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Swelling behavior of amphiphilic hydrogels of copolymers of the vinyl ether of ethylene glycol and vinyl isobutyl ether, and their interaction with cationic surfactant

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Abstract Amphiphilic hydrogels of copolymers of the vinyl ether of ethylene glycol and vinyl isobutyl ether were synthesized by γ-radiation-induced free radical polymerization. Hydrogels with certain copolymer compositions showed thermo-sensitive behavior in aqueous solutions. The swelling behavior of the hydrogels in cetylpyridinium bromide aqueous solution was studied. Increased swelling of the hydrogels was observed in the surfactant solutions. The increased swelling was more prominent for the hydrogels with a higher content of hydrophobic moiety in the copolymer composition, and with higher surfactant concentration. The reason for this phenomenon is discussed. Treatment of some hydrogels in the surfactant solutions resulted in higher swelling ability in distilled water with distinct thermo-induced contraction over a narrow temperature interval.

Keywords Vinyl ether · Hydrogel · Thermo-sensitive · Surfactant · Complex

Introduction

Some non-ionic amphiphilic polymers are able to self-associate in aqueous solutions and exhibit reversible phase transitions. Such behavior is related to the removal of hydrogen bonds between polymer and water molecules, and the presence of attractive hydrophobic interactions along the polymeric chains in response to changes in pH, temperature, light intensity, and other environmental factors. Although the nature of the hydrophobic interaction is not yet fully understood, it is widely used to explain the physicochemical behavior of many polymers.

Phase transitions of water-soluble amphiphilic polymers can be considered on a molecular scale as coil-globule conformational changes. In addition, as the environmental conditions promote hydrophobic association, individual globular macromolecules are organized into micelle-like structures to interact with each other. Polymers present at a lower concentration generally result in precipitation, while those at higher concentrations aggregate and interconnect into a network-like structure [1]. For cross-linked swollen polymer networks, the phenomenon of coil-globule conformational transition is usually expressed by a volume phase transition. In other words, when polymer-polymer interactions become preferable rather than polymer-solvent interactions, macromolecules accept a compacted globule conformation, and a hydrogel collapses, decreasing its volume, to exclude solvent [2].

Self-association can be caused by various external stimulations. Among all of the stimuli-sensitive polymers, those demonstrating temperature-dependent behavior have attracted great attention from both fundamental and practical points of view. In particular, thermo-sensitive polymers have been used to make sensors, actuators, controlled and targeted drug delivery systems [3], non-viral vectors for gene therapy [4], and preparation of cultured cell sheets [5]. In this paper, the term "thermo-sensitive polymers" means polymers containing both a hydrophilic part responsible for water solubility, and hydrophobic moieties providing hydrophobic interactions, in their structures. Thermo-sensitive polymers can change their solubility/volume in aqueous solutions significantly upon temperature changes between 0 °C and 100 °C at atmospheric pressure.

Poly(*N*-isopropylacrylamide) (poly(NIPAAm)) is a well-known representative of thermosensitive polymers. Its aqueous solutions show a lower critical solution temperature (LCST) at 32 °C, which does not depend on molecular weight [6]. Cross-linked poly(NIPAAm) exhibits a discontinuous volume phase transition behavior as temperature increases above the LCST.

The value of critical temperatures can be adjusted according to requirements by copolymerization with hydrophilic or hydrophobic comonomers. Therefore, introduction of hydrophilic or hydrophobic units into the poly(NIPAAm) structure leads to an increase or decrease in the LCST, respectively. With ionic comonomers in poly(NIPAAm)-based polymers, the copolymers exhibit pH-sensitivity in addition to their thermo-sensitivity [7, 8]. Except for poly(NIPAAm), there are other known thermo-sensitive polymers, such as *N*-vinylcaprolactam-based copolymers [9, 10], poly(vinyl methyl ether) [11], 2-hydroxyalkylacrylate-based copolymers, and other polymers [11, 12].

Another useful tool to modify thermo-sensitive properties of non-ionic polymers is to complex them with ionic surfactants through hydrophobic interactions. Normally this results in conversion of the non-ionic polymer into the ionic one bearing charged surfactant heads around its hydrophobic moieties. That enhances the polymer's solubility in aqueous environments, and this effect is more prominent with higher surfactant concentrations [2, 13]. The interaction efficiency between non-ionic polymer and ionic surfactant increases with the hydrophobicity of both of the reactants [13, 14]. Nevertheless, the driving forces for these polymer-surfactant interactions are not clearly understood. To investigate non-ionic polymer–ionic surfactant systems, the following polymers were used: poly(ethylene oxide) (PEO) [1, 15] and its hydrophobic modifications containing different numbers of methylene oxide units, such as poly(1,3,6,9-tetraoxacycloundecane), poly(1,3,6-trioxacyclooctane) and poly(1,3-dioxolane) [16] or PEO didodecyl ether [1], polyacrylamides hydrophobically modified with dihexylacrylamide [17], poly(*N*-vinylpyrrolidone) [18] and its thermally sensitive copolymer with *N*-vinylcaprolactam [14], ethyl (hydroxyethyl)cellulose [19], hydroxypropylcellulose [20], methyl cellulose [21], and poly(NIPAAm) microgel [2, 22, 23]. Interactions of these polymers with surfactants depend on the nature of the latter and temperature. Therefore, addition of sodium dodecyl sulfate (SDS), an anionic surfactant, to a thermo-sensitive poly(NIPAAm) microgel dispersion affects solubilization and swelling of the microgels, and subsequently increases the conformational transition temperature [2]. In contrast, in the presence of cationic surfactants (generally alkylammonium salts), the transition temperature decreases and no swelling is observed. For water-soluble non-ionic polymers such as PEO, the interaction with surfactants at room temperature, or changes in LCST usually do not occur. Recent studies, however, revealed the appearance of such interaction upon heating [16, 14]. This provides yet more evidence of the importance of hydrophobic "forces" involved in the interactions of amphiphilic non-ionic polymers with surfactants.

Therefore, one may consider the interactions of thermo-sensitive polymers with ionic surfactants as a promising method for controlling their stimuli-sensitive properties. In this paper, we have investigated the modification of the thermo-sensitive properties of non-ionic amphiphilic hydrogels based on the vinyl ether of ethylene glycol and vinyl isobutyl ether via interactions with the cationic surfactant *N*-cetylpyridinium bromide.

Experimental

Materials

The vinyl ether of ethylene glycol (VEEG), vinyl isobutyl ether (VIBE) and divinyl ether-like cross-linking agent were purchased from Alash Ltd., Kazakhstan. All of the monomers were purified by vacuum distillation under an argon atmosphere.*N*-cetylpyridinium bromide (CPB; Aldrich) was used as commercially obtained.

Synthesis of polymers

Vinyl ether monomers were mixed in a wide range of compositions and bubbled with argon for 30 min. Then the monomer mixtures were exposed to ^{60}Co gamma-radiation from the "MPX-γ-25M" device. The radiation dose was regulated by exposure time at the dose rate of 110 Mrad/s. The synthesis conditions are described elsewhere [24, 25, 26, 27]. Cross-linked copolymers were obtained using 4 mol% of cross-linker in the monomer mixtures, and the synthesized hydrogels were washed with isopropanol for two weeks before storing in distilled water.

Polymer characterization

The structure of the synthesized copolymer is presented in Fig. 1. The copolymer compositions were determined by elemental analysis on a PERKIN ELMER Series II CHNS Analyzer 2400. Swelling degree, α, was calculated as weight of water absorbed by 1 g of dry hydrogel at equilibrium.

Hydrogel-surfactant interaction

The hydrogel samples were kept in distilled water prior to interaction with surfactants. Disk-shaped samples of 0.50 ± 0.02 g were immersed into a surfactant solution (20 ml) of predefined concentration and the kinetics of the volume changes were examined. The volume of each hydrogel was calculated using the swelling ratio, V/V_0, where V means the volume of the gel at ambient conditions, and V_0 is its volume right after the synthesis. The sorption of the surfactant by the hydrogels was observed by a spectrophotometric method at a wavelength of 260 nm (UV-VIS spectrophotometer Shimadzu, Japan) under isothermal condition (25 °C). The extinction coefficient (ϵ) for $[\mathrm{CPB}] = 1 \times 10^{-3}$ mol/L at the selected wavelength was found to be 3850 L mol^{-1} cm^{-1}, as estimated by the follow equation: $A = \epsilon CL$, where A is absorbance, $C$is concentration (mol/L), and L is path length of the cell (cm).

The interaction between the polymer and the surfactant was considered to reach the equilibrium when V/V_0 and absorbance did not change further. Then the hydrogels were moved into distilled water at room temperature to remove excess surfactant molecules from the hydrogel surface, and the swelling ratio was observed with time.

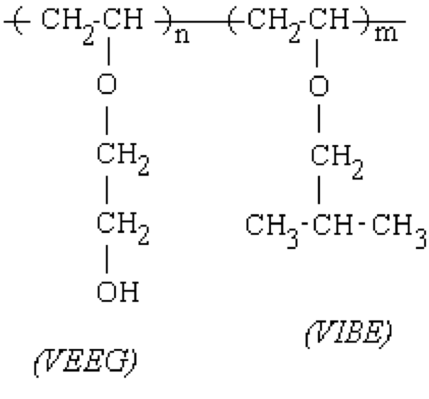

Fig. 1 Structure of VEEG-VIBE copolymer

Thermo-induced phase transition

The thermo-induced collapse phenomenon for the hydrogels was studied in water by monitoring the swelling ratio,V/V_0, of the hydrogels as a function of temperature. The temperature was gradually increased at 5 °C intervals, and the hydrogel samples were allowed to equilibrate for 30 min at each temperature.

Results and discussion

Hydrogel synthesis and characterization

In our previous studies [24, 25, 26], we synthesized water-soluble and water-swelling polymers based on the vinyl ether of ethylene glycol (VEEG) and vinyl butyl ether (VBE). Due to the presence of both hydrophilic (VEEG) and hydrophobic (VBE) units, those copolymers exhibited a lower critical solution temperature (LCST) or thermo-induced collapse behavior in water solutions. The value of LCST for the soluble copolymers was dependent on the copolymer composition, and it decreased as the VBE concentration increased. The hydrogel samples shrink dramatically in a quite narrow temperature range upon heating, due to hydrophobic interactions.

Recently, we have synthesized copolymers of VEEG with VBE's analogue – vinyl isobutyl ether (VIBE). Interestingly, this minor change in butyl radical structure from normal to isomeric resulted in a considerable increase in the extent of swelling and the critical temperatures for both soluble and swelling copolymers. This is expected to be due to less prominent hydrophobic properties of the isomeric butyl radical than the *n*-butyl moiety, as well as lower monomer activity of VIBE than VBE, as discussed in our previous paper [27].

In this work, we present our continuing investigation into the VEEG-VIBE thermo-sensitive hydrogels. We prepared several samples of VEEG-VIBE hydrogels under conditions described in Table 1. An unusual increase in the swelling degree of the hydrogels was observed with increasing hydrophobic component (VIBE) in the feed mixture, and consequently in the polymer network composition. As seen from Table 1a, an unusual increase of swelling degree in water was observed with the more hydrophobic hydrogel V3 than with hydrogels V1 and V2 that have less hydrophobic VIBE content. This was attributed to the differences in monomer activity of VEEG and VIBE, in analogy with data on the VEEG-VBE hydrogels [24, 26]. This can be explained by the decrease in cross-linking density of the hydrogel with increased concentration of less reactive VIBE in the reaction mixture [27]. The sample V4 was obtained at a higher radiation dose D: it is enriched with VIBE content and has a lower swelling degree than the sample V2 with the same monomer ratio, [VEEG]:[VIBE] = 80:20 mol%, in feed.

Table 1 Characterization of VEEG-VIBE copolymer hydrogels and their CPB absorption in water solutions

Sample	[VEEG]:[VIBE] (mol% in feed)	[VEEG]:[VIBE] (mol% in copolymer)	Synthesis conditions	Equilibrium swelling degree, α	Conditions of absorption	$Q(\times10^{-5}$ mol per 1 g dry gel)	$A(\times10^{-2}$ mol CPB per mol VIBE in copolymer)
V1	90:10	93:7	[CA] = 4 mol%;	29.7	$[CPB]_0 = 1\times10^{-3}$ mol/L;	1.90	2.35
V2	80:20	86:14	$D = 98$ kGy	35.1	$V = 20$ ml, $T = 25$ °C	5.24	3.44
V3	70:30	77:23		41.3		58.16	23.16
V4	80:20	81:19	[CA] = 4 mol%;	22.2	$[CPB]_0 = 5\times10^{-4}$ mol/L	4.05	1.92
			$D = 121$ kGy		$[CPB]_0 = 2.5\times10^{-4}$ mol/L	1.99	0.96
					$[CPB]_0 = 1\times10^{-4}$ mol/L	0.44	0.31

The copolymers VEEG-VIBE exhibit thermo-sensitivity in aqueous solutions. For those synthesized in this work, the swelling behavior as a function of temperature is presented in Fig. 2. For the samples V1 and V2 that are more hydrophilic but are cross-linked more densely, the contraction was not dramatic for a wide temperature range. The hydrophobic interactions in their macromolecules are not very cooperative and are weak due to a low content of the alkyl group. This means that a higher temperature is required to turn the macromolecules into a more collapsed state, where $V/V_0 = 1/2$. The difference in the swelling ratio V/V_0 at the lowest and the highest temperatures in the studied range for these samples is called "an amplitude of the contraction" here. It was significantly less than that for the sample V3. The sample V3 is characterized by the highest swelling degree and the highest content of the hydrophobic unit. That is why it exhibits such a distinct contraction with such high amplitude upon the temperature increase (Fig. 2, curve 3).

Interaction of the hydrogels with the surfactant

The interaction of non-ionic polymers containing hydrophobic moieties with ionic surfactants may increase the solubility of the polymers. Here, cationic cetylpyridinium bromide (CPB) was used as a surfactant.

To investigate the interactions between VEEG-VIBE hydrogels and the surfactant, the samples in the equilibrium-swollen state were transferred from water into CPB solutions at 25 °C. Their swelling behavior was examined using the swelling ratio, V/V_0. As seen from Fig. 3, the hydrogels swell more as the hydrophobic component of the polymer increases. An order of magnitude increase in the swelling ratio was observed for the most hydrophobic sample V3.

On transferring from water to the surfactant solution, the homopolymer poly(VEEG) shows only minor swelling ratio changes with time (data not shown). The difference in the homopolymer's and the copolymers' VEEG-VIBE behavior is due to the presence of hydrophobic isobutyl groups in the copolymer hydrogels, which are involved in the interaction with the ionic surfactant, and their absence in the homopolymer. The hydrophobic interaction appears to be a dominant driving force for the formation of complexes of these

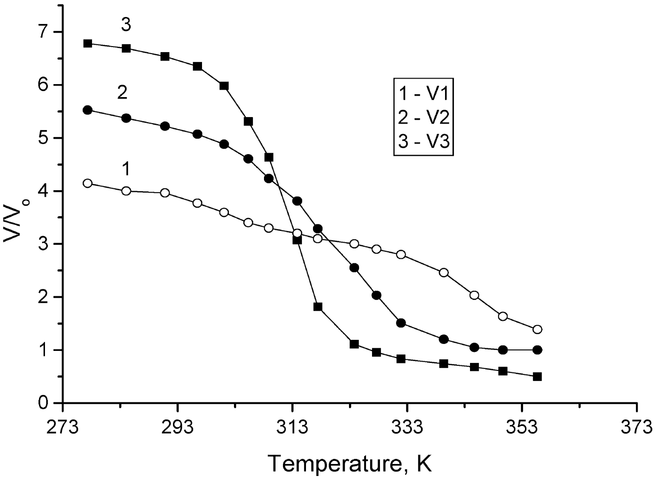

Fig. 2 Volume phase transition of VEEG-VIBE hydrogels with temperature. [VEEG]:[VIBE] (mol%): **1** 93:7; **2** 86:14; **3** 77:23

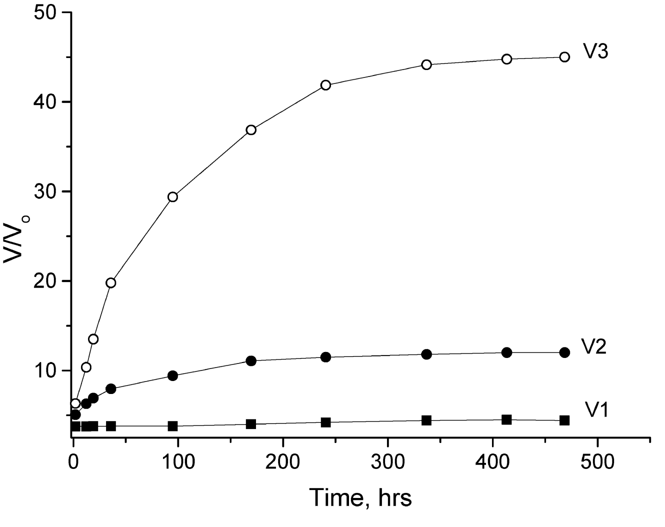

Fig. 3 Swelling of the VEEG-VIBE hydrogels in CPB solution. [VEEG]:[VIBE] (mol%): **1** 93:7; **2** 86:14; **3** 77:23. $[CPB] = 1\times10^{-3}$ mol/L

hydrogels with the surfactant. Generally, for a set of non-ionic VEEG-VIBE hydrogels with different compositions, the swelling extent in an ionic surfactant aqueous solution can be taken as an index of complex-forming ability of the hydrogels with ionic surfactants.

The amount of the surfactant absorbed by the hydrogels was calculated using data from UV-Vis spectrophotometry (Table 1, results for V1–V3). The molar quantity *Q* of the surfactant absorbed by the network was calculated with respect to 1 g of dry gel. The lowest value of *Q* was found for the V1 sample, the most hydrophilic hydrogel of VEEG-VIBE. The sample V2 absorbed almost three times more surfactant, and the higher order of magnitude was observed with the V3 samples. The value *A* in Table 1 describes the amount of the absorbed surfactant per 1 mol of VIBE in the copolymer, and a similar tendency was observed with the samples.

Figure 4 shows the influence of CPB concentration on the volume changes for the hydrogels. The rate and the amplitude of the hydrogel swelling in the surfactant solution were increased with the CPB concentration (Fig. 4). The swelling ratio growth is less significant at concentrations well below the critical micelle formation concentration (CMC) than at a concentration of $5{\times}10^{-4}$ mol/L which is closer to the CMC. This result is in accordance with the data obtained in [2], where the authors attributed their similar observation to the sorption data isotherm of poly(NIPAAm) microparticles and SDS. Indeed, as the hydrogels are immersed into CPB solutions with different concentration, the concentration of CPB in bulk solution decreases with time (Fig. 5). The data for CPB absorption as a function of its initial concentration are presented in Table 1, results for V4. The values *Q* and *A* increased when the absorption was carried out for more concentrated solutions. Interestingly, the sample V4, which is slightly more hydrophobic than V2, absorbed almost the same amount of CPB ($4.05{\times}10^{-5}$ mol per 1 g of dry gel) as the twice diluted solution ($5{\times}10^{-4}$ ml/L).

In Fig. 5, we use four curves to compare absorption of the surfactant within the hydrophilic poly(VEEG) network and the VEEG-VIBE copolymer hydrogels. The homopolymer also absorbed some amount of CPB, but this may simply be due to a physical diffusion rather than to any specific interaction, as in the case of the copolymers. However, there is no clear explanation of a precise mechanism of the interactions occurring between a non-ionic hydrogel and an ionic surfactant that can be found in the scientific literature at this moment. Most of the authors appeal to the hydrophobic interaction, while some of them suggest the possibility of independent surfactant aggregates composed of several molecules that interact with the polymers. A short review of the opinions on this topic are given in [2].

By comparing the data on the swelling parameter and the surfactant absorbance presented in Figs. 4 and 5, one can see that the active absorption of CPB by the hydrogels occurs during the first couple of hours, and any visible changes cease after 10 h (Fig. 4). Meanwhile, the swelling ratio, V/V_0, reaches the equilibrium state in approximately 4–5 days (Fig. 5). Presumably, at first the surface layers of the hydrogel absorb surfactant that forms a complex with the polymer network through

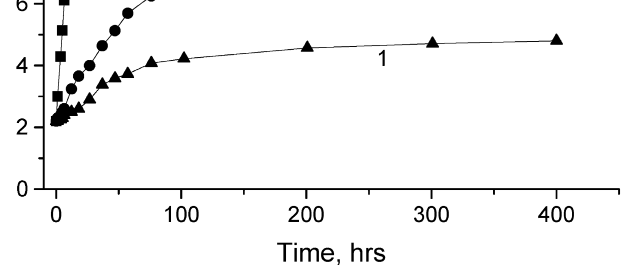

Fig. 4 The kinetics of swelling ratio changes of copolymers VEEG-VIBE in CPB solutions of different concentrations. [VEEG]:[VIBE] = 81:19 mol%; [CPB] ($\times10^{-4}$ mol/L): **1** 1.0; **2** 2.5; **3** 5.0

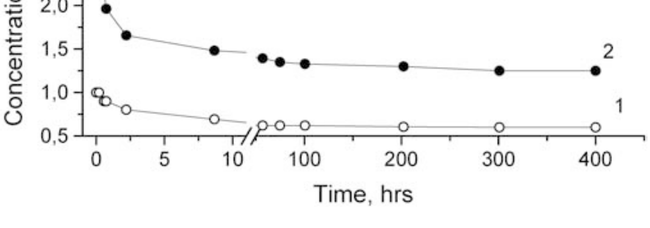

Fig. 5 Kinetics of CPB concentration change in the course of absorption by VEEG-VIBE (**1**, **2**, **3**) and poly(PVEEG) (**4**) hydrogels from concentrated surfactant solutions of various concentrations. [VEEG]:[VIBE] = 81:19 mol%. [CPB] ($\times10^{-4}$ mol/L): **1**,**4** 5.0; **2** 2.5; **3** 1.0. poly(VEEG) ($\alpha = 3.37$)

hydrophobic interactions between the hydrophobic surfactant tails and the radicals of hydrophobic isopropyl VIBE. Micelles of the absorbed surfactant form at sufficiently high concentration; it may also form a complex with the polymer network. On the one hand, this interaction results in the appearance of the charge on the nonionic VEEG-VIBE copolymer hydrogel and additional swelling due to the polyelectrolyte effect. This effect is illustrated in the scheme of the interaction between the polymer network and surfactant (Fig. 6a). But, on the other hand, such interaction leads to the formation of additional junctions, because the micelles act as additional cross-linking aggregates (Fig. 6b). We observed the additional swelling of hydrogels, which could be explained by the dominance of the first factor – the appearance of an ionic contribution in the total pressure of the polymer network swelling.

As the equilibrium state was reached, the samples were removed from the surfactant solutions and transferred into glass containers with distilled water. During this process, some contraction of the hydrogels was observed (data not shown). This may indicate a partial dissociation of the "gel-surfactant" complex. However, as time passed, the hydrogels swelled much more than their original size before the interaction with CPB.

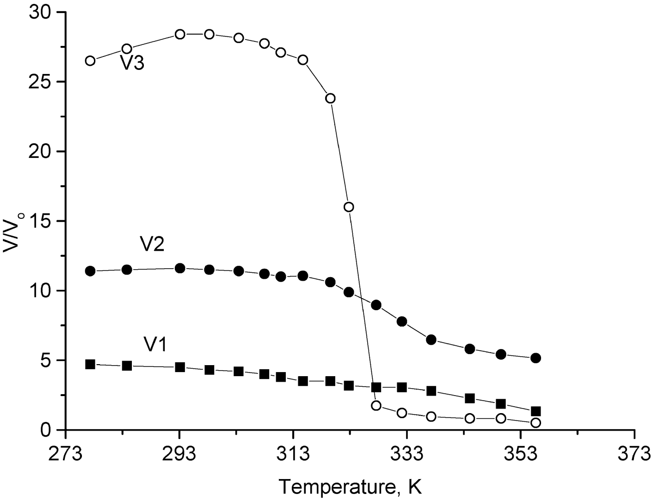

Fig. 7 Volume phase transition of VEEG-VIBE hydrogels with temperature after interaction with CBP. [VEEG]:[VIBE] (mol%): **V1** 93:7; **V2** 86:14; **V3** 77:23

The temperature-dependent swelling behavior of "VEEG-VIBE hydrogel-CPB" polycomplexes is shown in Fig. 7. The hydrogels contracted with an increase in temperature. Interestingly, for the less hydrophobic samples V1 and V2 there was no noticeable improvement in thermo-sensitivity: their contraction was not large, and the amplitude of the decrease in V/V_0 was about 3 and 6 units for V1 and V2, respectively. While

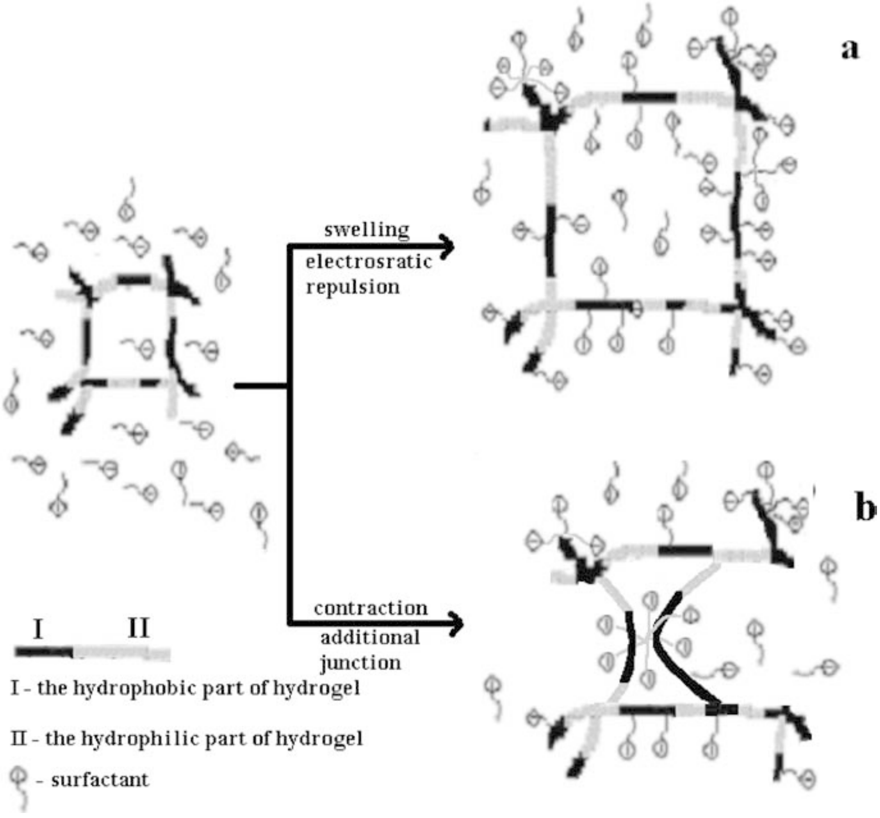

Fig. 6 Scheme for the interaction of the nonionic polymer network with the surfactant

the sample V3, with the highest content of the hydrophobic component, undergoes a significant collapse, with an amplitude of about 27 units of V/V_0, no changes were observed for the original parent hydrogels of any composition [24, 25, 26, 27]. The greatest value of the swelling ratio that we could achieve for VEEG-VIBE hydrogels in our laboratory did not exceed 12, even for very slightly cross-linked and therefore mechanically weak mucus-like samples. On the other hand, the hydrogels modified with CPB were quite elastic and demonstrated a V/V_0 of about 30 at room temperature.

Except for the noticeable increase in the amplitude and the narrowed temperature interval of the collapse transition, from 25 K for the V3 sample (from Fig. 2, curve 3) to about 10 K for the "V3CPB" complexed sample (from Fig. 7), about a 10 K shift to higher temperature of the onset of collapse should be noted. Obviously, the observed changes in the temperature interval, its narrowness, and the amplitude of the contraction are related to the increased solubilization and the simultaneously enhanced content of the hydrophobic species in the sample after modification by the surfactant.

The thermo-sensitive properties of the VEEG-VIBE hydrogels modified by complexing with the cationic surfactant CPB were much better than those of the initial hydrogels, and some samples showed very distinct thermo-induced collapse behavior.

Conclusions

The interactions of amphiphilic thermo-sensitive hydrogels based on VEEG-VIBE copolymers with the cationic surfactant cetylpyridinium bromide were investigated in aqueous solutions. The more hydrophobic hydrogels absorbed the surfactant more effectively because of hydrophobic interaction. A significant increase in swelling ratio was observed for all of the hydrogels, especially for those with a higher hydrophobic content in the molecular structure. Certain hydrogel samples showed considerable improvements in thermo-induced collapse behavior (higher amplitude and a narrower temperature interval of collapse). Enhanced solubilization with high hydrophobicity of the "gel-cationic surfactant" complexes is considered to be the reason for the observed phenomena.

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