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INFLUENCE OF INITIAL STATE OF HYDROGELS ON SELF-ORGANIZATION OF POLYMER NETWORKS OF POLYMETHACRYLIC ACID AND POLY-4-VINYLPYRIDINE AT THEIR REMOTE INTERACTION IN AN AQUEOUS MEDIUM

Abstract. Process of mutual activation of hydrogels of polymethacrylic acid (PMAA) and poly-4-vinylpyridine (P4VP) in intergel system on their basis is studied. Effect of dry initial state of hydrogels on their remote interaction, mutual activation and self-organization is studied by methods of conductometry, pH-metry, gravimetry. It is found that self-organization of macromolecules provides transfer of hydrogel of PMAA into highly ionized state in intergel system at gPMAA:gP4VP=1:5 ratio, and hydrogel of P4VP – at gPMAA:gP4VP=5:1 ratio of polymer hydrogels. Low values of swelling degree of gP4VP at gPMAA:gP4VP=1:5 ratio are due to formation of intermolecular cross-links leading to folding of macromolecular globe.

Keywords: intergel system, mutual activation, self-organization, initial state, hydrogels, polymethacrylic acid, poly-4-vinyl-pyridine.

In previous studies [1-6] it was found that remote interaction of rare-cross-linked polymer hydrogels has significant impact on their electrochemical and volume-gravimetric properties. Overwhelming majority of hydrogels are polyelectrolytes [7]. Conformational behavior of polyelectrolytes is influenced mainly by ionization degree of macromolecular globes [8-11]. In intergel systems ionization degree and conformational state of each hydrogel is significantly determined by concentration of another hydrogel. High sorption degree of polymers in intergel systems is due to absence of counter ions at ionized groups. This is consequence of intergel interactions, result of which is mutual activation of hydrogels and formation of uncompensated charges along polymer chain. Uncompensated charge is formed due to cleavage of proton from carboxyl groups during dissociation of acid hydrogel and binding of this ion with heteroatom of polybasis in an aqueous medium. Wherein charge density of basic hydrogels in limited by dissociation degree of acid hydrogel. Subsequently both hydrogels are ionized and do not have counter ions at major part of functional groups. Formation of ionized groups is caused by conformational changes of internode links of polymer chains due to what unfolding of macromolecular globe takes place. In this regard, the goal of the work is to study impact of dry initial state of polymer hydrogels of PMAA and P4VP on electrochemical and volume-gravimetric properties of intergel system gPMAA-gP4VP.

Experimental part

Equipment. For measurement of specific electric conductivity conductometer MARK 603 (Russia) was used, pH of solutions was measured on pH-meter Metrohm 827 pH-Lab (Switzerland). Mass of swollen samples of hydrogels for further calculation of swelling degree (α) was measured by weighing on electronic analytical scales SHIMADZU AY220 (Japan).

Materials. Investigations was carried out in distillated water. 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 made 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. After that, parameters (electric conductivity, pH and mass of samples) were measured. Measurement of electric conductivity and pH was made in absence of hydrogels in an aqueous medium. Swelling degree was calculated by the equation

$$\alpha = \frac{m_2 - m_1}{m_1}$$

where m_1 – mass of dry hydrogel, g, m_2 – mass of swollen hydrogel, g.

Results and discussion

In process of hydrogels remote interaction in intergel system hPMAA-hP4VP there are chages in specific electric conductivity of water solutions. Dependence of electric conductivity from time is presented on figure 1. As seen from data, increase of electric conductivity occur at hPMAA:hP4VP=3:3 ratio during all time of remote interaction. Maximum values of electric conductivity are observed at 48 hours. Minimum values of conductivity are reached in presence of only polybasis (ratio hPMAA:hP4VP=0:6), what is due to it's ionization in result of proton association, which were formed at water molecules dissociation.

For more clear description of low and high values of electric conductivity, it is necessary to consider processes of ionization and dissociation of hydrogels. In process of carboxyl group dissociation there is a formation of proton, further binding of which is occurred by nitrogen atom of vinylpyridine. This is the main cause of low values of conductivity. It should be noted, that high values of electric conductivity (ex. Ratio hPMAA:hP4VP=3:3) point to the fact that in result of

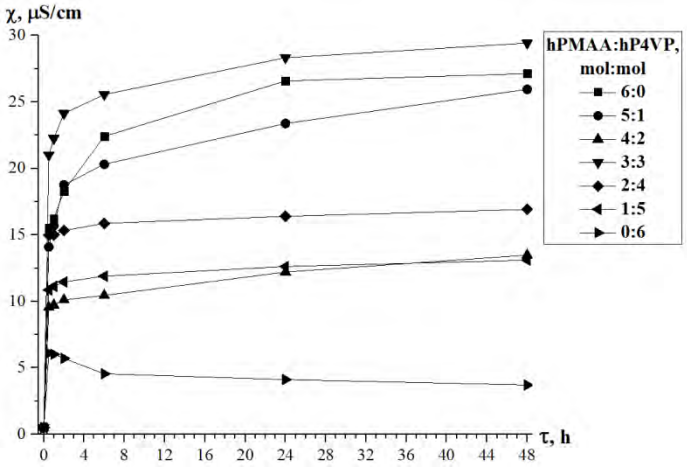

Figure 1 – Dependence of electric conductivity of aqueous solutions from time in presence of intergel system hPMAA-hP4VP

self-organization carboxyl groups dissociation process prevails over protons association by polybasis heteroatom. High conductivity values cannot point to high degree of mutual activation.

Dependence of hydrogen ions concentration from time is shown on figure 2. As seen from figure, increase of hydrogen ions concentration occur at ratio hPMAA:hP4VP=3:3. Comparison of this data with values of electric conductivity allows to conclude that carboxyl groups dissociation process prevails over protons association by vinylpyridine at this ratio.

As seen from figure 2, significant decrease of H^+ ions concentration occurs at hPMAA:hP4VP=1:5 during 6 hours of hydrogels remote interaction. In case with specific electric conductivity at this ratio it is seen, that values of electric

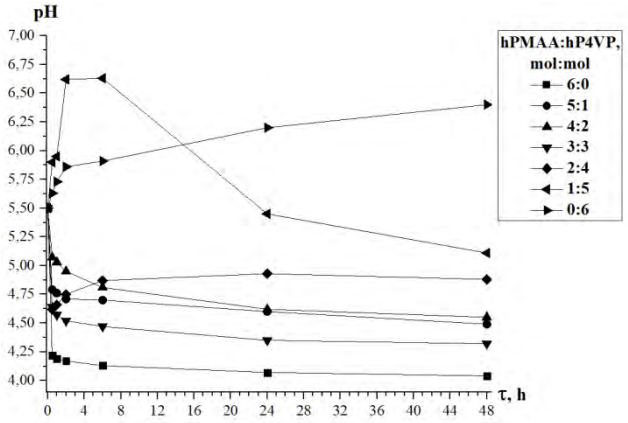

Figure 2 – Dependence of pH of aqueous solutions from time in presence of intergel system hPMAA-hP4VP

conductivity is not very high. Result of such interactions is formation of similarly charged groups without counter ions. And as consequence – transfer of acid and basic hydrogels into high ionized state. Maximum amount of protons is released in presence of polyacid (ratio hPMAA:hP4VP=6:0), what is directly connected with COOH-groups dissociation.

Appearance of H^+ ions excess is due to high swelling rate and COOH-groups dissociation, and not sufficient swelling rate of basic groups and their low concentration. Increase of OH^- concentration in an aqueous medium is due to low swelling rate and low concentration of COOH-groups, and high swelling rate and interaction of basic functional groups with H^+ ions.

Dependence of swelling degree of acid hydrogel of polymethacrylic acid in intergel system hPMAA-hP4VP from time is presented on figure 3. Increase of polyacid swelling degree occurs gradually with time. Wherein it should be noted that increase of α occurs with increase of polybasis concentration in solution. Minimum swelling occurs in presence of only polyacid in solution (ratio hPMAA:hP4VP=6:0), what is due to absence of phenomenon of mutual activation of polymer structures. As seen from obtained data, maximum swelling of poly-methacrylic acid hydrogel occurs at hPMAA:hP4VP=1:5 ratio at 48 hours of hydrogels remote interaction. Also there is strong increase at hydrogels ratio equal 2:4. Such swelling increase is due to predominance of proton association process over carboxyl groups dissociation. Result of this phenomenon is transfer of acid hydrogel into highly ionized state. Not sufficiently full ionization of the hydrogels occurs at ratios of hPMAA:hP4VP=5:1, 4:2 and 3:3 what is indicated by not significant increase of swelling degree values.

Figure 4 shows dependence of swelling degree of basic hydrogel of poly-4-vinylpyridine in intergel system hPMAA-hP4VP from time. Low values of α are

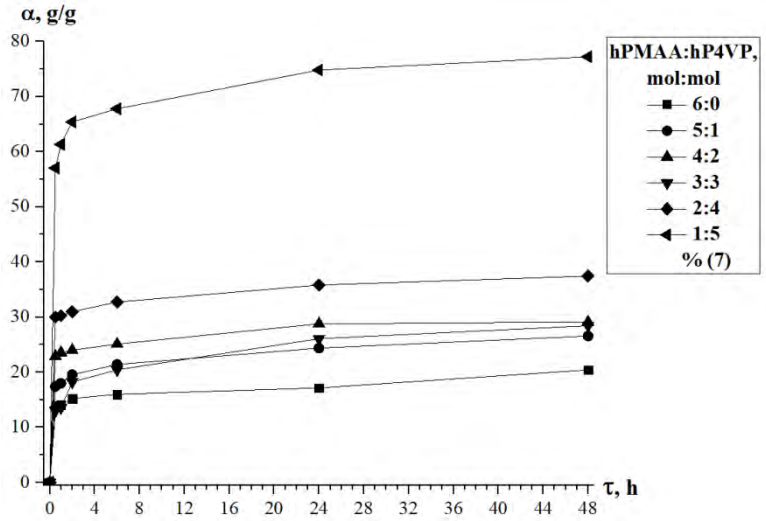

Figure 3 – Dependence of hPMAA swelling degree from time in presence of hP4VP

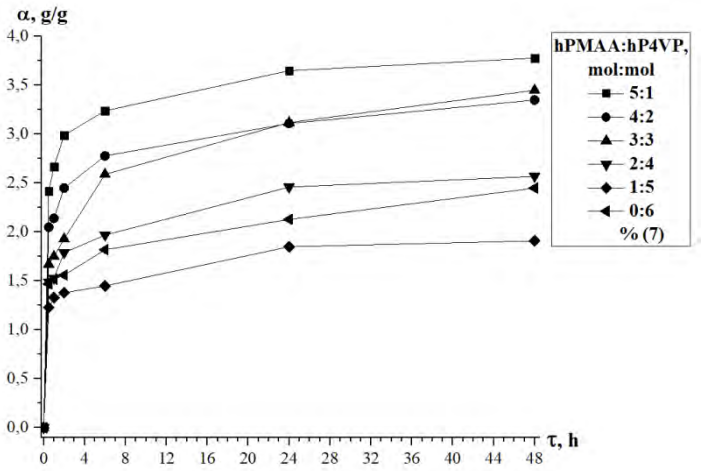

Figure 4 – Dependence of hP4VP swelling degree from time in presence of hPMAA

observed at hPMAA:hP4VP=0:6 ratio (individual hP4VP), what is caused by not very high ionization rate of individual basic hydrogel.

It should be noted that low swelling of polybasis occurs at hPMAA:hP4VP=1:5 ratio. This is due to formation of ≥N...H^+ …N≡ intermolecular cross-links, result of what is folding of polymer globe and swelling decrease. With increase of polyacid share swelling degree of polybasis increases in result of high ionization rate at mutual activation of both macromolecules. Area of maximum swelling is hPMAA:hP4VP=5:1 ratio, wherein maximum values of α are observed at 48 hours.

As seen from obtained data, self-organization of polymer networks of PMAA and P4VP mainly depends from ionization degree of macromolecules.

Conclusion.

1. Obtained experimental data on specific electric conductivity and pH of solutions and swelling degree of PMAA and P4VP hydrogels allow to conclude that mutual activation of polymer structures of acid and basic nature has significant influence on their electrochemical and conformational properties.

2. Significant increase of values of specific electric conductivity, concentration of hydrogen ions and swelling degree is directly connected with self-organization of polymer hydrogels of acid and basic nature at their mutual activation in intergel pairs.

3. Obtained results on specific electric conductivity, pH and swelling degree point to the fact, that high ionized state of hPMAA is observed at hPMAA:hP4VP=1:5 ratio, and hP4VP – at hPMAA:hP4VP=5:1 ratio.

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Резюме

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СПОРТТЫҢ САҚТАНДЫРУ ШАРУАШЫЛЫҒЫНДА ҚОЛДАНЫЛАТЫН ПОЛИМЕТАКЛИКАЛЫҚ ЖӘНЕ ПОЛИ-4-ВИНИЛ ПИРИДИНІ ПОЛИМЕР ЖЕЛІСІНІҢ ӨЗІ-ҰЙЫМДАСТЫРУҒА АРНАЛҒАН ГИДРОГЕЛЬДІҢ НЕГІЗГІ МЕМЛЕКЕТТІЛІГІН ҚАТЫСУЫ

Полиметакрил қышқылы (гПМАҚ) және поли-4-винилпиридин (гП4ВП) гидрогелдерінің интергелді жүйедегі өзара активтену процесі зерттелді. Кондуктометрия, pH-метрия және гравиметрия әдістерімен гидрогелдердің бастапқы құрғақ күйінің олардың қашықтан өзара әрекеттесуіне, өзара активтенуіне және су ортасында өзін-өзі ұйымдастыруына әсері зерттелді. Макромолекулалардың өзін-өзі ұйымдастыруына байланысты интергелді жүйеде ПМАҚ гидрогелі ПМАҚг: П4ВПг=1:5 қатынасында, ал П4ВП гидрогелі полимерлік гидрогелдердің 5:1 қатынасында жоғары ионизацияланған күйге өтетіні анықталды. Макромолекулярлы шумақтардың жиналуына әкелетін молекулаішілік тігілу өзгерісіне байланысты ПМАҚг: П4ВПг=1:5 қатынасында П4ВП гидрогелінің ісіну дәрежесі төмен болатыны белгілі блды.

Түйін сөздер: интергелді жүйе, өзара активтену, өзін-өзі ұйымдастыру, бастақы күй, гидрогелдер, полиметакрил қышқылы, поли-4-винилпиридин.

Резюме

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ВЛИЯНИЕ НАЧАЛЬНОГО СОСТОЯНИЯ ГИДРОГЕЛЕЙ НА САМООРГАНИЗАЦИЮ ПОЛИМЕРНЫХ СЕТЕЙ ПОЛИМЕТАКРИЛОВЫХ КИСЛОТ И ПОЛИ-4-ВИНИЛПИРИДИНА ПРИ ИХ ДИСТАНЦИОННОМ ВЗАИМОДЕЙСТВИИ В ВОДНОЙ СРЕДЕ

Исследован процесс взаимной активации гидрогелей полиметакриловой кислоты (гПМАК) и поли-4-винилпиридина (гП4ВП) в интергелевой системе на их основе. Методами кондуктометрии, pH-метрии, гравиметрии исследовано влияние сухого исходного состояния гидрогелей на их дистанционное взаимодействие, взаимную активацию, самоорганизацию в водной среде. Установлено, что гидрогель ПМАК переходит в высокоионизованное состояние в интергелевой системе при соотношении гПМАК:гП4ВП=1:5, а гидрогель П4ВП – при соотношении полимерных гидрогелей, равном 5:1, вследствие самоорганизации макромолекул. Низкие значения степени набухания гП4ВП при соотношении гПМАК:гП4ВП=1:5 связаны с образованием внутримолекулярных сшивок, приводящих к сворачиванию макромолекулярного клубка.

Ключевые слова: интергелевая система, взаимная активация, самоорганизация, исходное состояние, гидрогели, полиметакриловая кислота, поли-4-винилпиридин.