poly-4-vinylpyridine (hP4VP) and hydrogel of polyacrylic acid (hPAA) – hydrogel of poly-2-methyl-5-vinylpyridine (hP2M5VP) is studied. Found that self-organization of PAA hydrogels is in significant influence from structure of basic hydrogel. Absence of bulky methyl substituent in the structure of hP4VP provides faster ionization of the hydrogels in intergel system hPAA-hP4VP in comparison with system hPAA-hP2M5VP. Extraction degree of cerium ions of individual hydrogels of PAA, P4VP and P2M5VP is 63.33%, 56.67% and 50.00% respectively. At 17%hPAA-83%hP4VP and 33%hPAA-67%hP2M5VP ratios 92.33% and 90.67% cerium is extracted. PAA, P4VP, P2M5VP polymer hydrogels have not very high values of polymer chain binding degree (52.53%, 47.00% and 41.47% respectively). Maximum values of polymer chain binding degree in the intergel systems are observed at ratios: 17%hPAA-83%hP4VP (binding degree is 76.59%) and 33%hPAA-67%hP2M5VP (polymer chain binding degree is 75.21%).

**Keywords:** intergel system, self-organization, sorption,  $\text{Ce}^{3+}$  ions, hydrogels, polyacrylic acid, poly-4-vinylpyridine, poly-2-methyl-5-vinylpyridine.

In result of previous investigations [1-6] it was found that remote interaction of polymer hydrogels provides significant changes of their self-organization. In this regard goal of the present work is study of impact of second component (polybasis) on self-organization of polyacrylic acid polymer hydrogels in intergel systems as well as study of sorption properties of intergel systems hPAA-hP4VP and hPAA-hP2M5VP in relation to cerium ions.

### EXPERIMENTAL PART

*Equipment.* Measurements of optical density for further calculation of cerium ions concentration were carried out on spectrophotometer Jenway-6305 (UK).

*Materials.* Studies were carried out in 0.005 M solution of 6-water cerium nitrate. Hydrogels of polyacrylic acid were synthesized in presence of cross-linking agent N,N-methylene-bis-acrylamide and red-ox system  $\text{K}_2\text{S}_2\text{O}_8\text{-Na}_2\text{S}_2\text{O}_3$ . Hydrogel of poly-4-vinylpyridine (hP4VP) (2% of cross-linking agent) was synthesized by «Sigma Aldrich» company. Hydrogel of poly-2-methyl-5-vinylpyridine (hP2M5VP) was synthesized in dimethylformamide medium in presence of cross-linking agent epichlorohydrin. Synthesized hydrogels were put together to create intergel pairs hPAA-hP4VP and hPAA-hP2M5VP. Swelling degrees of the hydrogels are:  $\alpha_{(\text{hPAA})}=27.33$  g/g;  $\alpha_{(\text{hP4VP})}=3.27$  g/g;  $\alpha_{(\text{hP2M5VP})}=3.20$  g/g.

*Experiment.* Experiments were made at a room temperature. Study of the intergel systems 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 cerium ions determination.* Methodology of cerium ions determination in solution is based on formation of colored complex compound of organic analytic reagent arsenazo III with rare-earth metals ions [7].

Cerium ions extraction degree (sorption degree) was calculated in accordance with equation:

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

where  $C_{\text{initial}}$  – initial concentration of metal in solution, g/L;  $C_{\text{residual}}$  – residual concentration of metal in solution, g/L.

Total polymer chain binding degree was calculated as follows:

$$\theta = \frac{v_{\text{sorbed}}}{v} * 100\%$$

where  $v_{\text{sorbed}}$  – quantity of polymer links with sorbed metal, mol;  $v$  – total quantity of polymer mass (if there are 2 hydrogels in solution, it is calculated as sum of each polymer hydrogel mass), mol.

Effective dynamic exchange capacity was determined by calculations in accordance with equation:

$$Q = \frac{v_{\text{sorbed}}}{m_{\text{sorbent}}}$$

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

## RESULTS AND DISCUSSION

Sorption of cerium ions by the intergel systems hPAA-hP4VP and hPAA-hP2M5VP occurs by ionic and coordination mechanisms. Process of rare-earth elements sorption (on lanthanum example) is clearly described in previous works [8-10].

*Extraction of cerium ions by intergel system hPAA-hP4VP.* Dependence of cerium ions extraction degree of the intergel system hPAA-hP4VP from hydrogels molar ratios in time is presented on figure 1. Maximum quantity of cerium ions is sorbed by the intergel system at hydrogels ratio 17%hPAA-83%hP4VP. Extraction degree at 48 hours is 92.33%. Obtained results show that extraction degree of cerium ions of individual hydrogels of polyacrylic acid and poly-4-vinylpyridine is not high, values of the parameter are 63.33 and 56.67 respectively. The rest intergel pairs in the intergel system hPAA-hP4VP also have

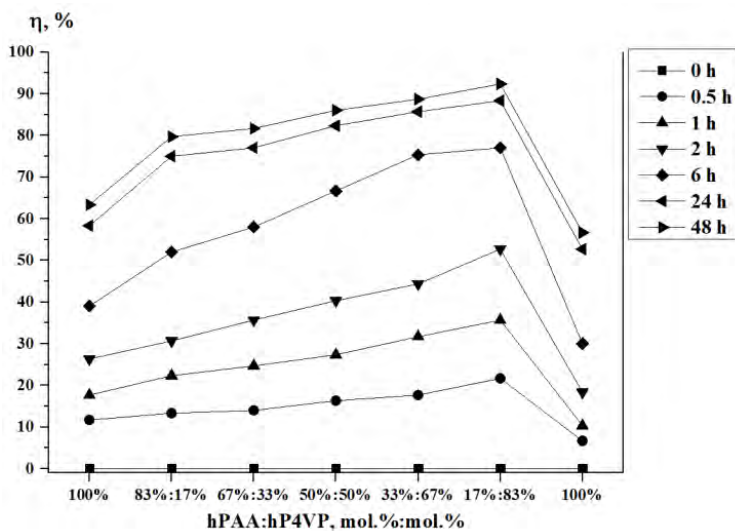


Figure 1 – Dependence of cerium ions extraction degree of the intergel system hPAA-hP4VP from hydrogels molar ratios in time

significantly higher values of cerium ions extraction degree comparatively with individual hydrogels of PAA and P4VP.

Figure 2 represents dependence of polymer chain binding degree (in relation to cerium ions) of the intergel system hPAA-hP4VP from time. Maximum values of binding degree in the intergel system at 48 hours are observed at hydrogels

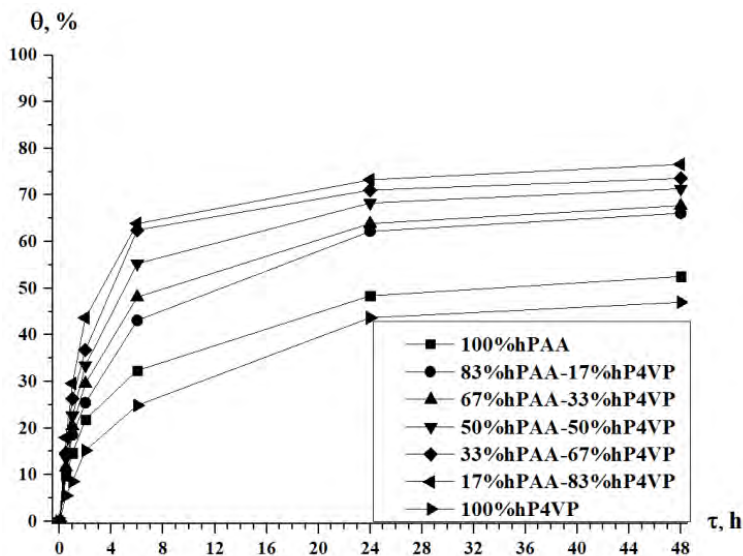


Figure 2 – Dependence of polymer chain binding degree of the intergel system hPAA-hP4VP from time

ratio 17%hPAA-83%hP4VP, it is 76.59%. High values of polymer chain binding degree are also observed at ratios 33%hPAA-67%hP4VP and 50%hPAA-50%hP4VP. It indicates to high ionization degree of the macromolecules in results of mutual activation of hydrogels of polyacrylic acid and poly-4-vinylpyridine. Polymer chain binding degree of the individual hydrogels of PAA and P4VP at 48 hours is 52.53% and 47.00%.

Dependence of effective dynamic exchange capacity of the intergel system hPAA-hP4VP from hydrogels molar ratios in time is shown on figure 3. Obtained data point to the fact that mutual activation of the polymer hydrogels in intergel pairs provides significant increase of values of exchange capacity in comparison with initial hydrogels. This is particularly pronounced at 6 hours of remote interaction. As seen from the figure, at this time of hydrogels interaction at ratio 17%hPAA-83%hP4VP values of exchange capacity are in 2.5 times higher than values of capacity of the individual hydrogels of PAA and P4VP. Further remote interaction of the polymers indicates that the intergel system hPAA-hP4VP approaches to equilibrium state, what is evidenced by not strong increase of effective dynamic exchange capacity as it was in the beginning of the hydrogels remote interaction. Maximum values of effective dynamic exchange capacity are reached at ratio 17%hPAA-83%hP4VP at 48 hours of remote interaction.

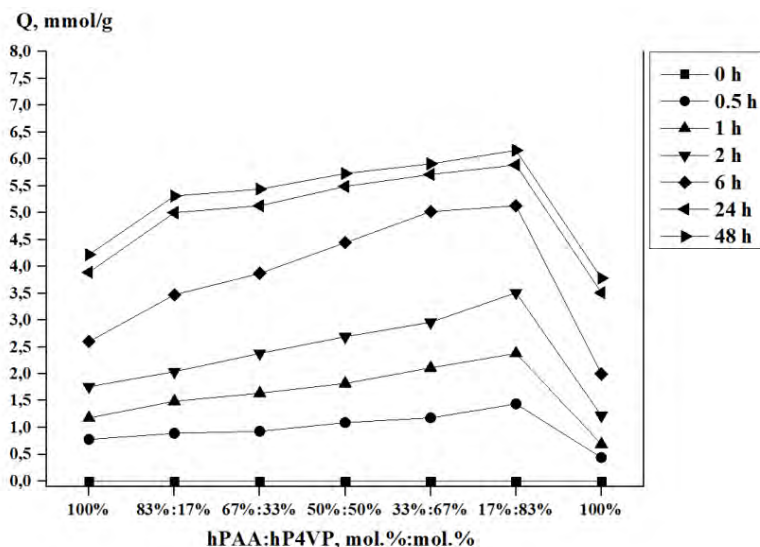


Figure 3 – Dependence of effective dynamic exchange capacity of the intergel system hPAA-hP4VP from hydrogels molar ratios in time

*Extraction of cerium ions by intergel system hPAA-hP2M5VP.* Figure 4 shows dependence of cerium ions extraction degree of the intergel system hPAA-hP2M5VP from hydrogels molar ratios in time. Extraction degree increases with time in intergel system. It should be noted that transfer of polymer

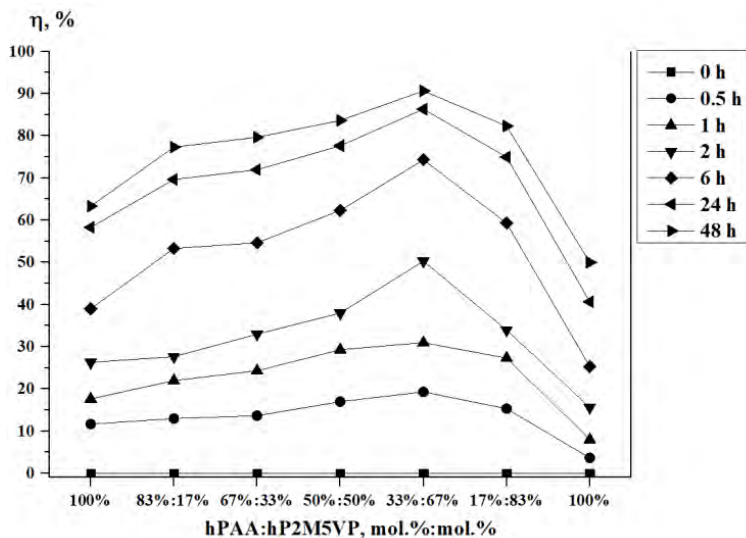


Figure 4 – Dependence of cerium ions extraction degree of the intergel system hPAA-hP2M5VP from hydrogels molar ratios in time

macromolecules into highly ionized state due to their mutual activation provides strong increase of extraction degree of cerium ions of polymer hydrogels in the intergel pairs comparatively with initial polymers. Maximum values of extraction degree of cerium ions in the intergel system are observed at ratio 33%hPAA-67%hP2M5VP. Extraction degree at this ratio is 90.67%. Sorption degree of cerium ions of individual polymer hydrogels of PAA and P2M5VP is 66.33% and 50.00% respectively.

Dependence of polymer chain binding degree (in relation to cerium ions) of the intergel system hPAA-hP2M5VP is presented on figure 5. Individual hydrogels of polyacrylic acid and poly-2-methyl-5-vinylpyridine have not sufficiently high values of binding degree (52.53% and 41.47% respectively). Maximum values of polymer chain binding degree in the intergel system hPAA-hP2M5VP are reached at 48 hours of PAA and P2M5VP hydrogels remote interaction at ratio 33%hPAA-67%hP2M5VP, binding degree is 75.21%.

Effective dynamic exchange capacity of the intergel system hPAA-hP2M5VP is shown on figure 6. The highest values of the parameter the intergel system hPAA-hP2M5VP reaches at 48 hours of PAA and P2M5VP remote interaction at ratio 33%hPAA-67%hP2M5VP. Minimum values of exchange capacity are observed in presence of only individual hydrogels of PAA and P2M5VP, what is result of absence of polymer hydrogels mutual activation phenomenon.

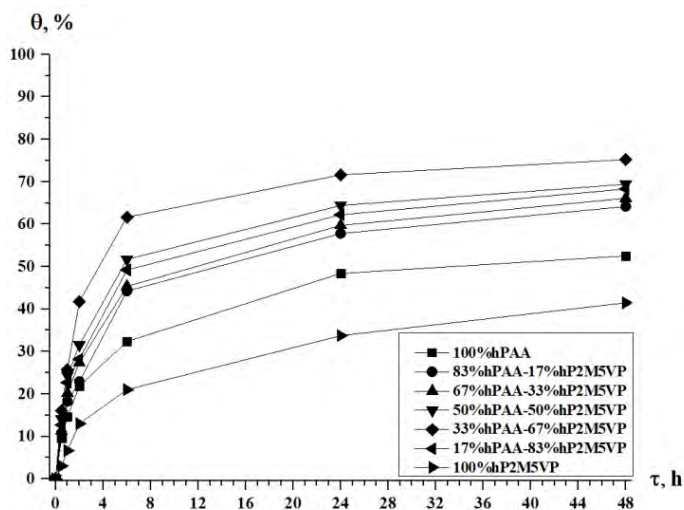


Figure 5 – Dependence of polymer chain binding degree of the intergel system hPAA-hP2M5VP from time

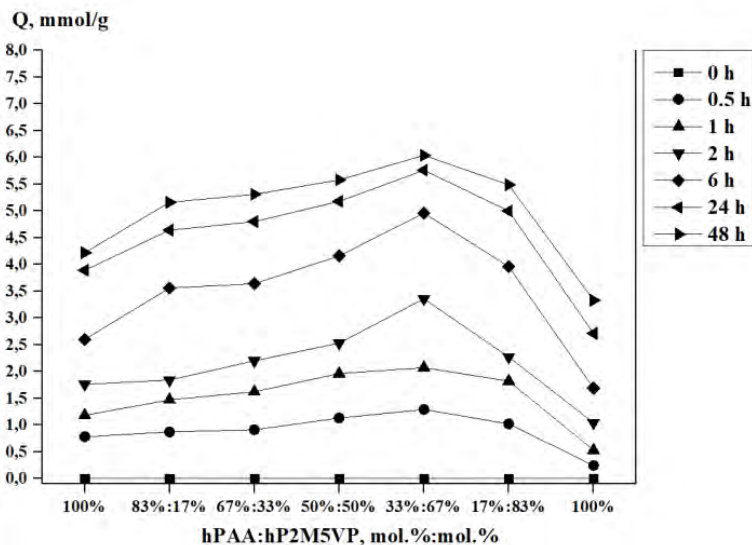


Figure 6 – Dependence of effective dynamic exchange capacity of the intergel system hPAA-hP2M5VP from hydrogels molar ratios in time

As seen from the obtained data, self-organization of polyacrylic acid hydrogels is significantly impacted by the structure of second component (polybasis). Absence of bulky methyl substituent in the structure of hP4VP provides faster ionization of the hydrogels in intergel system hPAA-hP4VP in comparison with system hPAA-hP2M5VP.

### **Conclusion.**

1. Individual hydrogels of PAA, P4VP, P2M5VP do not have high values of sorption properties. Cerium ions extraction degree of hPAA, hP4VP, hP2M5VP is 63.33%, 56.67%, 50.00%.

2. Significant increase of extraction degree in intergel systems hPAA-hP4VP and hPAA-hP2M5VP is result of mutual activation of polymers. Extraction degree of cerium ions in the intergel system hPAA-hP4VP reaches maximum values (92.33%) at ratio 17%hPAA-83%hP4VP at 48 hours. In intergel system hPAA-hP2M5VP maximum extraction of cerium ions occurs at ratio 33%hPAA-67%hP2M5VP, at 48 hours 90.67% of the metal is sorbed.

3. Polymer chain binding degree of hPAA, hP4VP, hP2M5VP is not high (52.53%, 47.00% and 41.47% respectively). This is consequence of absence of mutual activation between the polymers.

4. Maximum values of polymer chain binding degree in the intergel systems are observed at the following ratios: 17%hPAA-83%hP4VP (binding degree is 76.59%) and 33%hPAA-67%hP2M5VP (binding degree is 75.21%).

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## Резюме

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### ЦЕРИЙ ИОНДАРЫН СОРБЦИЯЛАУ БАРЫСЫНДА ИНТЕРГЕЛДІ ЖҮЙЕДЕГІ ПОЛИАКРИЛ ҚЫШҚЫЛЫНЫҢ ПОЛИМЕРЛІК ГИДРОГЕЛДЕРІНІҢ ӨЗІН-ӨЗІ ҰЙЫМДАСТЫРУЫ

**Аннотация.** Полиакрил қышқылы гидрогелі (ПАҚГ) – поли-4-винилпиридин гидрогелі (П4ВПГ) және полиакрил қышқылы гидрогелі (ПАҚГ) –поли-2-метил-5-винилпиридин гидрогелі (П2М5ВПГ) интергелді жүйелерімен церий иондарын сорбциялау процесі зерттелді. Полиакрил қышқылы гидрогелінің өзін-өзі ұйымдастыруына негізгі гидрогелдің құрылымы анағұрлым әсер ететіні анықталды. ПАҚГ-П2М5ВПГ жүйесімен салыстырғанда ПАҚГ-П4ВПГ интергелді жүйесінде П4ВПГ құрылымында үлкен метил алмастырғыштың болмауы гидрогелдердің неғұрлым жылдам ионизациялануына әкеледі. ПАҚ, П4ВП және П2М5ВП жекелеген гидрогелдерінің церий иондарын шығару дәрежесі сәйкесінше 63,33%, 56,67% және 50,00% құрайды. 17%ПАҚГ-83%П4ВПГ және 33%ПАҚГ-67%П2М5ВПГ қатынастарында 92,33% және 90,67% церий шығарылады. ПАҚ, П4ВП және П2М5ВП полимерлік гидрогелдері полимерлік тізбектердің байланысу дәрежесінің салыстырмалы төмен мәндеріне ие (сәйкесінше 52,53%, 47,00% және 41,47%). Интергелді жүйелердің мына қатынастарында полимерлік тізбектердің байланысу дәрежесі анағұрлым жоғары мәнге ие: 17%ПАҚГ-83%П4ВПГ (байланысу дәрежесі 76,59%-ға тең) және 33%ПАҚГ-67%П2М5ВПГ (полимерлік тізбектің байланысу дәрежесі 75,21%-ды құрайды).

**Түйін сөздер:** интергелді жүйе, өзін – өзі ұйымдастыру, сорбция,  $\text{Ce}^{3+}$  иондары, гидрогелдер, полиакрил қышқылы, поли-4-винилпиридин, поли-2-метил-5-винилпиридин.

Резюме

*Т. К. Джумадилов, Р. Г. Кондауров*

САМООРГАНИЗАЦИЯ ПОЛИМЕРНЫХ ГИДРОГЕЛЕЙ  
ПОЛИАКРИЛОВОЙ КИСЛОТЫ В ИНТЕРГЕЛЕВЫХ СИСТЕМАХ  
ПРИ СОРБЦИИ ИОНОВ ЦЕРИЯ

**Аннотация.** Изучен процесс сорбции ионов церия интергелевыми системами гидрогель полиакриловой кислоты (гПАК) – гидрогель поли-4-винилпиридина (гП4ВП) и гидрогель полиакриловой кислоты (гПАК) – гидрогель поли-2-метил-5-винилпиридина (гП2М5ВП). Установлено, что значительное влияние на самоорганизацию гидрогелей ПАК оказывает структура основного гидрогеля. Отсутствие объемного метильного заместителя в структуре гП4ВП приводит к более быстрой ионизации гидрогелей в интергелевой системе гПАК-гП4ВП по сравнению с системой гПАК-гП2М5ВП. Степень извлечения ионов церия индивидуальных гидрогелей ПАК, П4ВП и П2М5ВП составляет 63,33%, 56,67% и 50,00% соответственно. При соотношениях 17%гПАК-83%гП4ВП и 33%гПАК-67%гП2М5ВП извлекается 92,33% и 90,67% церия. Полимерные гидрогели ПАК, П4ВП, П2М5ВП обладают относительно невысокими значениями степени связывания полимерной цепи (52,53%, 47,00% и 41,47% соответственно). Наиболее высокие значения степени связывания полимерной цепи в интергелевых системах наблюдаются при соотношениях: 17%гПАК-83%гП4ВП (степень связывания равна 76,59%) и 33%гПАК-67%гП2М5ВП (степень связывания полимерной цепи составляет 75,21%).

**Ключевые слова:** интергелевая система, самоорганизация, сорбция, ионы  $\text{Ce}^{3+}$ , гидрогели, полиакриловая кислота, поли-4-винилпиридин, поли-2-метил-5-винилпиридин.