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INFLUENCE OF DISTANT ACTION EFFECT BETWEEN POLYMETHACRYLIC ACID AND POLY-4-VINYLPYRIDINE HYDROGELS ON THE SORPTION ABILITY OF ERBIUM IONS

Abstract. The phenomenon of sorption erbium ions by intergel system of polymethacrylic acid hydrogel (PMAA) and poly-4-vinylpyridine hydrogel(P4VP) was studied. It was established that the structure of the basic hydrogel has a significant influence on the self-organization of the PMAA hydrogels. The erbium ions extraction rateof individual hydrogels PMAA and P4VP was 42% and 16%, respectively. At ratios 5:1 (83% of gPMAA-17% gP4VP) and 4:2 (67% gMPAA-33% gP4VP), erbium ions were recovered up to 54% in both cases. The polymer PMAA and P4VP hydrogels have relatively low values of the polymer chain binding degree (0.54% and 0.20%, respectively).

The obtained results indicate the possibility of creating selective intergel systems for separation erbium ions.

Key words: intergel system, sorption, Er^{3+} ions, hydrogels, polymethacrylic acid, poly-4-vinylpyridine.

Introduction. After optimization of the most probable structures of the complex, the heat of formation was estimated. Calculations show that the formation of complex 4 (HF = -267.960 kcal/mol) is most profitable energetically. The main points for the generation of coordination bonds between the ligand molecule - 1-(2-etho-xyethyl)-4-(dimethoxyphosphoryl)-4-hydroxypiperidine, and the bivalent copper ion are nitrogen and oxygen with a double bond on phosphorus, which have the

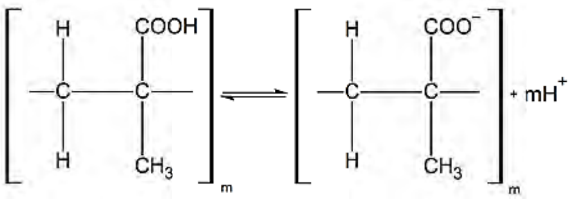
Rare-earth elements are used in various industries: radio electronics, instrument making, machine building, nuclear engineering, metallurgy, chemical industry, etc. Lanthanum, cerium, praseodymium, neodymiumare widely used in the glass industry in the form of oxides and other compounds [1]. These elements increase the translucence of the glass. Rare-earth elements are part of special-purpose glasses that transmit infrared rays and absorb ultraviolet rays, and heat-resistant glass [2].

Rare earth elements and their compounds are widely distributed in the chemical industry, for example, in the production of pigments, varnishes and paints, in the oil industry as catalysts. Rare-earth elements are used in the production of certain explosives, special steels and alloys, as degasifiers [3]. Single-crystal compounds of rare-earth elements (and also glasses) are used to create laser and other optically active and nonlinear elements in optoelectronics [4]. Based on erbium, neodymium, yttrium, samarium, europium with Fe-B mixture, alloys with recordable magnetic properties (high magnetizing and coercive forces) are produced to create permanent magnets of enormous power in comparison with simple ferroalloys [5]. Previous studies [6-9] have shown that mutual activation of polymer hydrogels leads to significant changes in their electrochemical and conformational properties. It should be noted that in previous studies, the starting polymers were applied in a dry state. Remote interaction is carried out by the following processes: rapid - hydration, ionization, dissociation, association and slow - change in the conformational state of inter-node links.It is obvious that the initial state of the rare-crosslinked hydrogels should influence the rate of interactions in the intergel system. Swollen polymers are better subjected to mutual activation due to the fact that the macromolecular ball unfolds during swelling, as a result, the activity of functional groups increases. In connection with this, the purpose of this work was to study the sorption ability of the intergel system gPMAA-gP4VP consisting of preliminary swollen hydrogels with respectto erbium ions.

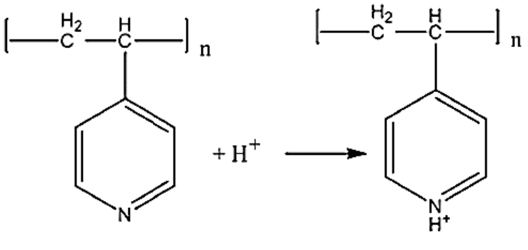
As a result of previous studies [1-6], it was established that the remote interaction of polymer hydrogels in intergel systems leads to significant changes in the conformational state as a result of their self-organization.In connection with this, the aim of this work was to study the effect of the second component (poly-base) on the self-organization of polymer hydrogels of polymethacrylic acid in the intergel system, as well as the study of the sorption properties of the gPMAA-gP4VP intergel systems with respect to erbium ions**.**

Two main reactions occur in intergel systems:

1. Acid hydrogel dissociation:



2. Binding of cleaved proton by nitrogen heteroatom:



EXPERIMENTAL PART

Equipment. Optical density measurements for the subsequent calculation of the erbium nitrate concentration were made using a Jenway-6305 (SC) spectrophotometer.

Materials. The studies were carried out in an erbium(III) nitrate pentahydrate solution. The hydrogels of polymethacrylic acid were synthesized in the presence of the cross-linking agent N,N-methylene-bis-acrylamide and the oxidation-reduction system $K_2S_2O_8$-$Na_2S_2O_3$. The poly-4-vinylpyridine hydrogel (gP4VP) was synthesized by Sigma-Aldrich (2% cross-linking agent). The synthesized hydrogels in the aqueous medium constituted the intergel pair «polymethacrylic acid hydrogel – poly-4-vinylpyridine hydrogel» (gPMAA-gP4VP). The hydrogels swelling degrees were: α (gPMAA) = 20.65 g/g; α (gP4VP) = 2.65 g/g., respectively.

Experiment. The experiments were carried out at room temperature. Investigations of the intergel system were carried out as follows: the calculated amount of each hydrogel in dry form was placed in special polypropylene nets, the pores of which are permeable to low molecular ions and molecules, but impermeable to the dispersion of hydrogels. Then, an aliquot was taken for subsequent optical density measurements.

Methodology of erbium ions determination. The method for determining erbium ions in solution was based on the formation of a colored complex compound of the organic analytic reagent arsenazo III with erbium ions [7].

Extraction (sorption) degree was calculated by the following equation:

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

where C_{initial} is the initial concentration of erbium in solution, g/L; C_{residue} is theresidual concentration of erbium in solution, g/L.

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

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

where ν_{sorbed} – the quantity of polymer links with sorbed erbium, mol; ν – thetotal quantity of polymer links (if there are two hydrogels in solution, it is calculatedas sum of each polymer hydrogel links), mol.

The effective dynamic sorption capacity was calculated by the following equation:

$$Q = \frac{\nu_{\text{sorbed}}}{m_{\text{sorbent(s)}}},$$

where ν_{sorb} is the amount of sorbed metal, mole; $m_{\text{absorbent}}$ – the mass of the sorbent (if there are two hydrogels in solution, it is calculated as the sum of the two hydrogels masses), g.

RESULTS AND DISCUSSION

The erbium ions sorption by thegPMAA-gP4VP intergel system occurs by ionic and coordination mechanisms. The process of rare-earth elements sorption by the example of lanthanum is described in detail in our previous works [8-10].

Erbium ions extraction by the gPMAA-gP4VPintergel system. The dependence of erbium ions extraction degree by the gPMAA-gP4VP intergel system on the mole ratio of hydrogels in time is shown in figure 1. The maximum amount of erbium ions was extracted by the gPMAA-gP4VP intergel system at the ratio of hydrogels 5:1 (83%gMPAA-17%gP4VP) and 4:2 (67%gPMAA-33%gP4VP). The degree of erbium ions extraction after 48 hours at these ratios was 54%. The obtained results indicate that the degree of erbium ions extraction by individual hydrogels of polymethacrylic acid and poly-4-vinylpyridine is low, the extraction rates were 42% and 16%, respectively. The remaining ratios of the intergel pair in the gPMAA-gP4VP intergel system also have much higher erbium ion extraction rates compared to the erbium ions extraction of the PMAA and P4VP individual hydrogels.

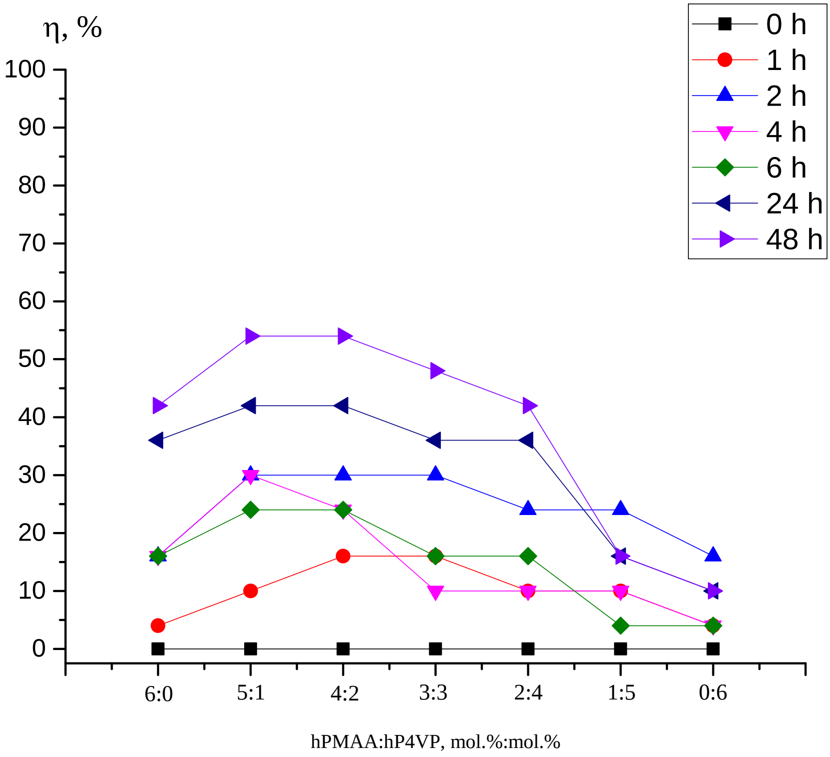


Figure 1 – The dependence on the erbium ions extraction degree by the gPMAA-gP4VP intergel system versus of the mole ratio of hydrogels at the various duration

Figure 2 shows the dependence on the polymer chain binding degree (with respect to erbium ions) of the gPMAA-gP4VP intergel system versus of duration of time. The maximum values of the polymer chain binding degree in the intergel system after 48 hours were 0.7% at ratios of gPMAA-gP4VP 5:1 and 4:2. The polymer chain binding degree values of polymethacrylic acid and poly-4-vinylpyridine individual hydrogels after 48 hours were 0.54% and 0.13%, respectively. At 2 hours of sorption, a certain increase in the polymer chain binding degree was achieved. At 24 and 48 hours, a significant increase in the polymer chain binding degreewas observed; this is particularly noticeable for 4:2 and 3:3 ratios.

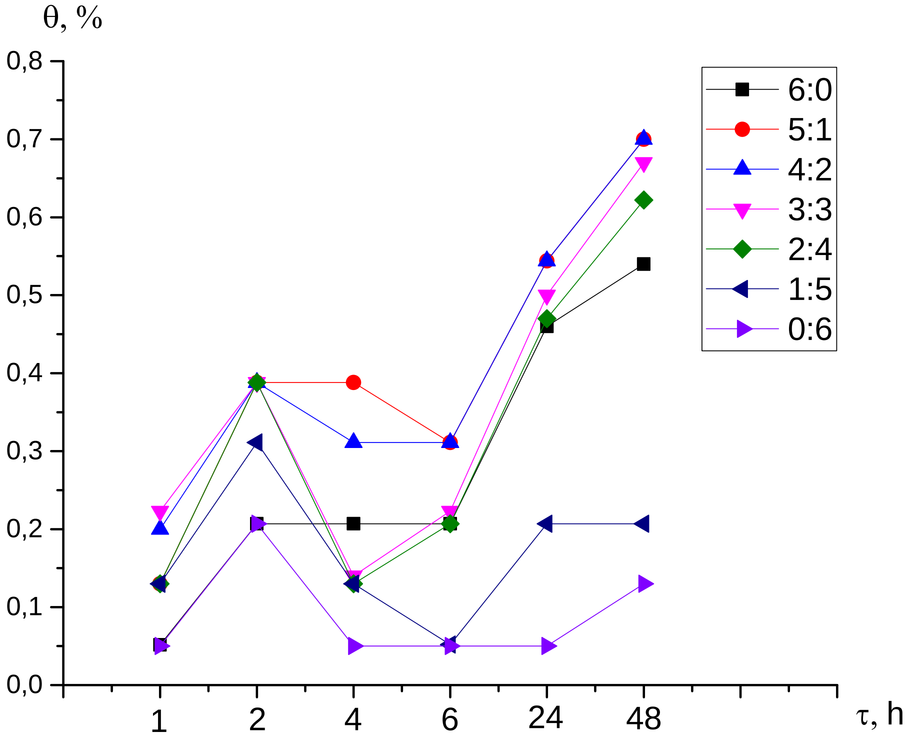


Figure 2 – The dependence on the polymer chain binding degreeof the gPMAA-gP4VP intergel system versus of duration of time in the erbium(III) nitrate pentahydrate medium

Figure 3 shows the dependence of the effective dynamic exchange capacity of the gPMAA-gP4VP intergel system on the molar ratio of hydrogels in time. The obtained data indicate that the mutual activation of polymer hydrogels in the intergel pair leads to a significant increase in the values of the exchange capacity in comparison with the individual hydrogels. The maximum value of the effective dynamic exchange capacity was achieved atgPMAA-gP4VPratio of 5:1 at 48 hours of remote interaction of the hydrogels. Further remote interaction of polymer hydrogels indicates that the gPMAA-gP4VP intergel system approaches

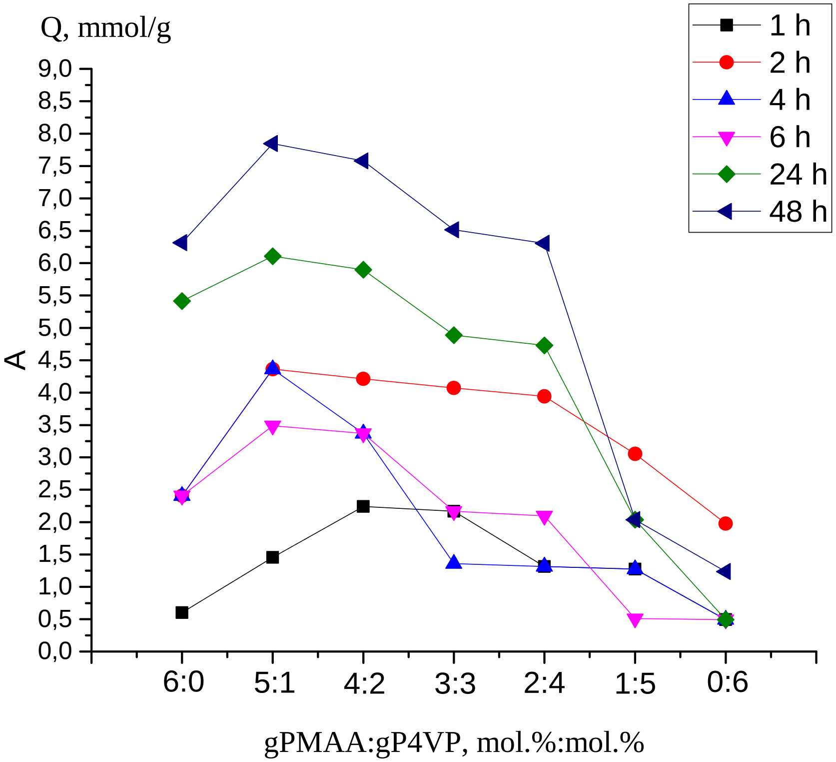


Figure 3 – The dependence on the effective dynamic exchange capacity of the gPMAA-gP4VP intergel system versus of mole ratio of hydrogels at the various duration

the equilibrium statewhich evidenced by slower growth of the effective dynamic exchange capacity as at the beginning of the remote interaction of the hydrogels.

The following ions are present in the solution: -COO^{-}, H^{+}, Er^{3+} and NO_3^{-}. There is an occurrence of these chemical reactions in solution:

1. Dissociation of erbium nitrate along with carboxyl groups dissociation:

$$\text{-COOH} \leftrightarrow \text{-COO}^{-} + H^{+}$$

$$Er(NO_3)_3 \times 5H_2O \leftrightarrow Er^{3+} + 3NO_3^{-} + 5H_2O$$

2. Sorption oh erbium ions by polymer hydrogels:

$$3\ \text{-COO}^{-} + Er^{3+} \rightarrow \text{-COO}_3Er$$

$$3 \equiv N + Er^{3+} \rightarrow \equiv N^{+}{}_3Er$$

Electrochemical equilibrium in solution depends on these reactions and therecould be changes of electrical conductivity values in dependence of dominance ofany one of them.

Conclusions.

1. Individual hydrogels PMAA and P4VP do not possess sufficiently high sorption properties. The degree of erbium ions extraction is 42% and 16% for gPMAA and gP4VP, respectively.

2. The degree of erbium ions extraction in the intergel system reaches the maximum values of 54% at gPMAA-gP4VP ratios of 5:1 and 4:2 after 48 hours.

3. Individual polymer hydrogels PMAA and P4VP have relatively low values of the polymer chain binding degree (0.54% and 0.2%, respectively) with respect to erbium ions due to the absence of the mutual activation phenomenon.

4. The maximum values of the polymer chain binding degreein the intergel systems are 0.7% at gPMAA-gP4VP ratios of 5:1 and 4:2.

5. The obtained results show the possibility of creating erbium sorbents based on intergel systems when the conditions of activated hydrogels interaction with Er^{3+} ions change.

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Резюме

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ЭРБИЙ ИОНДАРЫН СОРБЦИЯЛАУ БАРЫСЫНДА ИНТЕРГЕЛЬДІ ПОЛИМЕТАКРИЛ ҚЫШҚЫЛЫ ЖӘНЕ ПОЛИ-4-ВИНИЛПИРИДИН ГИДРОГЕЛЬДЕРІНІҢ ӨЗАРА ӘСЕРЛЕРІ

Полиметакрил қышқылы гидрогелі (ПМАҚг) – поли-4-винилпиридин гидрогелі (П4ВПг) интергелді жүйесімен эрбий иондарын сорбциялау процесі зерттелді. Полиметакрил қышқылы гидрогелінің өзін – өзі ұйымдастыруына негізгі гидрогелдің құрылымы анағұрлым әсер ететіні анықталды. ПМАҚ және П4ВП жекелеген гидрогелдерінің эрбий иондарын шығару дәрежесі сәйкесінше 42% және 16% құрайды. 83%ПАҚг-17%П4ВПг және 67%ПАҚг-33%П4ВПг қатынастарында 54% эрбий шығарылады. ПАҚжәне П4ВП полимерлік гидрогелдері полимерлік тізбектердің байланысу дәрежесінің салыстырмалы төмен мәндеріне ие (сәйкесінше 0,54% және 0,20%).

Түйін сөздер: интергельді жүйе, сорбция, Er^{3+} иондары, гидрогельдер, полиметакрил қышқылы, поли-4-винилпиридин.

Резюме

Т. К. Джумадилов, Р. Г. Кондауров, Х. Химерсен, А. М. Имангазы

ВЛИЯНИЕ ЭФФЕКТА ДАЛЬНОДЕЙСТВИЯ МЕЖДУ ПОЛИМЕТАКРИЛОВОЙ КИСЛОТОЙ И ПОЛИ-4-ВИНИЛПИРИДИНОМ НА СОРБЦИОННУЮ СПОСОБНОСТЬ К ИОНАМ ЭРБИЯ

Изучен процесс сорбции ионов эрбия интергелевой системой гидрогель полиметакриловой кислоты(гПМАК) – гидрогель поли-4-винилпиридина (гП4ВП). Установлено, что значительное влияние на самоорганизацию гидрогелей ПМАК оказывает структура основного гидрогеля. Степень извлечения ионов эрбия индивидуальных гидрогелей ПМАК и П4ВП составляет 42 и 16%, соответственно. При соотношениях 5:1 (83%гПМАК-17%гП4ВП) и 4:2 (67%гПМАК-33%гП4ВП) извлекается до 54% эрбия в обоих случаях. Полимерные гидрогели ПМАК и П4ВП обладают относительно невысокими значениями степени связывания полимерной цепи (0,54 и 0,20%, соответственно).

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