

Interaction of Polyelectrolyte Gels and Surface Active Agents

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Abstract

Hydrogel polymers can absorb surface active agents from the water environment, which can be practically applied for their removal from waters polluted with detergents.

This investigation involved the interaction of maleic anhydride copolymers with vinyl ethers when subjected to crosslinking with various crosslinking agents, as well as cationic, anionic and non-ionic surfactants generated in Poland.

A very high absorption of cationic surfactant by the hydrogels has been found, which can be applied in the vicinity of plants using such surfactants, e.g. dairies.

Poly(vinyl) alcohol crosslinked with glutaraldehyde was used as hydrogel, too; it does not absorb cationic surfactants.

Keywords: hydrogels, surfactants, wastes

Introduction

Hydrogels are three-dimensionally crosslinked polymers capable of swelling in water. The first generation of hydrogels with swelling up to 40-50 % appeared in the late 1950s. Intensive development of hydrogels with ultra-high absorbing power began in the 1980s thanks to their expanding application.

The basic application potentials of the described polymers involves the production of sanitary goods used to absorb water solutions and physiological liquids (e.g. diapers of the "Pampers" type). A very important factor involving such applications is the fact that the polymers are not toxic. They are resistant to ultraviolet rays and microorganisms, and after they absorb liquid, they still seem to be dry.

Hydrogel polymers are used in medicine as surgical tampons and dressings. They can also be used in situations where it is necessary to stop the flow of water, e.g. in mining or civil engineering. In agriculture, through the sorption of fertilizing agents on supersorbents, the time of their operation in the soil can be prolonged [1].

It has been observed that polyelectrolyte gels can absorb a very large amount of water and undergo sharp volume transitions induced, for example, by small changes in pH, solvent quantity and temperature, or by the presence of salts.

This phenomenon is known as polymer network collapse. A similar effect has been observed for polyelectrolyte gels interacting with ionic surfactants. The interaction of the polyelectrolyte gel and the ionic surfactant can lead to the formation of unusual structures. This feature can be of pronounced practical interest, in particular for the purification of raw water from detergents.

There is a significant number of papers [2-6] dealing with gel-surfactant interactions, but only a few studies on the polymeric gels as absorbents of ionic surfactants.

The structure of the gel-surfactant complexes is believed to be due to a combination of hydrophobic and electrostatic interactions between the polyelectrolyte gel and the ionic surfactant.

Benjamin Chu and workers [7] reported the existence of highly ordered supramolecular structures in the complexes formed as a result of the interaction of cationic gels based

on poly- and copoly(diallyldimethylammonium chloride) and anionic sodium alkyl sulfate surfactant. These complexes exhibited nanostructures or ordering with a periodicity of approximately twice the surfactant molecule length.

Filippova et al. [8] studied the interaction of hydrophobically-modified poly(acrylic acid) gels in acid or salt form containing up to 20 mol% of n-alkyl acrylate units of different alkyl chain lengths. It was found that an uncharged modified poly(acrylic acid) gel absorbs anionic as well as cationic surfactants. An unmodified poly(acrylic acid) gel can absorb anionic surfactant - sodium dodecylbenzenesulfonate even below the critical micelle concentration. The swelling behaviour of the gel depends strongly on the charge sign of the absorbed surfactant ions.

A particularly interesting feature of the polymer and surfactant system is their interaction between copolymers of maleic acid - and surface active agents. These copolymers occur most often in 1:1 alternation with a comonomer in the polymer chain. Crosslinked copolymers of maleic anhydride (MA) prepared as an insoluble polyelectrolytes has been useful for removing organic impurities from waste water [9]. By carefully selecting comonomers one can design polymer chains with varying lipophilicity and polarity.

Based on these facts, the overall plan of the present investigation was to evaluate of crosslinked polyanionic copolymers of maleic acid as potential absorbers of surface active agents.

It would be very interesting to effect the absorbency of cation active surfactants in view of the protection of the natural environment in the area where the plants utilizing such surfactants are located, e.g. dairies or breweries. The introduction of wastes containing cation active surfactants to biological treatment plants would lead (due to their microbes-killing properties) to a negative influence on the bacteria in biofilters and activated sludge of the treatment plant.

In the present paper the investigation concentrated on the interaction of hydrogel polymers with cation active, anion active and non-ionic surfactants.

Experimental Procedure

Materials - Polymeric Matrixes

Copolymerization

Each polymerization was carried out in a glass tube in argon atmosphere.

Monomers mixture: ethyl vinyl ether (EtVE), isobutyl vinyl ether (isBVE) and maleic anhydride (MA) (molar ratio 1:1) were dissolved in dioxane with AIBN as an initiator and the solution was heated at 40°C for several hours. After termination of polymerization, the polymer was added to a large excess of ethanol. The crude polymer was purified by extraction in a Soxhlet apparatus with the same solvent.

The crosslinked structure of MA copolymers was prepared using the following procedure:

Ethyl vinyl ether - maleic anhydride (EtVE-MA), isobutyl vinyl ether - maleic anhydride (isBVE-MA) or vinyl acetate - maleic anhydride - isobutyl vinyl ether (VA-MA-isBVE), 10 g was dissolved in 100 ml of THF and 1,6-he-

xamethylenediamine (10% per anhydride group) in 50 ml THF was added. Then the reaction mixture was heated to boiling for 2 h, filtered off and dried [10].

The EtVE-MA-DMP copolymer (with molar ratio 0.8 : 1.0 : 0.1) is crosslinked with dimethallylidene-penterythritol (DMP) during copolymerization.

The structure of some crosslinked copolymers has been studied by high resolution ¹³C DD/CP/MAS/NMR [11].

Preparation of MA Hydrogels

Potassium hydroxide (0.95 to 6.5 g) was added to crosslinked MA copolymer (10 g) in aqueous suspension (100-300 ml). The mixture was stirred at room temperature for 24 h. Then, the resin was filtered off and washed (10 times, 100 ml of water) and dried.

Preparation of PAV Hydrogel

Polyvinyl alcohol (PVA) - 20 g was dissolved in 300 ml of water, 3.4 g of glutaraldehyde (50%) and 2.45 g of butyraldehyde and catalytic amount of p-toluenesulfonic acid, were added. The reaction mixture was allowed to stand for 24 h at room temperature. The hydrogel was washed with 5% NaHCO₃, washed extensively with distilled water and dried in vacuo.

Applied Surfactants

I. Cation active N-cetylpyridinium bromide - BR (Merck, 99%)

II. Anion active sodium dodecylbenzenesulfonate - DBS (Marlon A390, Hiils, powder, active detergent 90 ± 1%, sodium sulphate 7-9%, sodium chloride < 0.5%)

III. Non-ionic Rokafenol N8 (oxyethylated nonylphenol) - RF (Rokita SA in Brzeg Dolny, 99%)

Methods

50 ml of model surfactant solutions of considerable concentration were poured on 0.1 g of hydrogel and let for absorption over different time periods (45 min to 7 days). Every experiment was made separately, without mixing. Then the solution was filtered through the swelled hydrogel and the number of surfactant moles was determined in the filtrate. The absorption degree of surfactants by hydrogels was determined using UV spectrophotometry. The absorption degree of surfactants by hydrogels was also determined using UV spectrophotometry. The aqueous solutions of DBS, RF and BR of various, exactly known concentrations, were made. The samples were placed in a "Shimadzu" UV-2102PC spectrophotometer, connected with a computer, and their absorbances (by $\lambda = 224$ nm for DBS and RF, and $\lambda = 260$ nm for BR) were determined. Having concentration data and absorbances corresponding to them, analytical curves were made. The solutions of surfactants after absorption by hydrogels and after respective dilution were set up into the cuvette of spectrophotometer and computer based measurements of absorbance were made. Unknown concentrations of surfactants in filtrates were analyzed, based on analytical curves.

Results and Discussion

Our approach to the preparation of hydrogels as potential absorber of ionic or nonionic surfactants was to synthesize the alternating maleic anhydride copolymers with ethyl vinyl ether (EtVE-MA), isobutyl vinyl ether (isBVE-MA), vinyl acetate - isobutyl vinyl ether (VA-MA-isBVE) and ethyl vinyl ether - dimethylidene - pentaerythritol (EtVE-MA-DMP). The copolymers EtVE-MA, isBVE-MA and VA-MA-isBVE were crosslinked with 1,6-hexamethylenediamine.

In order to form the hydrogels the copolymers were subjected to hydrolysis of anhydride groups with potassium hydroxide.

The quantitative analysis of potassium ions in the polymeric matrix was developed by the flame photometric method [10]. It has been proved that K^+ ions cannot be eluted from the polymer matrix when the potassium salt of the copolymer is subjected to numerous washings. The treatment of copolymers using a deficiency of KOH (25%, 50% to a total content of anhydride groups in the crosslinked polymer) causes restricted hydrolysis, as proved by the low

Table 1. Absorbing power of N-cetylpyridinium bromide (BR) by polymers.

Polymer		Amount of BR moles in filtrate $\times 10^{-5}$							
		concentration 2 g/l 50 ml of solution contains 24.85×10^{-5} m BR			concentration 3 g/l 50 ml of solution contains 37.27×10^{-5} m BR			concentration 5 g/l 50 ml of solution contains 62.12×10^{-5} m BR	
		45 min	3 days	7 days	45 min	3 days	7 days	3 days	7 days
1	EtVE-MA (HMDA)	1.77	1.60	0.974	2.30	-	-	-	-
2	EtVE-MA (DMP)	0.001	0.001	0.000	0.242	0.148	0.149	2.92	1.42
3	isBVE-MA (HMDA)	1.56	0.912	0.385	7.93	4.24	2.03	36.2	33.2
4	VA-isBVE-MA (HMDA)	0.935	0.597	0.133	6.81	0.141	0.084	5.18	1.63
5	PAV (GA)	13.6	13.5	13.6	32.2	31.7	22.5	61.2	58.6

Table 2. Absorbing power of sodium dodecylbenzenesulfonate (DBS) by polymers.

Polymer		Amount of DBS moles in filtrate $\times 10^{-3}$					
		concentration 2 g/l 50 ml of solution contains 0.287×10^{-3} m DBS		concentration 3 g/l 50 ml of solution contains 0.430×10^{-3} m DBS			concentration 4.5 g/l 50 ml of solution contains 0.646×10^{-3} m DBS
		3 days	7 days	45 min	3 days	7 days	45 min
1	EtVE-MA (HMDA)	-	-	0.398	0.328	0.331	0.637
2	EtVE-MA (DMP)	0.275	0.246	0.419	0.404	0.201	0.635
3	isBVE-MA (HMDA)	0.238	0.233	0.429	0.429	0.397	0.633
4	VA-isBVE-MA (HMDA)	0.283	0.276	0.430	0.369	0.405	0.634
5	PAV (GA)	0.283	0.256	0.394	0.337	0.339	0.631

Table 3. Absorbing power of Rokafenol (RF) by polymers.

Polymer		Amount of RF moles in filtrate $\times 10^{-3}$					
		concentration 2 g/l 50 ml of solution contains 0.175×10^{-3} m RF			concentration 3 g/l 50 ml of solution contains 0.262×10^{-3} m RF		
		45 min	3 days	7 days	45 min	3 days	7 days
1	EtVE-MA (HMDA)	0.150	0.171	0.162	0.188	0.165	0.104
2	EtVE-MA (DMP)	0.170	0.174	0.139	0.155	0.137	0.138
3	isBVE-MA (HMDA)	0.164	0.167	0.090	0.189	0.134	0.059
4	VA-isBVE-MA (HMDA)	0.133	0.138	0.113	0.189	0.059	0.088
5	PAV (GA)	0.176	0.173	0.162	0.179	0.088	0.086

potassium contents in the analyzed samples (from 0.25 to 2.7%). It is preferable to use an excess of KOH in respect to the theoretically calculated anhydride groups. The potassium salts of polyions (7.0 to 10%) are stable and unreacted KOH can be easily removed from gel-form polymer by washing with water.

Dry samples of polymers were suspended in aqueous solutions of surfactants. The gel samples were left in these solutions for different time periods (from 45 min to 7 days) and then taken out. The degree of absorption of surfactants by hydrogels was determined by UV spectrophotometry.

The results of experimental data are shown in Tables 1-3.

Polyanions hydrogels based on the copolymers of maleic acid having a high carboxylate group absorb cationic surfactant (N-cetylpyridinium bromide) in some cases lowering its concentration in the filtrate almost to zero (Table 1, no. 2 - copolymer of maleic acid and ethyl vinyl ether crosslinked by dimethylolidene-pentaerythritol). It was shown that the anionic surfactant DBS does not bind to polyanionic network and poly(vinyl)alcohol (Table 2).

It should be noted that the absorption of Rokafenol from aqueous solutions onto poly(vinyl alcohol) crosslinked with glutaraldehyde has been observed at higher surfactant concentration and at prolonged time of interaction (Table 3, no. 5).

From the data presented here it can be concluded that the polyanions of maleic acid copolymers may probably be used effectively for removal of cation active surfactants from wastes. It can be of significance for the protection of the natural environment in the area where there are plants using such surfactants.

Further studies should be concentrated on the search of polymers of the cationic type which could be able to absorb the most commonly used anion active surfactants.

Opening investigations of multiple application and regeneration of crosslinked maleic anhydride copolymers showed the stability of polymeric matrixes. In the conditions of the conducted experiments the degradation of the polymers chain does not occur. The absorbing power of regenerated hydrogels and initial ones is similar.

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