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INFLUENCE OF HYDROGELS INITIAL STATE ON THEIR ELECTROCHEMICAL AND VOLUME-GRAVIMETRIC PROPERTIES IN INTERGEL SYSTEM POLYACRYLIC ACID HYDROGEL AND POLY-4-VINYLPYRIDINE HYDROGEL

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Abstract. Electrochemical properties of intergel system polyacrylic acid (gPAA) and poly-4-vinylpyridine hydrogels (gP4VP) and conformational properties of initial hydrogels were studied depending on hydrogels initial state. Maximum activation area is: for dry hydrogels – gPAA:gP4VP ratios 5:1 and 1:5, for swollen – ratios 5:1, 2:4 and 1:5.

Keywords: intergel systems, remote interaction, initial state.

1. Introduction

Previous studies showed that result of hydrogels remote interaction is their mutual activation, in the result of which their electrochemical and volume-gravimetric properties are changed significantly [1-5]. Level of mutual activation in turn determines selectivity and sorption activity of hydrogels in intergel systems. The goal of this work is study of hydrogels initial state influence on their electrochemical and conformational properties. In this regard influence of dry and swollen hydrogels on their mutual activation in intergel system polyacrylic acid hydrogel (gPAA) and poly-4-vinylpyridine hydrogel (gP4VP) was studied by the following methods: conductometry, pH-metry and gravimetry.

2. Experimental

Specific electric conductivity of solutions was measured on conductometer "MARK-603" (Russia), hydrogen ions concentration was determined on pH-meter Seven Easy (METTLER TOLEDO, China). Swelling coefficient K_{sw} of initial substances was measured on analytical scales SHIMADZU AY220 (Japan). Measurement errors did not exceed 1 %.

Studies were carried out in medium of distillated water. Hydrogels of polyacrylic acid were synthesized in the presence of crosslinking agent *N*,*N*-methylene-bis-acrylamide and redox system $K_2S_2O_8 – Na_2S_2O_3$ in water medium. Synthesized hydrogels were milled into small dispersions and continuously washed with distilled water until a constant conductivity value of aqueous solutions appeared. Poly-4-vinylpyridine hydrogel (Sigma-Aldrich), crosslinked by divinylbenzene, was used. After synthesis obtained hydrogels were purified from impurities by extraction with water-organic substance extractant, after that hydrogels were washed with distilled water for a long time. Purification degree was 99.99 %.

For research task an intergel pair from synthesized hydrogels was formed. Swelling coefficients of hydrogels were $K_{sw(gPAA)} = 18.6$ g/g, $K_{sw(gP4VP)} = 2.06$ g/g. Studies were carried out at the temperature of 296 ± 0.5 K. Studies were carried out in the following way: each hydrogel was put into glass filter with pores permeable for low-molecular ions and molecules but impermeable for hydrogels dispersion. After that filters with hydrogels were put into glasses with distillated water. Electric conductivity and pH of solutions were measured in the presence of hydrogels. Swelling coefficient was estimated by this equation:

$$K_{sw} = \frac{m_2 - m_1}{m_1} \quad (1)$$

where m_1 – mass of dry hydrogel; m_2 – mass of swollen hydrogel.

3. Results and Discussion

3.1. Study of Properties of gPAA:gP4VP Intergel System Consisting of Dry Hydrogels

Figs. 1 and 2 show dependencies of electric conductivity and solutions pH change on hydrogels molar ratios in time.

As it can be seen from Fig. 1, electric conductivity of solution increases in time almost for all ratios of hydrogels. Nevertheless character of electric conductivity change is different for various hydrogels ratios. It should be noted that there is an appearance of maximum and minimum electric conductivity areas. Clear maximum is observed for 24 h of hydrogels remote interaction at gPAA:gP4VP ratio 2:4. Also at this ratio there is a further electric conductivity increase and maximum value is reached for 48 h. Minimum of electric conductivity is observed for 24 h of interaction at gPAA:gP4VP ratio 5:1. Change of hydrogen ions concentration in the presence of gPAA:gP4VP intergel system is shown in Fig. 2. Primarily it can be noted that on dependence curves of solutions pH there is no linear dependence, which indicates hydrogels remote interaction in intergel system. As it can be seen from Fig. 2 there is an increase of solutions pH with time. This occurs due to an addition of cleaved proton, which was cleaved from carbonyl group, to vinylpyridine. This is evidenced by maximums of pH at hydrogels ratio 2:4, which corresponds to remote interaction time of 24 and 48 h. Minimum of pH is observed at initial moment of time at the ratio 1:5. As it was mentioned above maximum conductivity is observed at the ratio of 2:4. It occurs due to appearance of different charged particles in solution: ions (H^+, OH^-) and groups ($-COO^-$, $\equiv NH^+$). Reactions which describe in details appearance of these particles are given in previous works [5]. At the ratio 2:4 there are pH maximums; due to this fact it is possible to say that COOH groups dissociation rate is less than nitrogen heteroatom of vinylpyridine protonation rate. It indicates to basic hydrogels ionization process. And, finally, as a result of remote interaction both hydrogels are transferred into highly-ionized state being exposed to mutual activation.

Swelling coefficients dependence of acid and basic hydrogels on hydrogels molar ratios in time is shown in Figs. 3 and 4.

Change of swelling coefficient of acid hydrogel is showed in Fig. 3. The increase of polybasis share provides gradual increase of gPAA swelling coefficient. Maximum swelling of polyacid is observed at the ratio of 1:5 for 48 h of remote interaction. Area of gPAA minimum swelling is observed at the presence of only polyacid (ratio 6:0) in initial moment of time. Dependence of poly-4-vinylpyridine hydrogel swelling in the presence of polyacrylic acid hydrogel is shown in Fig. 4. Minimum swelling of polybasis occurs at hydrogels ration 1:5 at all remote interaction time. Clear maximum of swelling is seen at the ratio of 5:1 for 48 h of remote interaction.

Comparing the values of conductivity, pH and swelling coefficient, it can be concluded that as in the result of mutual activation hydrogels are transferred into highly-ionized state. The highest ionization of gP4VP hydrogel occurs at the ratio of 5:1. In turn, gPAA swelling increases significantly when there is a predominance of polybasis in solution (ratio 1:5).

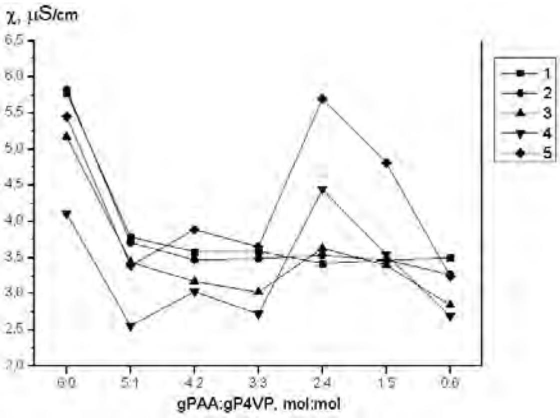

Fig. 1. Dependence of electric conductivity change of solutions of intergel system, which consists of gPAA and gP4VP dry hydrogels on hydrogels molar ratio in time: 0.0833 h (1); 1 h (2); 6 h (3); 24 h (4) and 48 h (5)

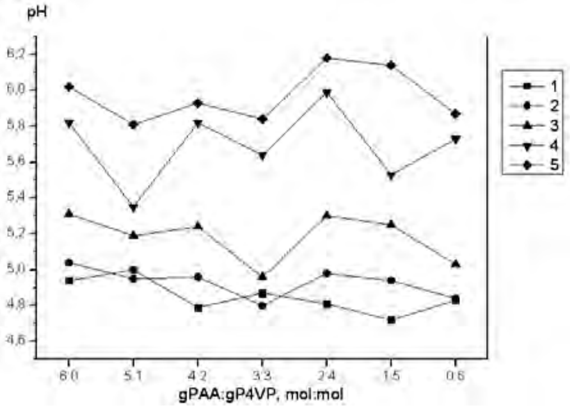

Fig. 2. Dependence of pH change of solutions of intergel system consisting of gPAA and gP4VP dry hydrogels on hydrogels molar ratio in time: 0.0833 h (1); 1 h (2); 6 h (3); 24 h (4) and 48 h (5)

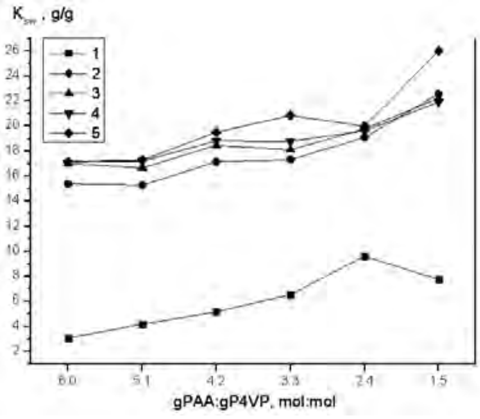

Fig. 3. Dependence of polyacrylic acid hydrogel swelling coefficient on gPAA:gP4VP hydrogels molar ratios in time at macromolecules dry initial state: 0.0833 h (1); 1 h (2); 6 h (3); 24 h (4) and 48 h (5)

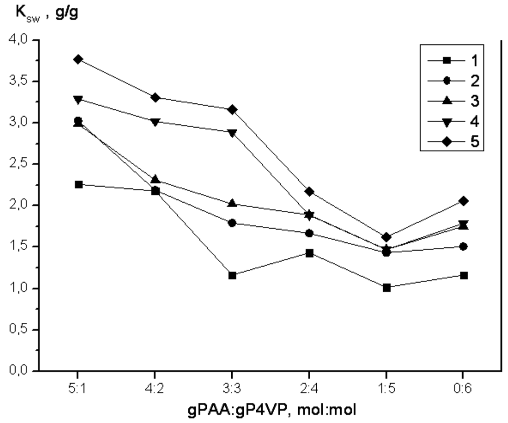

Fig. 4. Dependence of poly-4-vinylpyridine hydrogel swelling coefficient on gPAA:gP4VP hydrogels molar ratios in time at macromolecules dry initial state: 0.0833 h (1); 1 h (2); 6 h (3); 24 h (4) and 48 h (5)

3.2. Study of Properties of gPAA:gP4VP Intergel System Consisting of Swollen Hydrogels

To study the influence of initial state on physical-chemical properties, properties of intergel system consisting of swollen hydrogels were studied. Obtained experimental data showed that electrochemical and volume–gravimetric properties of intergel system are under great influence of initial conformational state of polymer networks. In contrast to intergel system consisting of dry hydrogels, in the case with swollen hydrogels there is a decrease of electric conductivity of solutions with remote interaction time increase (Fig. 5). The difference is that minimum conductivity occurs when there is only polybasis in system (ratio 0:6) for 24 h interaction. However, maximums are seen at hydrogel ratios 1:5 and 6:0 (presence of only polyacrylic acid) at time of remote interaction 5 min and 48 h, respectively. But maximums are seen at the ratios of gPAA:gP4VP=5:1 and 1:5 for 48 h of remote interaction. Comparing values of intergel system solutions electric conductivity, which are formed from dry and swollen hydrogels, it can be seen that conductivity values in case with swollen hydrogels are 1.3–1.5 times lower than in case with dry hydrogels.

Minimum pH values are observed in initial moment of time (Fig. 6). Moreover, strong minimum is observed in the presence of only poliobasis (ratio 0:6). Further a gradual increase of pH with time occurs for all ratios. Maximums at gPAA:gP4VP ratios 3:3 and 1:5 for 24 h of remote interaction are strongly pronounced, conductivity decreases with time for all hydrogels ratios. The sharp pH increase at the ratios 3:3 and 1:5 indicates that proton association by basic hydrogel completely predominates over carboxyl groups dissociation.

Swelling of polyacrylic acid hydrogel in swollen hydrogels intergel system occurs similarly to polyacid swelling in case with dry hydrogels. This is evidenced by the fact that there is a sharp swelling increase since hydrogels ratio 3:3 with increase of polybasis share. This phenomena indicates that there is a predominance of proton association process by nitrogen heteroatom over carboxyl group dissociation process, which, in turn, provides conformational changes of macromolecule structure, and, as a consequence, additional swelling. Minimum area of swelling is observed when there is only polyacid in solution (ratio 6:0) at initial moment of time. Maximum swelling of polyacid occurs at hydrogels ratio 1:5 for 48 h of remote interaction.

Swelling of poly-4-vinylpyridine hydrogel (Fig. 8) occurs not as intensive as in case of polyacid. This indicates to the fact that ionization degree of vinylpyridines links is quite small. Minimum swelling occurs at the ratio of of gPAA:gP4VP=1:5 for 24 h of interaction. A clear maximum appears at hydrogels ratio 5:1 at initial moment of time. It should be noted that values of K_{sw} are higher than values in case with dry hydrogels. Sharp change of gP4VP swelling indicates formation of intramolecular crosslinks of ≡NH…N≡ or ≡NH^{+}…N≡ type, which are stabilized by hydrophobic fragments of vinylpyridine.

Analyzing the dependence of electric conductivity, pH, and swelling coefficient of swollen hydrogels it can be concluded that highly-ionized state of gPAA is observed at hydrogels ratios 2:4 and 1:5, and for gP4VP – at the ratios of 5:1 and 2:4. It should be noted that it is confirmed by the hydrogels swelling increase, which is the evidence of additional activation of its links. High values of electric conductivity in this case, as in the case with dry hydrogels, show only that there is a predominance of charged groups. But it should be remembered that conformational properties of hydrogels are in direct dependence on links ionization of high molecular structures, but not on concentration of charged groups.

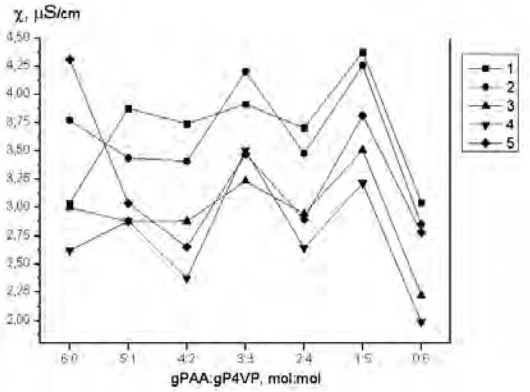

Fig. 5. Dependence of electric conductivity change of solutions of intergel system consisting of gPAA and gP4VP swollen hydrogels on hydrogels molar ratio in time: 0.0833 h (1); 1 h (2); 6 h (3); 24 h (4) and 48 h (5)

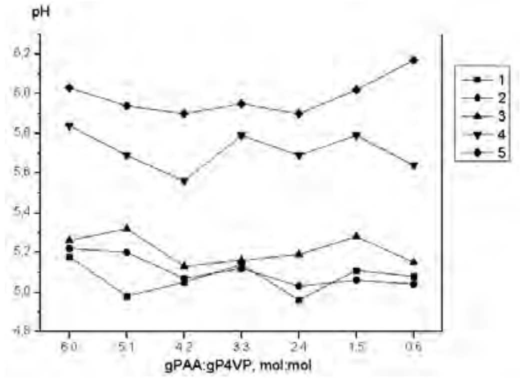

Fig. 6. Dependence of pH change of solutions of intergel system consisting of gPAA and gP4VP swollen hydrogels on hydrogels molar ratio in time: 0.0833 h (1); 1 h (2); 6 h (3); 24 h (4) and 48 h (5)

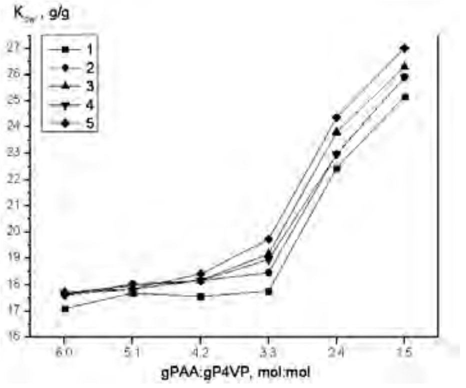

Fig. 7. Dependence of polyacrylic acid hydrogel swelling coefficient on gPAA:gP4VP hydrogels molar ratios in time at macromolecules swollen initial state: 0.0833 h (1); 1 h (2); 6 h (3); 24 h (4) and 48 h (5)

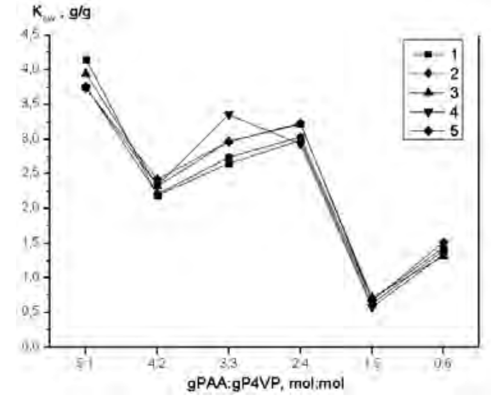

Fig. 8. Dependence of poly-4-vinylpyridine hydrogel swelling coefficient on gPAA:gP4VP hydrogels molar ratios in time at macromolecules swollen initial state: 0.0833 h (1); 1 h (2); 6 h (3); 24 h (4) and 48 h (5)

4. Conclusions

Obtained results allow to make the conclusion that initial state of hydrogels has a significant effect on electrochemical and properties of individual hydrogels and intergel systems on their basis. This is pointed by volume–gravimetric significant changes in electric conductivity, pH of medium and swelling coefficient of initial hydrogels depending on their aggregate state in intergel system.

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ВПЛИВ ПОЧАТКОВОГО СТАНУ ГІДРОГЕЛЮ НА ЕЛЕКТРОХІМІЧНІ ТА ОБ‘ЄМНО-ГРАВИМЕТРИЧНІ ВЛАСТИВОСТІ ГІДРОГЕЛІВ В ІНТЕРГЕЛЕВІЙ СИСТЕМІ ГЕЛЬ ПОЛІАКРИЛОВОЇ КИСЛОТИ І ГЕЛЬ ПОЛІ-4-ВІНІЛПІРИДИНУ

Анотація. *Досліджено електрохімічні властивості інтергелевої системи гідрогель поліакрилової кислоти (гПАК) – гель полі-4-вінілпиридину (гП4ВП) та конфірмаційні властивості вихідних гідрогелів в залежності від початкового стану гідрогелів. Області максимальної активації: для сухих гідрогелів – гПАК:гП4ВП = 5:1 і 1:5, для набухлих – 5:1, 2:4 и 1:5.*

Ключові слова: *інтергелева система, дистанційна взаємодія, початковий стан.*