

Adsorption of Surfactant by Hydrophobically Modified Poly[2-(diethylamino)ethylmethacrylate-co-N-vinyl-2-pyrrolidone/octadecyl acrylate] Hydrogels and Effect of Surfactant Adsorption on the Volume Phase Transition

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ABSTRACT: Hydrophobically modified poly[2-(diethylamino)ethylmethacrylate-co-N-vinyl-2-pyrrolidone/octadecyl acrylate] [P(DEAEMA-co-NVP/OA)] hydrogels were synthesized by free-radical crosslinking copolymerization of 2-(diethylamino)ethylmethacrylate (DEAEMA), N-vinyl-2-pyrrolidone (NVP) with different amounts of hydrophobic comonomer octadecyl acrylate (OA) in *tert*-butanol with ethylene glycole dimethacrylate (EGDMA) as a crosslinker. The swelling equilibrium of the hydrogels was investigated as a function of temperature and hydrophobic comonomer content in aqueous solutions of the anionic surfactant sodium dodecyl sulfate (SDS) and the cationic surfactant dodecyltrimethylammonium bromide (DTAB). The

results indicated that the swelling behavior and temperature sensitivity of the hydrogels were affected by the type and concentration of surfactant solutions. Additionally, the amount of the adsorbed SDS and DTAB molecules onto the hydrogels was determined by fluorescence measurements. An increase of OA content in the hydrogel caused an increase in the amount of adsorbed surfactant molecules in both media. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 103: 3771–3775, 2007

Key words: poly[2-(diethylamino)ethylmethacrylate-co-N-vinyl-2-pyrrolidone/octadecyl acrylate]; hydrophobically modified hydrogels; surfactant; adsorption

INTRODUCTION

The interaction of surfactants with hydrogels has been the subject of active research for many years. Early investigations were mainly concerned with the effect of synthetic detergents on natural proteins.^{1,2} These studies were motivated by observations of biological phenomena involving surfactants and proteins such as the inactivation of bacterial metabolism by synthetic detergents. There are several pieces of evidence that the ionic surfactant interacts with non-ionic hydrogel by hydrophobic bonding. Such interaction depends on the physicochemical properties of the hydrogel and surfactant as well as on the medium, in which they are swelled, and it increases with increasing hydrophobic chain length.³ The hydrogel hydrophilicity can be adjusted by synthesizing copolymers of appropriate composition using two or more comonomers that exhibit contrasting interactions with water.⁴ Meguro et al.⁵ have ob-

served that the adsorption of anionic and cationic surfactants on the hydrogels in multiple layers depend on their orientation results in aqueous solutions.

On the other hand, the interaction between surfactants and hydrogels is of great importance in understanding the fundamentals of hydrogel volume transition because of the amphoteric property of surfactants. In Mashelkar and coworkers' study,⁶ they investigated the swelling behavior of hydrophobically modified poly(*N*-isopropylacrylamide) (PNIPA) copolymeric hydrogels in aqueous sodium dodecyl sulfate (SDS). The swelling ratios and the lower critical solution temperature were found to be remarkably enhanced, which was interpreted on the basis of electrostatic repulsion due to binding of SDS to polymer chains. The change in the transition temperature was found to be influenced strongly by the addition of small amounts of ionic surfactants.

In this study, we attempted to perform quantitative measurements of the adsorption of surfactant molecules by hydrophobically modified P(DEAEMA-co-NVP/OA) hydrogels and to explain the effect of surfactant binding on the temperature-induced volume phase transition of the hydrogels. The anionic surfactant SDS and the cationic surfactant dodecyltrimethylammonium bromide (DTAB) were selected as the surfactants used in this study due to their pos-

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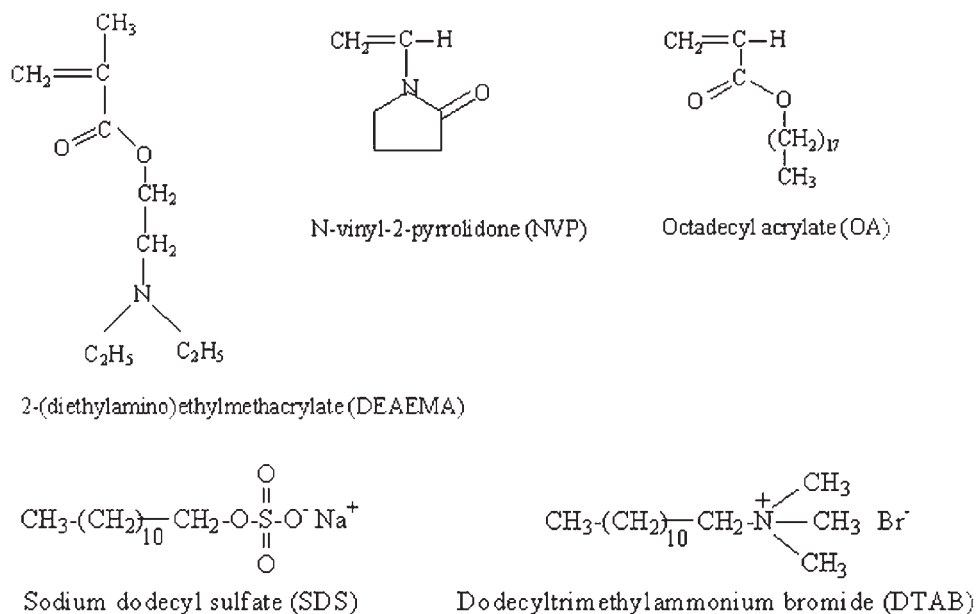


Figure 1 Chemical structure of the monomers and surfactants used.

session of a fluorescent emission band at ~ 373 nm, which permits a highly accurate determination of the difference in the amounts present before and after adsorption during the measurements.

EXPERIMENTAL

Materials

The monomers 2-(diethylamino)ethylmethacrylate (DEAEMA), *N*-vinyl-2-pyrrolidone (NVP), octadecyl acrylate (OA), the crosslinker 1,2-ethyleneglycol dimethacrylate (EGDMA), the initiator ammonium persulfate (APS), the accelerator *N,N,N',N'*-tetramethylethylenediamine (TEMED), surfactants sodium dodecyl sulfate (SDS), and dodecyltrimethylammonium bromide (DTAB) were purchased from Aldrich Chemical and were used as received. All aqueous solutions were prepared using deionized water. The chemical structures of both the monomers and the surfactants are shown in Figure 1.

Hydrogel synthesis

P(DEAEMA-*co*-NVP/OA) hydrogels were prepared by the free-radical crosslinking copolymerization of the DEAEMA, NVP, and OA in aqueous solution at 22°C for 24 h. The solutions containing DEAEMA (0.7 mL), NVP (0.3 mL) EGDMA (0.036 mL), APS (1.0 mL, 0.53M), TEMED (0.15 mL), and OA (1.7, 2.6, 3.4, and 4.3 mol %) were prepared in 4.0 mL of *tert*-butanol. After bubbling nitrogen for 15 min, these solutions were placed in poly(vinylchloride) straws of 4-mm diameters and about 20-cm long. The poly

(vinylchloride) straws were sealed and immersed in a thermostated water bath at 22°C, and the polymerization was conducted for 24 h. Upon completion of the reaction, the hydrogels were cut into specimens of ~ 10 mm in length and immersed in large excess of water to wash out any unreacted monomers and the initiator. The hydrogel samples were then dried at 50°C under vacuum to constant weight.

Determination of equilibrium swelling

For the swelling measurements in aqueous surfactant solutions, the hydrogels were immersed in vials filled with aqueous surfactant solutions (SDS or DTAB). Aqueous surfactant solutions were prepared by the dilution of 30-mM surfactant stock solutions with required volumes of water. The volume of the surfactant solutions in the vials was much larger than the hydrogel volume so that the concentration of the solution was practically unchanged. The hydrogels were equilibrated in aqueous surfactant solutions at temperatures ranging from 10 to 60°C. The hydrogels were allowed to swell in aqueous surfactant solutions for at least 24 h at each predetermined temperature. After immersion in aqueous surfactant solutions at a predetermined temperature, the hydrogels were removed from the aqueous surfactant solutions and blotted with wet filter paper for the removal of excess water on the hydrogel surface; they were then weighed. After a particular measurement, the hydrogels were reequilibrated in aqueous surfactant solutions at another predetermined temperature, and their swollen weight was also determined. The average values of three mea-

measurements were taken for each hydrogel, and the equilibrium swelling ratio was calculated as follows:

$$\text{ESR} = \frac{m_s - m_d}{m_d} \quad (1)$$

where m_d and m_s denote the masses of the dry and swollen hydrogel, respectively.

Determination of surfactant adsorption

For fluorescence measurements, the dry hydrogels (~0.05 g) were immersed into a 10-mL aqueous surfactant solution with different initial concentrations and allowed to stand for 48 h at 22°C. Fluorescence spectra were recorded with a Jobin Yvon-Horiba photoluminescence spectrometer. The system consists of a 450 W Xenon light source, a double-grating excitation monochromator (1200 grooves/mm), a single-grating emission monochromator (1200 grooves/mm), and a UV-vis detector (photomultiplier tube). Excitation wavelength was set to 330 nm. Both excitation and emission slit widths were adjusted to 3 nm. The intensity of the emission peak, observed at 373 nm, was recorded before and after the addition of the hydrogel. The amount of adsorbed surfactant molecules on the hydrogels was determined from the difference of the emission peak intensities. The average value of three measurements is reported.

RESULTS AND DISCUSSION

Figures 2 and 3 show the temperature-dependence of the equilibrium swelling ratio of the P(DEAEMA-*co*-NVP/OA) hydrogels with different OA contents in aqueous SDS and DTAB solutions with various concentrations. These figures illustrate the equilibrium swelling ratios versus temperature of P(DEAEMA-*co*-NVP/OA) hydrogels as a function of OA content in 4.15, 8.30, and 16.60 mM SDS and in 3.90, 7.80, and 15.60 mM DTAB solutions, respectively.

SDS and DTAB molecules have a long aliphatic hydrocarbon chain. Similarly, P(DEAEMA-*co*-NVP/OA) hydrogels also have long aliphatic hydrocarbon pendant groups due to the OA units. When SDS or DTAB molecules diffuse into the hydrogel, strong association takes place through the hydrophobic interactions between the aliphatic hydrocarbon pendant groups of the OA units and the long chain alkyl groups of the SDS and DTAB, resulting in a decrease in the equilibrium swelling ratio with increasing hydrophobic OA content in the hydrogel. Similar results have been reported by Mashelkar and coworkers⁶ for their hydrophobically modified poly(*N*-isopropylacrylamide) hydrogels.

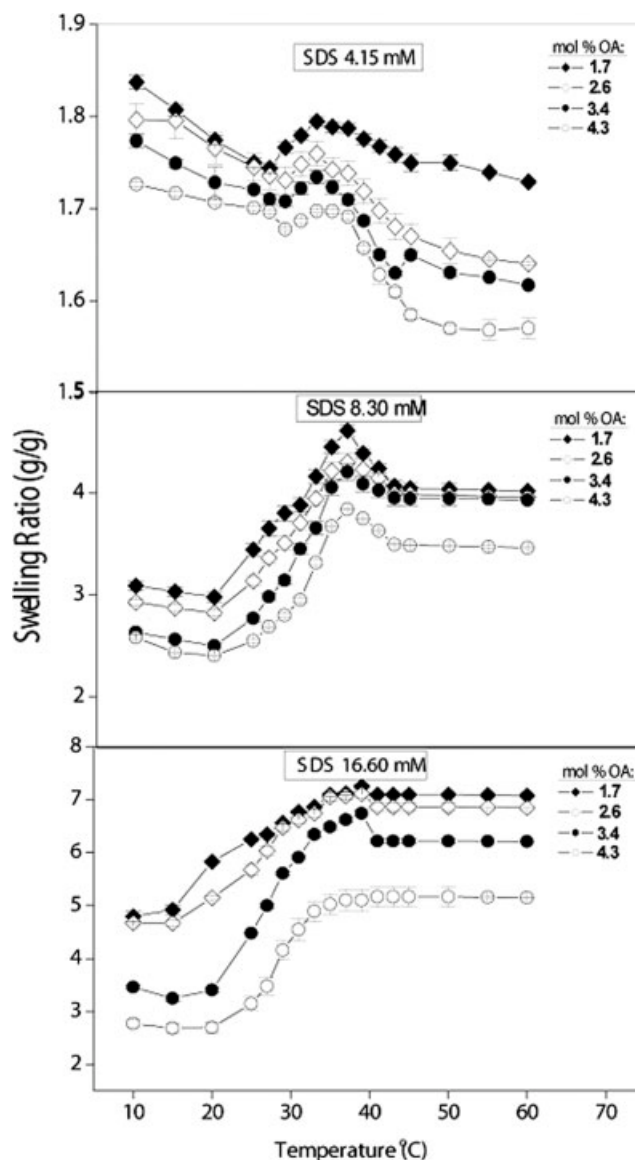


Figure 2 Equilibrium swelling ratio of the P(DEAEMA-*co*-NVP/OA) hydrogels in SDS solutions shown as a function of temperature. The concentrations of SDS solutions and OA contents are indicated in the legend.

The data in Figures 2 and 3 clearly showed that the equilibrium swelling ratios of these hydrogels increased with increasing initial surfactant concentration. Since, increasing the surfactant concentration in the external solution increases the counterion concentration (Na^+ or Br^-) inside the hydrogel and the neutral polymer chains become polyelectrolytes. These acquired network charges and the counterions associated with them exert an extra osmotic pressure on the network. As a result, the polymer conformation will become more like that of an expanded coil than a globule, and therefore the equilibrium swelling ratio of the hydrogels will be increased. The effect of the surfactant molecules in inducing some measure of polyelectrolyte behavior with chain

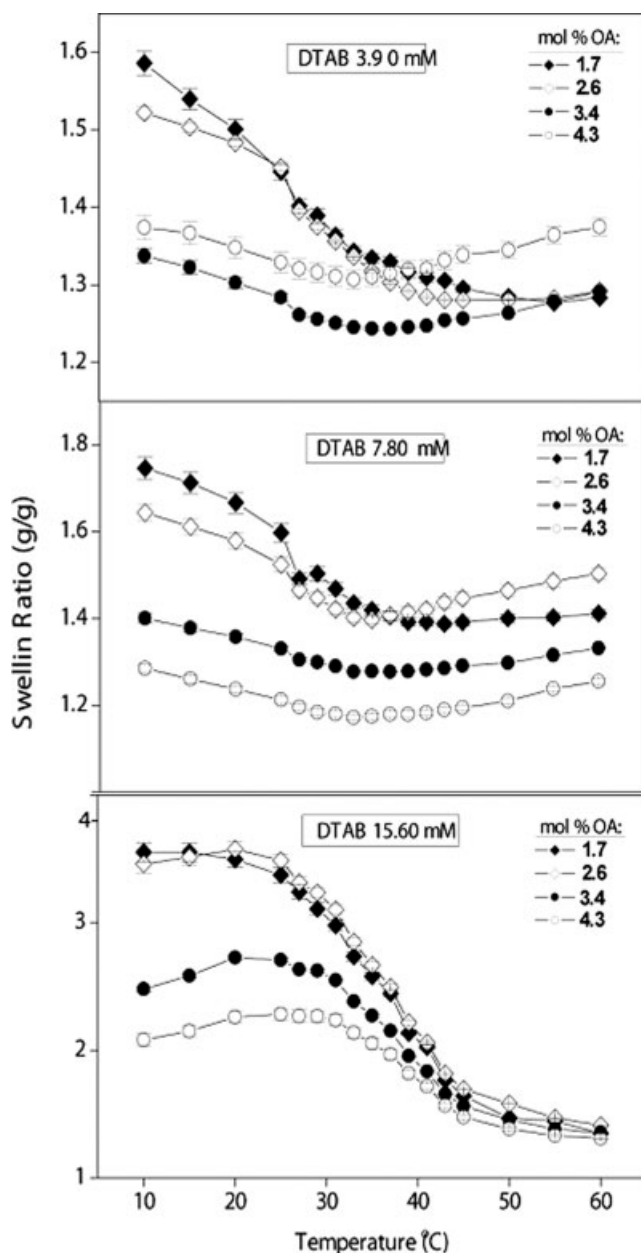


Figure 3 Equilibrium swelling ratio of the P(DEAEMA-*co*-NVP/OA) hydrogels in SDS solutions shown as a function temperature. The concentrations of DTAB solutions and OA contents are indicated in the legend.

expansion has been demonstrated by viscometric measurements on aqueous solution of the uncharged polymer, poly(*N*-vinyl-2-pyrrolidone).⁷

The critical micelle concentration (CMC) of SDS and DTAB are 8.30 and 15.60 mM at room temperature, respectively.⁸ At surfactant concentrations, beyond this characteristic concentration, the excess "free" surfactant is in a dual equilibrium with micelle formation and binding to the hydrogel. Both cases would result in a saturation value for the amount of surfactant bound to the hydrogel.

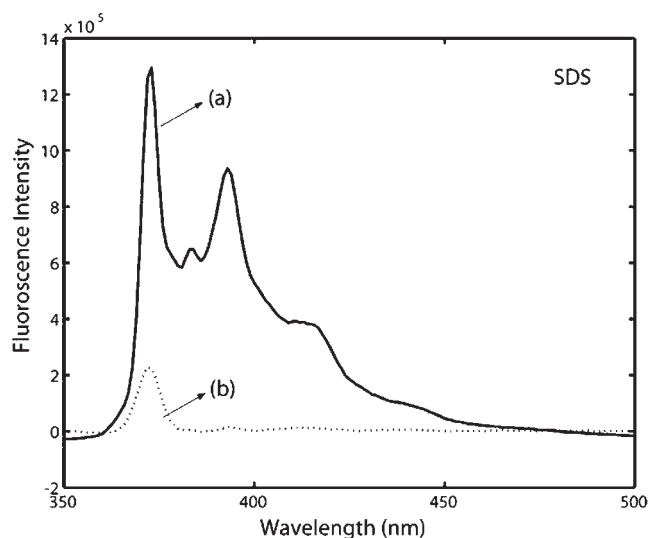


Figure 4 Fluorescence spectra of SDS solutions (a) before and (b) after adsorption by the P(DEAEMA-*co*-NVP/OA) hydrogels.

In 8.30 mM (at the CMC) and in 16.60 mM (above the CMC) SDS solutions (Fig. 2), the negative temperature-coefficient of the hydrogels in 4.15 mM (below the CMC) was converted into the positive temperature-coefficient, and in this case, the maximum swelling was observed in the range of 36–60°C. However, in the DTAB solutions (Fig. 3), the hydrogels exhibited a negative temperature-coefficient with increasing of temperature from 10 to 60°C. Another important characteristic of surfactant effects is the large differences in the values for the equilibrium swelling ratio observed between SDS and DTAB solutions. In this case, since the hydrophobic chain

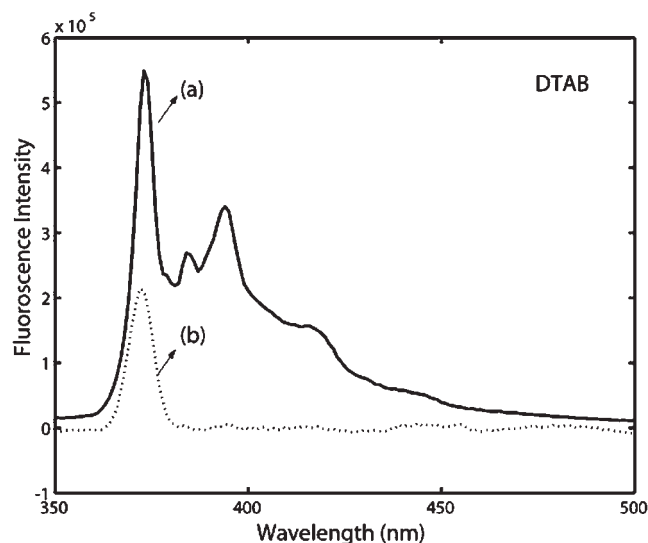


Figure 5 Fluorescence spectra of DTAB solutions (a) before and (b) after adsorption by the P(DEAEMA-*co*-NVP/OA) hydrogels.

TABLE I
The Effect of Initial Concentration of SDS and DTAB Solutions (mmol/g dry gel) on the Adsorption Capacities of the P(DEAEMA-*co*-NVP/OA) Hydrogels

OA (mol %)	In SDS			In DTAB		
	4.15 mM	8.30 mM	16.60 mM	3.90 mM	7.80 mM	15.60 mM
1.7	0.071 ± 0.012	0.109 ± 0.002	0.117 ± 0.008	0.216 ± 0.011	0.387 ± 0.004	0.603 ± 0.004
2.6	0.081 ± 0.007	0.114 ± 0.011	0.137 ± 0.013	0.236 ± 0.007	0.421 ± 0.011	0.607 ± 0.009
3.4	0.085 ± 0.017	0.130 ± 0.017	0.180 ± 0.017	0.238 ± 0.002	0.480 ± 0.003	0.640 ± 0.005
4.3	0.094 ± 0.002	0.132 ± 0.006	0.300 ± 0.014	0.246 ± 0.006	0.520 ± 0.009	0.750 ± 0.011

SDS, sodium dodecyl sulfate; DTAB, dodecyltrimethylammonium bromide.

length is the same for SDS and DTAB molecules, it cannot be responsible for the large differences in the equilibrium swelling ratio and the temperature-coefficient of the hydrogels. These changes may be attributed to the type and nature of the water binding sites, such as $-\text{O}-\text{SO}_3^-$ and $-\text{N}^+(\text{CH}_3)_3$, of surfactant molecules, the differences in the counterions, the ionizable groups, and the bound amounts of surfactants.

The adsorption of surfactant molecules to the hydrogels with different OA contents was also determined via fluorescence measurements of SDS and DTAB solutions (Figs. 4 and 5). The results were given in Table I. Although the anionic SDS and cationic DTAB surfactants are unlike molecules, the fluorescence spectrum of SDS and DTAB surfactants in their aqueous solutions are exactly the same. They have a fluorescence band at the same wavelength ($\lambda = 373$ nm). SDS molecules may have a fluorescence band due to its $-\text{OSO}_3^-$ groups conjugation. However, the fluorescence band of DTAB molecules is due to the twisted intramolecular charge transfer related to the torsional motion of the $-\text{N}^+(\text{CH}_3)_3$ groups.^{9,10} It can be said that the adsorption of SDS and DTAB molecules by the P(DEAEMA-*co*-NVP/OA) hydrogels occurs primarily due to hydrophobic interactions and that the fluorescence intensities of the solutions are proportional to the concentration of surfactant solutions. As shown Table I, in SDS solutions, the adsorption capacity of the P(DEAEMA-*co*-NVP/OA) hydrogels increased ~ 1.32 , 1.21 , and 2.56 fold in 4.15 , 8.30 , and 16.60 mM, respectively, with increasing OA content in the hydrogel. Similarly, in DTAB solutions, the increase in the adsorption values was ~ 1.14 , 1.34 , and 1.24 fold in 3.90 , 7.80 , and 15.60 mM, respectively, at the same hydrogel

compositions. As a result, the observed effects of both the anionic surfactant SDS and the cationic surfactant DTAB on the P(DEAEMA-*co*-NVP/OA) hydrogels can thus be readily understood by assuming that the hydrogel acquires a partially ionic character upon binding of SDS or DTAB molecules on the hydrogel. It is reasonable to suppose that the SDS or DTAB adsorbs towards the hydrogel within the gel phase through hydrophobic interactions. The strong hydrophobic interactions between DTAB or SDS molecules and the P(DEAEMA-*co*-NVP/OA) hydrogel enable the surfactants to adsorb towards hydrogel not only from free SDS or DTAB molecules but also from micelles of these, through the destruction or breakdown of the latter. The specificity of the surfactant hydrophobic side group might also have contributed to this high adsorption capacity.

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