

Features of Electrochemical and Conformational Behavior of Intergel System Based on Polyacrylic Acid and Poly-4-Vinylpyridine Hydrogels in an Aqueous Medium

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Received: June 17, 2014 / Accepted: June 23,, 2014 / Published: June 25, 2014.

Abstract: The goal of work is study of polyacrylic acid hydrogel (gPAA) and poly-4-vinylpyridine hydrogel (gP4VP) remote interaction influence on their electrochemical and conformational properties. The dependences of the swelling coefficient, conductivity and pH of intergel systems aqueous solutions with different ratios polyacid:polybasis from times are considered. It is established that maximum conductivity is observed at ratios of gPAA:gP4VP 5:1, 3:3 and 1:5, while minimum conductivity is observed at ratios 4:2 and 2:4. Increasing of medium's pH is observed at ratio 1:5. Swelling coefficient of polyacrylic acid hydrogel increases monotonically with increase of poly-4-vinylpyridine share in an aqueous medium. In dependence of swelling coefficient from ratios polyacid:polybasis conformational transition region of poly-4-vinylpyridine is detected in area 3:3-1:5. The obtained results can be explained by remote interaction of polyacrylic acid hydrogel with poly-4-vinylpyridine hydrogel, during which mutual activation of hydrogels occurs due to proton transfer from polyacid to polybasis.

Key words: Polyacrylic acid, poly-4-vinylpyridine, intergel system, swelling, hydrogels.

1. Introduction

Earlier in the systematic study of interaction of hydrogels with various compounds it was found that hydrogels remote interact with each other, noticeably change electrochemical, volume and hydrodynamic properties [1-5]. Subsequently is established that high sorption of low-molecular salts by intergel system at certain molar ratios of hydrogels is observed [6-10]. The obtained results are explained by mutual activation of hydrogels, resulting in internodal links of individual hydrogels uncompensated charges appear. To check this assumption it is necessary to conduct investigation of interaction between two hydrogels in an aqueous medium without salt. In this regard, aim of this work is investigation of electrochemical and volume-gravimetric properties of intelgel system, consisting of rarelinked polyacrylic acid and poly-4-vinylpyridine.

2. Materials and Methods

For measurement of electroconductivity conductometer "MARK 603" (Russia) was used, pH of solutions was measured on pH meter "Seven Easy" (METTLER TOLEDO, China). Swelling coefficient K_{sw} was defined by weighting of hydrogel swollen samples on electronic scales "SHIMADZU AY220" (Japan).

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Studies were carried out in distillated water medium. Polyacrylic acid hydrogels were synthesized in the presence crosslinking N.Nof agent methylene-bis-acrylamide and redox system K₂S₂O₈, Na₂S₂O₃. Poly-4-vinylpyridine (gP4VP) hydrogel was synthesized by crosslinking of a linear polymer in a medium of dimethylformamide with epichlorohydrin at 60 °C. In solution of linear polymer added 2ml epichlorohydrin solution (t⁰ \approx 40-50 °C). After full mixing of components temperature lifted to 65 °C. The reaction mixture was stirred before formation of dense gel mass. Formed gel was transferred to distilled water, then was filtered, was milled and was washed with distilled water. The degree of purification controlled by conductometer.

Intergel pair consists of synthesized hydrogels in an aqueous medium polyacrylic acid gel and poly-4-vinylpyridine gel. Swelling coefficients of hydrogels were $K_{sw}(gPAA) = 10.1 \text{ g/g}$, $K_{sw}(gP4VP) = 0.86 \text{ g/g}$ Experiments were carried out at a room temperature. Study of intergel systems was made by this way: each hydrogel was located in separated glass filters pores of which are permeable for low-molecular ions and molecules, but it is not permeable for a dispersion hydrogels.

Then weighing bottles with hydrogels were located in glasses with distilled water. Electroconductivity and pH of overgel liquid was measured by taking out of glass filters with hydrogels from the glass. Swelling coefficient was calculated as the difference of weights of glass filters with hydrogel and empty glass filters according to this equation:

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

where, m_1 is weight of dry hydrogel, m_2 is weight of swollen hydrogel

3. Results and Discussion

Obtained dependences of the intergel system electrical conductivity at different molar ratios from time are presented in Fig. 1. The figure shows that electrical conductivity increases with time for all ratios gPAA:gP4VP. However, electrical conductivity change behavior for different ratio is different. With increasing contact time with an aqueous medium maximum and minimum conductivity regions are observed. At 20 min (1/3 h) minimum becomes noticeable at a ratios 4:2 and 2:4. At ratios 5:1, 3:3 and 1:5, maximum conductivity field appearance can be seen.

At the time of interaction with the aqueous medium 24 and 48 h dependencies character varies considerably. Maximum at a 5:1 ratio shifts to 4:2 at 24 h. Weak maximum at 2:4 becomes the strongest at 48 h.

Intergel system's minimum conductivity caused by binding of proton cleaved from the carboxyl group by nitrogen heteroatom of vinylpyridine. At the moment of immersion in aqueous medium, both hydrogels begin to swell as a result of interactions with water molecules. The carboxyl groups firstly ionize and then dissociate on -COO⁻ carboxylate anion and hydrogen ions H⁺.



Fig. 1 Dependence of specific electrical conductivity of intergel system polyacrylic acid gel: poly-4-vinylpyridine gel from their molar ratios.

Curves' description: (1) 0 h; (2) ¹/₃ h; (3) ²/₃ h; (4) 1 h; (5) 2 h; (6) 4 h; (7) 6 h; (8) 24 h; (9) 48 h.

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Thus, a mutual activation of macromolecules occurs. In other words both hydrogels transfer into more highly ionized state. In the process of dissociation in an aqueous medium proton ions appear. Cationic hydrogel of poly-4-vinylpyridine is ionized in the aqueous medium under hydrogen ions acceptance formed by carboxyl groups dissociation and water molecules into ions H^+ , OH⁻. During these interactions total content of positive charges in an aqueous medium decreases.

Due to the bulky sizes hydrogels with charged ions have no mobility in an aqueous medium.

High electrical conductivity values indicate that at two hydrogels of intergel system certain ratios carbonyl groups dissociation prevails over proton association process by nitrogen heteroatoms. This may be due to decrease of hydrogen ions association by nitrogen atoms of vinylpyridine. Cause of this may be conformational changes in the links of internode chains. At certain concentrations NH⁺ charged groups can form intramolecular crosslinks such as $\geq N...H^+...N\equiv$, which leads to folding of a polymer coil and a decrease in proton binding.

Fig. 2 shows the change in hydrogen ion concentration in an aqueous medium in presence of intergel system PAA gel and P4VP gel. Obtained results show that in the initial moment when the system is dominated polyacid (Fig. 2, curve 1) pH value of the solution is low. With increasing of polyvinylpyridine share pH of solution gradually increases, passing through a maximum at ratio gPAA:gP4VP = 1:5. Low concentrations of hydrogen and high electrical conductivity values observed for intergel system at ratios gPAA:gP4VP = 1:5 show that the growth of the electrical conductivity is due to increasing concentration of OH anions.

For a description of the obtained data equilibrium in solution must be analyzed the. In an aqueous medium the following processes occur:

(1) -COOH: groups of internodal links dissociate according to the scheme:

$$-\text{COOH}=\text{COO}^-\text{H}^+ \rightarrow \text{COO}^- + \text{H}^+$$

Firstly ionization with formation of ion pairs occurs, then ion pairs partially dissociate on individual ions.

(2) The atom of nitrogen in a pyridine ring is ionized and partially dissociates:

 $\equiv N + H_2 O \rightarrow \equiv NH^+ \dots OH^- \rightarrow \equiv NH^+ + OH^-$

(3) Further the atom of nitrogen also interacts with the proton, cleaved from carboxyl group:

$$\equiv N + H^+ \rightarrow \equiv NH^+$$

 H^+ and OH^- groups formed as a result of functional groups interaction with water molecules form water molecules.

$$H^+ + OH^- \rightarrow H_2O$$

The result of these interactions is the lack of counterions at some part of charged functional groups of hydrogels. Concentration of ionized groups without counterions depends from initial ratio of polymeric networks and other factors.

The appearance of hydroxyl ions high concentration is possible in case of interaction of vinylpyridine links with water molecules by mechanism described on reaction 2.

Concentration of ions in studied intergel systems is determined by swelling rate and concentration of hydrogels in an aqueous medium. Generally, the concentration of H^+ and OH^- ion is proportional to concentration of hydrogels and their swelling degree. The rate of swelling and deprotonization depends on hydrogel nature, degree of crosslinking, dispersion and longitudinal size of polymeric hydrogels.



Fig. 2 Dependences of intergel system polyacrylic acid gel: poly-4-vinylpyridine gel solutions pH from various time of remote interaction.

Curves' description: (1) 0 h; (2) ¹/₃ h; (3) ²/₃ h; (4) 1 h; (5) 2 h; (6) 4 h; (7) 6 h; (8) 24 h; (9) 48 h.

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The appearance of excess H^+ ions is caused by the high swelling rate, COOH groups dissociation, insufficient swelling rate of basic groups and their low concentration. Increasing of OH⁻ ions the content in an aqueous medium is due to low swelling rate, low concentration of COOH groups, high swelling rate and interaction between the main functional groups and H⁺ ions.

It is possible in case of second reaction's occurrence at which hydroxyl anions are allocated in solution, in parallel the third reaction also proceeds as a result the free proton binds to pyridine ring and concentration of positively charged ions in the solution decreases sharply.

Fig. 3 shows that as a result of polymeric hydrogels long-range effect polyacid swelling coefficient change is observed. On dependencies K_{sw} -ratio gPAA:gP4VP, we observe significant increase of polyacid swelling with increasing of gPAA molar content. These results indicate that at this ratio maximum density of charged groups appears along internode links of polyacid due to high ionization of acid groups providing unfolding of acid hydrogel polymer chains. K_{sw} also increases at a ratio of 2:4.

Fig. 4 represents the K_{sw} change of basic hydrogel poly-4-vinylpyridine in an aqueous medium in the presence of a polyacrylic acid hydrogel. With the increase of polyacid share additional swelling of gP4VP is observed. This indicates to additional activation of polybasis links. Due to the proximity of curves maximum and minimum points are difficult to detect. General appearance of the curves indicates an increase in K_{sw} of cationic hydrogel in presence of acid hydrogel. However, in a time interval of 20-120 min maximum appears, indicating to a significant increase in polybasis swelling. This effect is probably due to the destruction of hydrophobic intramolecular associates $\equiv NH^+...N \equiv$, formed with participation $\equiv NH$ groups.

As is known, poly-4-vinylpyridine gel slightly swells in an aqueous medium due to it is a weak polybasis. Increase of gP4VP swelling coefficient by



Fig. 3 Dependencies of polyacrylic acid hydrogel swelling coefficient in presence of poly-4-vinylpyridine hydrogel in an aqueous medium.

Curves' description: (1) 0 h; (2) ¹/₃ h; (3) ²/₃ h; (4) 1 h; (5) 2 h; (6) 4 h; (7) 6 h; (8) 24 h; (9) 48 h.



Fig. 4 Dependencies of poly-4-vinylpyridine hydrogel swelling coefficient in presence of polyacrylic acid hydrogel in an aqueous medium.

Curves' description: (1) 0 h; (2) ¹/₃ h; (3) ²/₃ h; (4) 1 h; (5) 2 h; (6) 4 h; (7) 6 h; (8) 24 h; (9) 48 h.

2.0 times indicates to a strong degree of vinylpyridine's links ionization. This may be due to hydration of vinylpyridines links in aqueous medium and binding of proton, cleaved from the carboxyl group of polyacid.

4. Conclusions

The obtained experimental data of specific electric conductivity, pH of solution and K_{sw} of hydrogels indicates that between polyacrylic acid and

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poly-2-methyl-5-vinylpyridine hydrogels remote interaction influencing physical-chemical properties of solution and initial polymer network occurs.

At the last ratios gPAA:gP4VP there are areas of abnormally high electric conductivity, indicating to a high concentration of charged ions At equimolar ratios of gPAA:gP4VP practically complete association of H^+ and OH⁻ ions between themselves and internodal links of hydrogels occurs.

In results of remote interaction additional hydrogel's activation consisting in the fact that the internodal chain acquires an additional charge without counterions occurs.

Remote interaction leads to conformational change of both hydrogels's internodal links which causes them to significant additional swelling.

At certain ratios of gPAA:gP4VP at P4VP hydrogel the formation area of the intramolecular associates, leading to folding of polymer networks is revealed.

References

- A.B. Talgatovna, K.Z. Kozhamberdikyzy, H. Huangul, K.R. Gennadievich, J.T. Kozhataevich, Features of polymethacrylic acid and poly-2-methyl-5-vinylpyridine hydrogels remote interaction in an aqueous medium, J. Chem. Chem. Eng. 8 (3) (2014) 265-269.
- [2] J.T. Kozhataevich, K.S. Sericovna, K.R. Gennadievich, E. Bakhytzhan, E. Barnagul, Mutual activation and high selectivity of polymeric structures in intergel systems, in:

Proceedings of symposium ICSP&AM3, Tbilysi, 2013, Nova Science Publishers, Inc. USA., 2014, pp. 191-196.

- [3] T.K. Jumadilov, Electrochemical and conformational behaviour of intergel systems based on the rare crosslinked polyacid and polyvynilpyrydines, in: 25th International Conference of Lithuanian Chemical Society "Chemistry and Chemical Technology" Proceedings of the International Conference, Kaunas, Lithuania, 2014, pp. 226-229.
- [4] B.T. Alimbekova, T.K. Jumadilov, Zh.K. Korganbayeva, B. Erzhan, B. Erzhet, Some features of polymer hydrogels interraction with low-molecular salts, Bulletin d'EUROTALENT-FIDJIP 5 (2013). 28-32.
- [5] B. Erzhet, T.K. Jumadilov, Zh.K. Korganbayeva, Electrochemical and volume–gravimetric properties of intergel system based on polyacrylic acid hydrogel and poly-4-vinylpyridine hydrogel, Bulletin d'EUROTALENT-FIDJIP. 5 (2013) 41-45.
- [6] T.K. Jumadilov, Effect of remote interaction of polymeric hydrogels in innovative technology, Industry of Kazakhstan 2 (2011) 70-72.
- [7] E.A. Bekturov, I.E. Suleimenov, Polymeric hydrogels, 1998, p. 133.
- [8] E.A. Bekturov, T.K. Jumadilov, New approaches to study of remote influence effect of hydrogels, News of National Academy of Sciences of Republic of Kazakhstan 1 (2009) 86-87.
- [9] E.A. Bekturov, T.K. Jumadilov, Zh.K. Korganbayeva, Remote effect in polymeric systems, Herald of Al-Farabi Kazakh National University, Chemical Series 3 (59) (2010) 108-110.
- [10] T. Jumadilov, D. Shaltykova, I. Suleimenov, Anomalous ion exchange phenomenon, in: Austrian-Slovenian Polymer Meeting, ASPM 2013, Slovenia, 2013, p. 51.