

Fig. 1. Effect of the pH of the medium on the size V/V_0 of polymer hydrogels based on β -VOEA AA copolymers with (1) MAA and (2) AA; $[\beta$ -VOEA AA] = (1) 13.2 and (2) 9.8 mol %.

of interest to study the properties of β -VOEA AA copolymers with unsaturated carboxylic acids.

In this study, the effect of external factors on the behavior of hydrogels based on copolymers of β -VOEA AA with AA and MAA is considered. Figure 1 illustrates the influence of the pH of the medium on the swelling capacity of hydrogels of β -VOEA AA copolymers with MAA and AA. The swelling of gels of PAA and PMAA depending on pH was studied by Filippova et al. [6]. A comparison of swelling curves shows that the gels can pass from the swollen state to the collapsed state in a narrower range of variation in pH (3.2–3.8) for the system under investigation. At the same time, the sorption capacity of the gel for water is lower, a fact that may be due to a high crosslinker content of the copolymers of β -VOEA AA with AA and MAA. At an approximately equal crosslinking-agent content, the gel of MAA copolymers exhibits a higher swelling capacity. A similar effect was observed by other researchers [7].

One of the most likely causes of this effect is a denser structure of the β -VOEA AA copolymer, in spite of a lower amount of crosslinker units in this polymer.

Recent decades have seen a rise of attention paid by researchers to the problem of interaction with low-molecular-mass compounds. Figure 2 presents plots of the swelling ratio for gel networks based on β -VOEA AA copolymers with AA and MAA of different molar compositions versus the logarithm of concentration of the added low-molecular-mass electrolyte NaCl. The pattern of the curves is characteristic of polyelectrolyte gels that have likely charged units and are classified with anionic networks in terms of composition.

The transition of gels from the swollen to the collapsed state is discrete in character; for copolymers containing MAA units, this process is observed at a

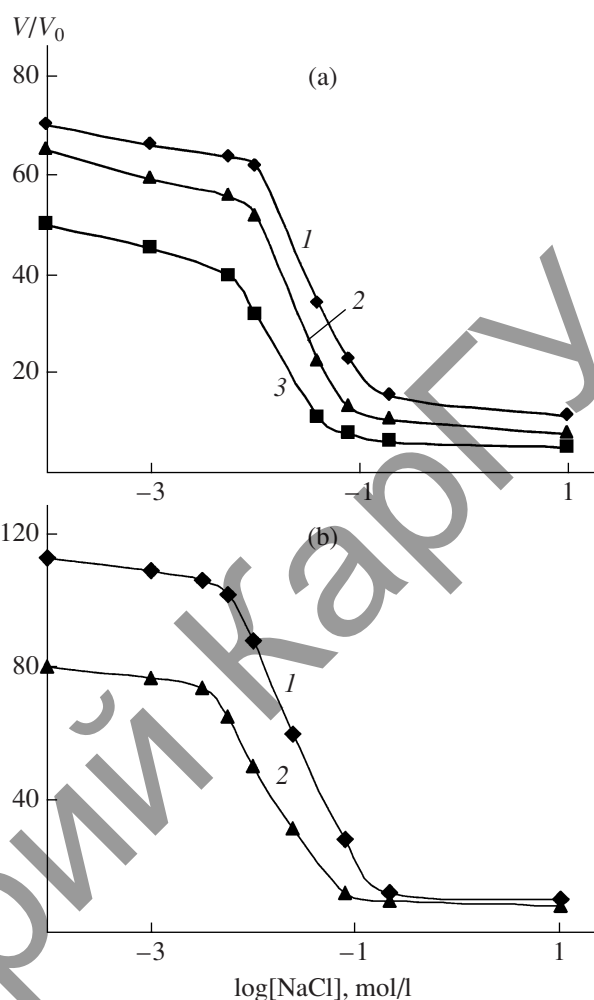


Fig. 2. Swelling of hydrogels based on copolymers of β -VOEA AA with (a) AA and (b) MAA depending on NaCl concentration. (a) $[\beta$ -VOEA AA] = (1) 7.1, (2) 9.8, and (3) 16.8 mol %; (b) $[\beta$ -VOEA AA] = (1) 13.2 and (2) 23.8 mol %.

lower concentration of the low-molecular-mass salt. An increase in the amount of carboxylic groups in the series of test substances enhances the sensitivity to the admixture of the low-molecular-mass salt, whereas an increase in the relative amount of β -VOEA AA units, which act as a crosslinking agent, results in a denser polymer network and, as a consequence, decreases the sorption capacity of the gel.

Numerous studies [8–10] concerning the effect of solvent quality on the behavior of gels demonstrate an important role of mixed solvents in the theory and practical application of hydrogels. It is well known that the presence of particular compounds initiates the volume-phase transitions in hydrogels accompanied by a sharp decrease in the specific volume of macromolecule. The presence of a poor solvent is a necessary condition for the onset of critical phenomena in the polymer network.

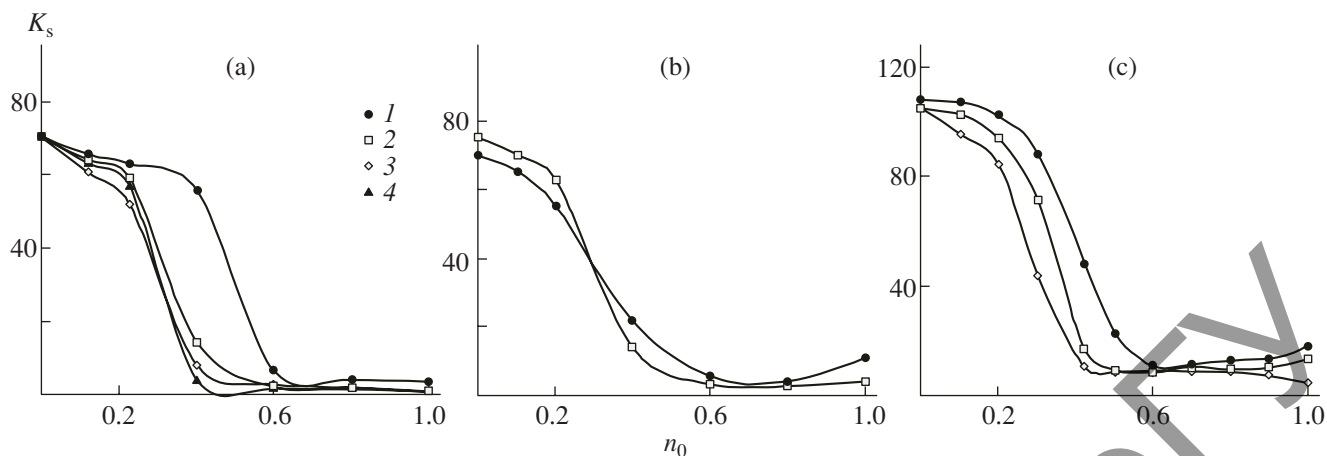


Fig. 3. Effect of the volume fraction of organic solvent n_0 on the swelling of hydrogels based on β -VOEA AA copolymers with (a, b) AA and (c) MAA; [β -VOEA AA] = (a, b) 9.8 and (c) 13.2 mol %: (a) (1) water–DMF, (2) water–DMSO, (3) water–dioxane, and (4) water–acetone; (b) (1) a dry sample, (2) the sample swollen in water and the DMF–water mixture; (c) (1) water–DMF, (2) water–ethanol, and (3) water–acetone.

The founder of the theory of such processes was Flory [11].

To add new data to the results of previous works on this subject matter, we studied the effect of composition of a binary solvent blend on the bulk characteristics of gels based on β -VOEA AA copolymers with AA and MAA. The following mixed solvents were chosen as model systems: water–ethanol, water–DMF, water–DMSO, water–acetone, and water–dioxane. The volume fraction of the precipitant in the blend was varied from 0 to 1.

The degree of swelling plotted versus the fraction of organic solvent n_0 (Fig. 3a) demonstrates the behavior typical of polymer networks with charged subchains. Notice that the nature of organic solvent has an effect on the pattern of the curves. The change of DMSO and DMF for acetone and dioxane shifts the transition from the swollen to the collapsed state toward lower organic-solvent concentrations, a development that is presumably due to a decrease in the permittivity of the precipitant.

In the above experiment, the solvent composition was characterized by the precipitant volume fraction calculated on the assumption of the additivity of volumes upon mixing. The solvents were replenished several times within 3–4 weeks to attain the equilibrium between the gel and the medium as in [7]. The performance of the experiment under these conditions was of interest from the practical standpoint. According to classical physical chemistry, the behavior of a polymer in solution will depend on its state before the immersion in the medium. When a dry polymer sample is placed in a mixed aqueous–organic solvent, the observed picture is somewhat different from that presented in Fig. 3a, when the swollen sample was placed into the mixed solvent. As can be seen from Fig. 3b,

when a dry polymer sample is introduced into a mixed aqueous–organic solvent, the hydrogel experiences contraction even at the minimum volume fraction of the organic solvent and the process is continuous in character. Filippova et al. [10] explained the differences in the swelling curves for gels in aqueous–organic mixtures at various initial states of gels in terms of the formation of nonequilibrium structures. Likewise, the differences in the behavior of the dry and swollen polymer samples can be attributed to polymer solvation in the gel. Thus, during swelling of polymers, a portion of the solvent is strongly retained by macromolecules in the form of solvation shell, thereby ensuring a relative stability of hydrogels toward an increase in the concentration of organic solvent up to a certain critical value.

When a dry polymer sample is placed in an aqueous–organic mixture, the copolymer swells to a considerably lesser extent than in water already at a volume fraction of the organic solvent above 0.2. It seems that the initial contraction of water-swollen samples requires a greater amount of the precipitant than the antagonistic action on the dry sample.

The hydrogel is collapsed to the least extent at an organic-solvent volume fraction of the order of 0.6. In the water–DMF blend at $n_0 > 0.6$, the degree of swelling of the β -VOEA AA copolymer is lower than in the individual solvents.

The deviation from the additivity of the action of mixed solvents can be explained in terms of the thermodynamic quality of solvent. For example if the interaction parameters of the components of the water and DMF pair are smaller than the solvent–polymer interaction parameters, the polymer is displaced from the solution, thus resulting in compaction of unfolded macrochains [11].

In continuation of this investigation, we studied the behavior of β -VOEA AA-MAA copolymers in aqueous-organic solvents. As can be seen from Fig. 3, the addition of organic solvents has an antagonistic effect on the water-swollen β -VOEA AA-MAA copolymer as well. On passing to organic solvents, the volume of hydrogels is reduced by more than a factor of 10. The sensitivity of hydrogels to the solvent quality shows an especially marked growth in the volume fraction range of 0.2–0.6, depending on the solvent nature.

The greater the values of the parameters that determine the polarity of solvents, the stronger the swelling of polymers in these solvents. The permittivity of solvents drops in the order H₂O-DMF-ethanol-acetone. The swelling capacity of polymers changes in the same order. The β -VOEA AA-MAA copolymer can absorb a significantly higher amount of both water and organic solvents relative to the copolymer with AA, a difference that is presumably due to a looser structure of the copolymer because of a lower degree of crosslinking. In addition, methacrylic acid has a higher affinity for organic medium than acrylic acid.

Thus, the nature and composition of comonomers and the amount of a crosslinking agent have a significant effect on the pH sensitivity of hydrogels, a factor that is important in the search for promising and efficient areas of practical application of the synthesized polymers. On the basis of the experimental data on the effect of concentration of inorganic salts and organic solvents, it may be concluded that the interaction of low-molecular-mass substrates with polymer networks

features a complex character and depends on external conditions.

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