

ORIGINAL ARTICLE

A dynamic light scattering study of hydrogels with the addition of surfactant: a discussion of mesh size and correlation length

Wei Wang¹ and Sverre Arne Sande²

We report a study of the interaction of sodium dodecyl sulfate (SDS) with hydrogels made of hydroxyethylcellulose (HEC) and hydrophobically modified hydroxyethylcellulose (HMHEC) by means of dynamic light scattering. The results reveal that the interaction between the hydrogels and SDS only affects the cooperative diffusion, while the slow relaxation of the hydrogels was not influenced by the interaction. Gel swelling due to the presence of SDS is also examined by measuring the weight change of the gel. The main observation is that when the gel swells due to increasing SDS concentration, the cooperative diffusion becomes faster. As such, we raise the question of whether the correlation length obtained from DLS is still proportional to the mesh size inferred from gel swelling. In the discussion, we attribute the cause to the quantity of bound surfactants. The mutual diffusion of SDS micelles could be detected at high SDS concentrations, and the diffusion coefficient of SDS in the gel matrix was determined.

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INTRODUCTION

Hydrogel-surfactant systems have been of great interest due to extensive industrially relevant applications, such as drug delivery, inks, cosmetics and detergents.^{1–4} Diffusion in a polymeric network is the pivotal process in most of these applications, and a study of polymer dynamics would help us to understand the diffusion process in a polymer matrix.

For a semidilute polymer solution at an infinitesimal time interval, the system could be considered as a transient gel. The many-body dynamics is reduced to the problem of the diffusion of one polymer chain in the transient gel.⁵ In dealing with the dynamics of one polymer chain in a gel, the crucial point in establishing the theory is the existence of a single characteristic length (mesh size) defining the average distance between entanglement points at a certain concentration.⁶ In a good solvent, the mesh size and the correlation length obtained in a dynamic light scattering (DLS) experiment are proportional, which provides the theoretical foundation for characterizing the mesh size of a gel system using the DLS method.⁷

In the DLS measurement with VV scattering configuration, the scattered light is a superposition of isotropic and anisotropic components, where the isotropic component is due to density fluctuations. It is closely related to the relaxation behavior of the bulk modulus (K) and shear modulus (μ).⁸ The cooperative diffusion coefficient (D_c) can be expressed in terms of the bulk modulus and shear modulus as $K + \frac{4}{3}\mu$, which is essentially caused by longitudinal displacements of the gel fiber network.^{9–11} The method has been successfully employed in predicting mesh size and extracting information on the elastic

properties of polyacrylamide gels.⁸ The results obtained by DLS were in strong agreement with those obtained using a hydrostatic method.

Most studies have been focused on binary systems with and without hydrodynamic interactions. The aim of the present study is therefore to employ DLS to study two ternary systems with electrostatic force and hydrophobic interactions between sodium dodecyl sulfate and HEC (or HMHEC) hydrogels. The effects of SDS concentration on the dynamics of the polymer chains, and thereby the diffusion of solutes through the gel, was studied. The correlation length of the hydrogels obtained from DLS measurements was compared with the mesh size obtained by using gel-swelling experiments. The trend of the mesh size with increasing SDS concentration was found to be the opposite of what was found for the correlation length.

MATERIALS AND METHODS

Materials

HEC and hydrophobically modified hydroxyethylcellulose (HMHEC) were obtained from Ashland with commercial names NatroSolPharm and NatroSol and LOT numbers H-0048 and NT1E9478, respectively. The chemical structures of HEC and HMHEC are shown in Figure 1a. The hydrophobic groups of HMHEC are hexadecyl chains, and the molecular weight of each polymer is 300 000 Da, calculated from intrinsic viscosity measurements. The polymers were purified by dialysis with a cutoff size of 8000 Da. Sodium dodecyl sulfate (SDS, >98.5%), sodium hydroxide (NaOH) and 1,4-butanediol diglycidyl ether (BDGE, >95%) were purchased from Sigma-Aldrich and used without further purification. Milli-Q water was used in all experiments, and the resistivity of the water was ~18.2 M Ω cm.

¹Center for Pharmacy and Department of Chemistry, University of Bergen, Bergen, Norway and ²Department of Pharmacy, University of Oslo, Oslo, Norway
Correspondence: Professor W Wang, Department of Chemistry, Institute of Chemistry, Allegaten 41, Bergen 5007, Norway.
E-mail: wei.wang@kj.uib.no

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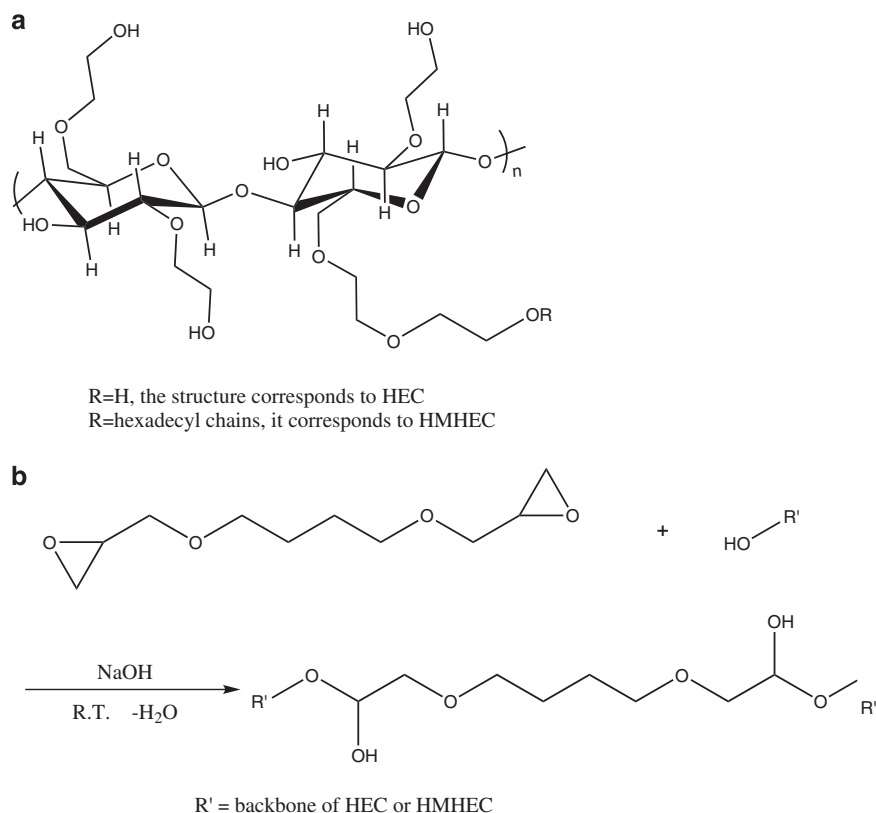


Figure 1 (a) The chemical structure of HEC and HMHEC; (b) the chemical reaction for synthesis of crosslinked HEC and HMHEC.

Sample preparation

Ten-millimeter NMR tubes (Wilma Glass, Vineland, NJ, USA) were used for preparing samples for the DLS experiments. The tubes were cleaned by a standard procedure including general cleaning with a boiled soap solution and subsequently water, followed by ethanol steaming for 40 min. The cleaned sample tubes were covered by aluminum foil to prevent dust contamination. The tubes were dried in a thermostatic oven for at least 24 h before use. All samples were prepared in a dust-free glovebox.

The hydrogels of HEC and HMHEC were prepared by chemical crosslinking. The chemical reaction for the synthesis of the crosslinked hydrogel is shown in Figure 1b. A solution of HEC (or HMHEC) and BDGE was mixed and filtered (5 μm). A stock solution of NaOH (10 mol l⁻¹) was prepared and filtered (200 nm) and then added to the mixed polymer solution. The final concentrations of the polymer and BDGE were 2 and 10 wt%, respectively, with pH = 14. The mixed solution (1.5 ml) was transferred to the NMR tubes, which were sealed before being removed from the glovebox. The samples were centrifuged (4000 r.p.m., 10 min). Two samples of HEC and HMHEC were measured immediately after preparation to monitor the gelation process. The remaining samples were kept at room temperature for 30 h to ensure the completion of the gel formation. The seal was then opened, and the samples were placed in pure water for dialysis to remove excess BDGE and NaOH. The dialysis lasted for 2 weeks, and the dialysis medium was changed twice a day.

Five concentrations of aqueous SDS solutions were prepared. Following the dialysis, the NMR tubes with samples were placed in bottles filled with 200 ml SDS solution. The gels were kept in the solution at 25 °C for 2 months to reach equilibrium and were thereafter measured according to the following procedure.

Dynamic light scattering

The DLS experiments were conducted with an ALV/CGS-8F multi-detector compact goniometer system with eight fiber-optical detection units. The beam from a Uniphase cylindrical 22 mW HeNe-laser, operating at a wavelength of 632.8 nm with vertically polarized light, was focused on the sample through a

temperature-controlled cylindrical quartz container (with two plane-parallel windows), filled with a refractive index matching liquid (cis-decalin). All measurements were taken at 25 °C.

The scattered light was detected at scattering angles of 22° to 141°, corresponding to a scattering vector (q) regime of $5.03 \times 10^6 \sim 2.49 \times 10^7 \text{ m}^{-1}$. The scattered light intensity autocorrelation function $\langle I(q, 0)I(q, t) \rangle$ ($\langle G^2(t) \rangle$) was measured for the equilibrated hydrogel-SDS samples. Owing to the nonergodicity of the gel system, the sample cell was equipped with a rotating device able to hold the sample tube and rotate it. The ensemble-averaged ICF ($\langle \langle G^2(t) \rangle \rangle_E$) was recorded for at least 60 different scattering volumes, and the same procedure was performed for all equilibrated samples. The ensemble-averaged ICF was used to calculate the background-subtracted and normalized dynamic structure factor, $f(q, t) = \frac{\langle I(q, 0)I(q, t) \rangle - B}{\langle I(q) \rangle^2 - B}$. The background B was determined from the value of $\langle I(0)I(t) \rangle$ at a sufficiently long time to ensure negligible further decay ($< 1\%$).¹² A Kohlrausch–Williams–Watts (KWW) stretched exponential function was used to fit the ICF, and is expressed as by $f(q, t) = \sum_j \{ x_j \exp[-(t/\tau_j)^{\beta_j}] \}$ where τ_j is the characteristic relaxation time, β_j is the Kohlrausch stretching exponent and x_j measures the strength of mode j . For cooperative diffusion, $\beta_j = 1$ was used in the data analysis. Unless otherwise indicated, data at a scattering angle of 90° were used for analysis, corresponding to a scattering vector of $1.87 \times 10^7 \text{ m}^{-1}$. The angular dependence was only applied to the q -dependence of the cooperative diffusion scaling.

Gel weight after interaction with SDS

Gel weight was measured by separately prepared samples with a gel volume of 0.5 ml before dialysis. The same procedure was used in dialyzing the gel samples as was used in preparing the DLS samples, and they were weighed afterwards. The samples were kept in SDS solutions of different concentrations for 2 months, and the gel weights were then measured to compare with the ones measured immediately after dialysis.

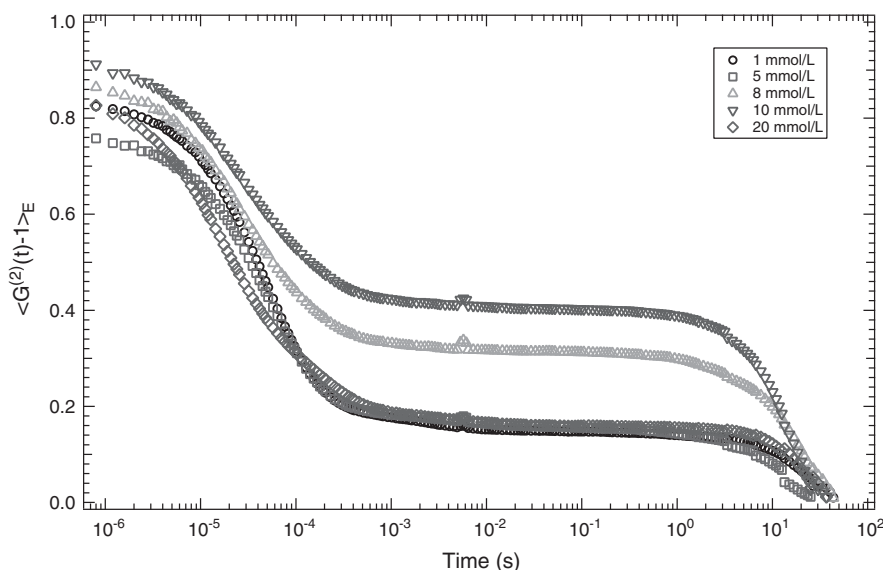


Figure 2 The ensemble-averaged intensity autocorrelation function obtained for the HEC gel with SDS at different concentrations. A full color version of this figure is available at *Polymer Journal* online.

RESULTS

The interaction between HEC and SDS

Figure 2 shows the ensemble-averaged intensity autocorrelation function for HEC gels measured after immersion in SDS solutions of various concentrations. Three relaxation processes could be observed over the measured time scales.

Fast relaxation occurs in the time scale of $10^{-7} \sim 10^{-4}$ s. The rapid decay indicates that it may be described by a mono-exponential function. This decay was assigned to cooperative diffusion, which is related to longitudinal fluctuation. However, when the SDS concentration is higher than the critical micelle concentration of SDS (8.2 mmol l^{-1} at 25°C), free micelles start to form in the gel media.¹³ The relaxation of the free micelles may also take place within this time scale. In Figure 2, a clear double exponential decay in the time scale can be observed for the 20 mmol l^{-1} SDS sample that is not observed for the sample with 10 mmol l^{-1} SDS. The reason that only a mono-decay was detected may be that the amount of scattered photons from the free micelles was not sufficient to be detected at 10 mmol l^{-1} . Please note that, although the decay caused by the free micelles extended up to 10^{-3} s on the time scale (shown below), in our discussion it is included in the fast decay (denoted inter-) because the decay is rather rapid and similar to the first one.

Following the fast decay is a slow and broad relaxation stretched over four decades in time on the time scale of $10^{-4} \sim 10^0$ s. For relaxations of gels, many cases show that the cooperative diffusion is truncated by a power-law decay. However, we did not observe the power-law decay in our system. A similar stretched exponential decay was also observed in chemically crosslinked gel systems after the fast mode. The physical picture of the slow mode in a gel system has not yet been made very clear. It has been variously attributed to viscoelastic relaxation,¹⁴ mode coupling,¹⁵ and analogies between the slow relaxation in a gel system and α -relaxation in a glassy material were suggested.^{5,16,17} Although the slow mode was analyzed by the procedure provided in the Materials and Methods section, it will not be further discussed, as it is not the main aim of the study. The terminal relaxation is on the time scale between $10^0 \sim 10^2$ s. It is considered to be an artifact of the correlator, and similar decays in the

intensity autocorrelation function were also observed by other researchers.¹⁸

As an example, Figure 3a shows the data analysis for the HEC gel with 5 mmol l^{-1} SDS. From the fitted line, we can observe that the combination of a single exponential and a stretched-exponential decay fits the measured data well. The two functions are also plotted separately in the figure, illustrating that the stretched exponential decay covers many decades.

In Figure 3b, a similar analysis of the scattering function for the HEC gel with 20 mmol l^{-1} SDS is presented. Obviously, there are two modes mixed together on the time scale of $10^{-7} \sim 10^{-3}$ s. As mentioned above, when the SDS concentration is sufficiently high, we expect the diffusion of free SDS micelles in the interior gel to contribute to the correlation function. A mono-exponential function was used for analyzing this inter-diffusion mode. For the slow mode between 10^{-3} and 10^0 s, a stretched-exponential was fitted to the ICF.

The parameters used in the fitting are presented in Table 1 and Figure 4. A clear decrease in the first relaxation time was obtained. As the decay is attributed to cooperative diffusion, the relation ($\Gamma \sim \tau_1 \sim \xi$) is applicable, indicating that the correlation length (ξ) is decreasing with increasing SDS concentration. This finding is rather interesting because increasing surfactant concentrations in general should lead to an increase in the gel volume. Therefore, an increase in mesh size would be expected, which contradicts with what is observed here. Although at high surfactant concentrations the gel volume tends to decrease, this change is rather small compared with the volume change close to the critical aggregation concentration (CAC). For the angular dependence of the fast mode, the results are presented in Supplementary Figure S1. A linear relationship between the linewidth and q^2 is found, which indicates that the mode is diffusive.

For the stretched-exponential decay, the relaxation time shows a decrease with SDS concentration before the critical micelle concentration (CMC) and an increase afterward, although the changes are rather small. This trend is similar to what was observed in the gel swelling experiment of Sjöström and Piculell.¹⁹ In this study, the maximum change in gel volume was observed at 10 mmol l^{-1} SDS, corresponding to the concentration where the lowest value is obtained in the present study.

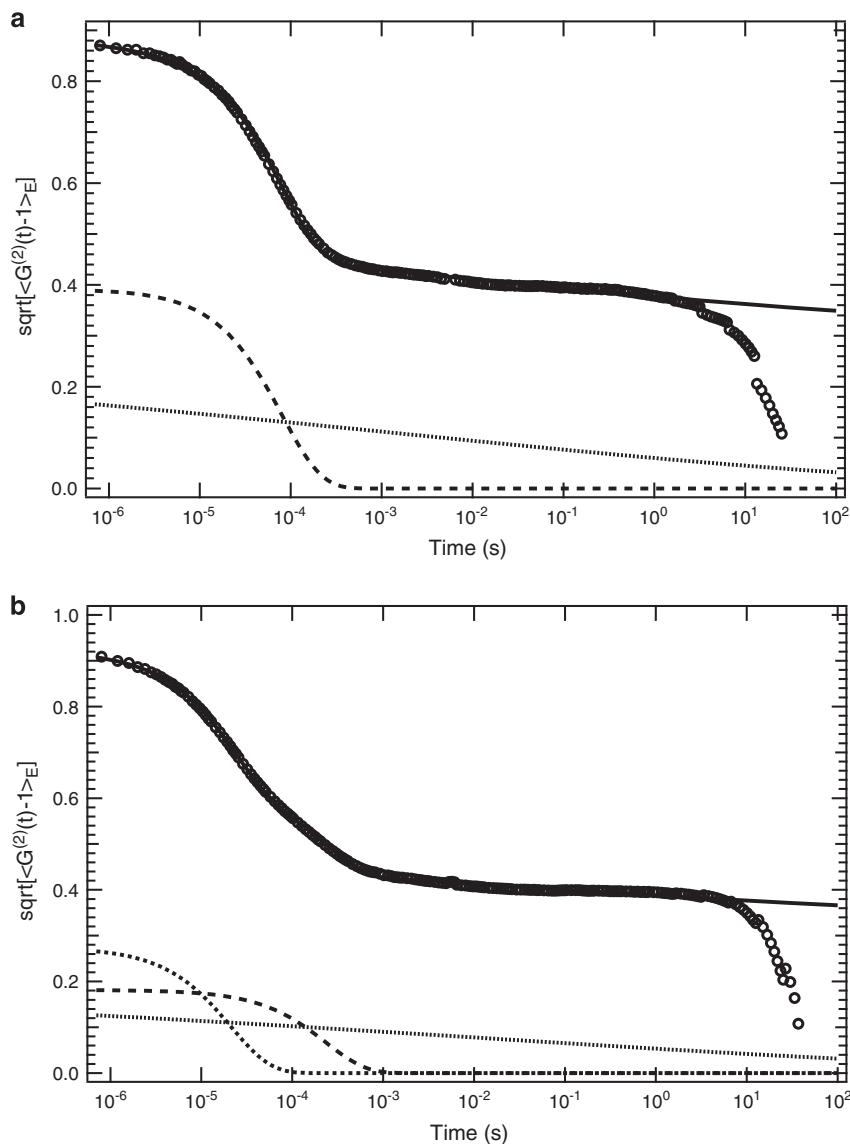


Figure 3 $\sqrt{\langle G^2(q, t) - 1 \rangle_E}$ obtained for (a) 5 and (b) 20 mmol l⁻¹ SDS with HECs divided into contributions from processes of the first decay (-----), the second decay (.....) and total curve-fit (—).

Table 1 Parameters used in the fitting for the HEC-SDS system and their values. τ_f refers to the first relaxation time, and so on. β represents the power of the stretched-exponential function

Concentration of SDS (mmol l ⁻¹)	τ_f	τ_i	τ_s	β
1	1.28E-4		0.010	0.04
5	9.20E-5		0.0081	0.07
8	8.03E-5		0.0019	0.07
10	8.39E-5		0.0027	0.05
20	2.16E-5	2.36E-4	0.012	0.07

The amplitude of these two decays is fairly similar for all of the functions. As shown in Figures 3a and b, the amplitude of the stretched-exponential decay is ~ 0.14 . For the HEC gels, the contributions of the mono-exponential decays are much larger than for the stretched-exponential decay. No evaluation of the exponent

in the stretched exponential decay is possible because it is strongly correlated to the choice of baseline and the process of normalization.

The interaction between HMHEC and SDS

The same decay pattern in the ensemble-averaged ICFs that was observed for HEC was also found for the HMHEC gel system shown in Figure 5, and was consequently analyzed with the same methods. The fast relaxation occurred on the time scale of $10^{-7} \sim 10^{-4}$ s, and the second one on the scale of $10^{-4} \sim 10^0$ s. Compared with the HEC system, the second decay is more pronounced. As an example, the ICF for the HMHEC gel with 5 mmol l⁻¹ SDS is shown in Figure 6a. Two decays are singled out and fitted with mono-exponential and stretched exponential functions for the first and second decays, respectively. In Figure 6b, the ICF obtained from the HMHEC gel in equilibrium with 20 mmol l⁻¹ SDS is presented. As for the HEC-SDS system at the same SDS concentration, an extra mono-exponential decay was identified in addition to the two decays found for the other samples.

The amplitude of the first decay is small compared with that of the HEC-SDS system, while the amplitude of the stretched exponential is much larger than for the mono-exponential decay.

Table 2 Parameters used in the fitting for the HMHEC-SDS system and their values. τ_f refers to the first relaxation time and, so on. β represents the power of the stretched-exponential function.

Concentration of SDS (mmol l^{-1})	τ_f	τ_i	τ_s	β
1	1.56E-4		0.0087	0.06
5	8.45E-5		0.038	0.15
8	8.33E-5		0.0068	0.09
10	6.91E-5		0.0085	0.09
20	2.53E-5	3.55 E-4	0.045	0.13

The values of the parameters obtained from fitting the models are shown in Table 2. The trends with respect to the SDS concentration are comparable to what was found for the HEC gel. For the first decay, the calculated relaxation time shifts to smaller values with increasing SDS concentration. For the sample with 20 mmol l^{-1} SDS, the decay rate of the inter mode was found to be on the same order of magnitude as the value obtained for the HEC-SDS system. For the stretched-exponential, a clear comparison is precluded due to the variation in β , but for comparable β , the results are fairly similar. The angular dependence was also determined for the fast mode and the inter-mode, and the results are presented in Supplementary Figure S2. The linewidth is plotted as a function of q^2 , and linear dependence is observed for all samples, which indicates that the fast mode and the inter-mode are diffusive.

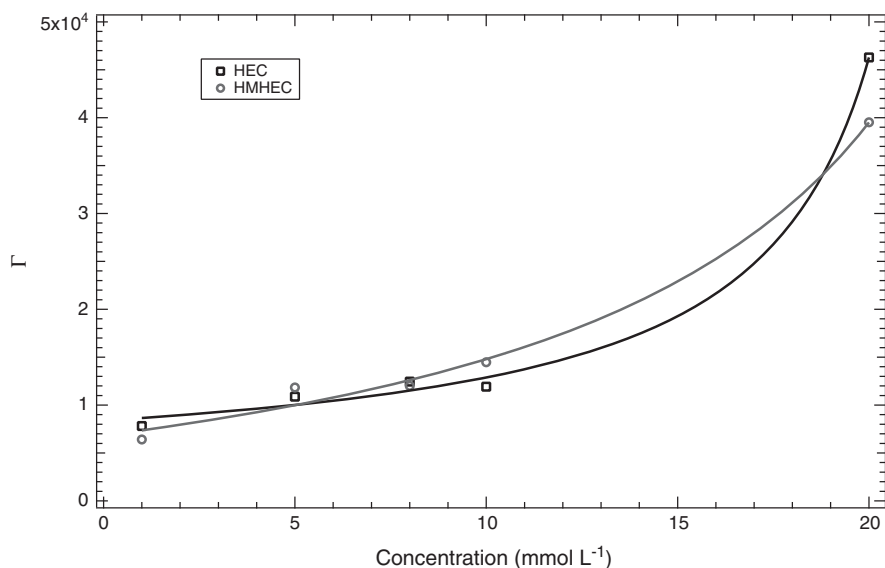


Figure 4 The linewidth of the fast mode is presented for comparison of the HEC and HMHEC systems. A full color version of this figure is available at *Polymer Journal* online.

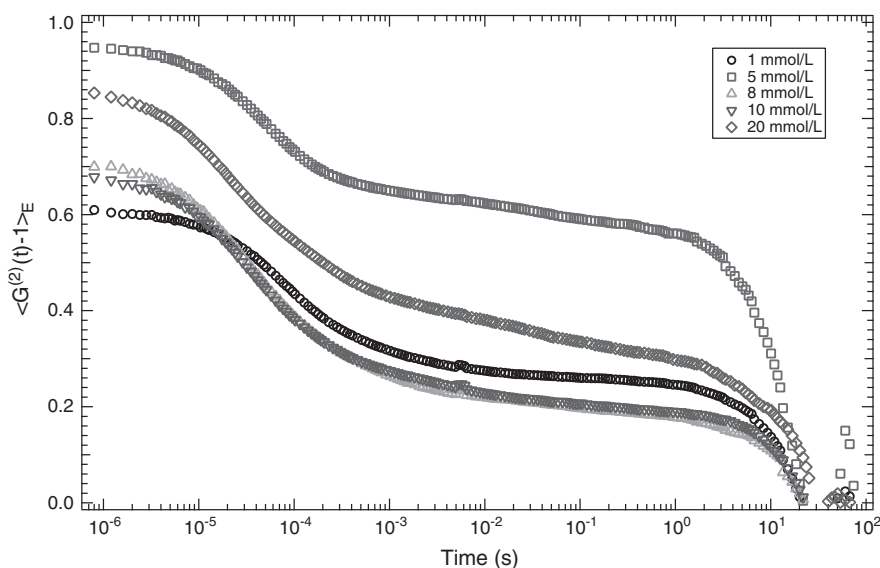


Figure 5 The ensemble-averaged intensity autocorrelation function obtained for the HMHEC gel with SDS at different concentrations. A full color version of this figure is available at *Polymer Journal* online.

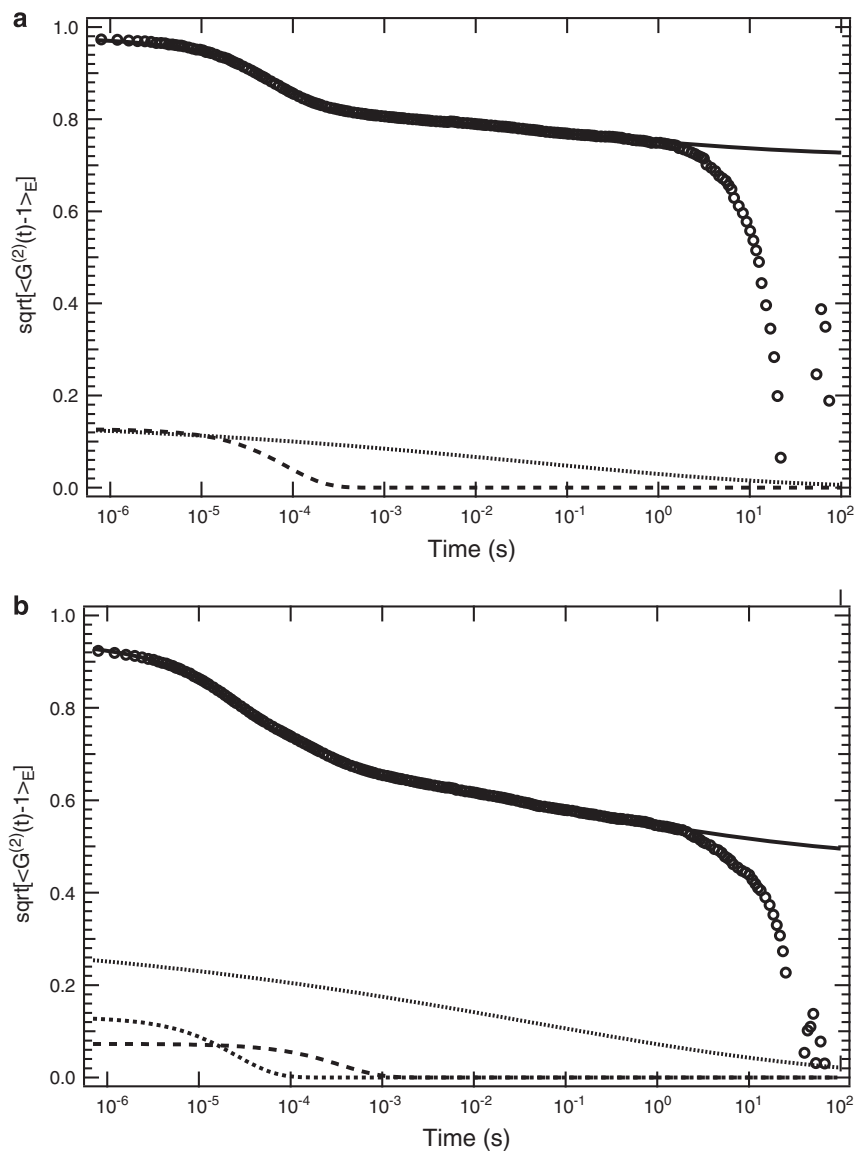


Figure 6 $\sqrt{\langle G^2(q, t) - 1 \rangle_E}$ obtained for (a) 5 and (b) 20 mmol l⁻¹ SDS with HMHEC are divided into contributions from processes of the first decay (-----), the second decay (.....) and total curve-fit (—), respectively.

Change in gel volume after the interaction

As shown in Figure 7, the gel weight changed after the interaction with SDS. Corresponding results reported by other researchers are consistent with the results found here.²⁰ At low surfactant concentrations, the gel volume remained constant with no swelling or shrinking. At this stage, the surfactant molecules dispersed in the gel and media evenly. The gel volume started to increase at 5 mmol l⁻¹ SDS and approached its maximum volume at 10 mmol l⁻¹. This abrupt increase of the gel volume indicates that the SDS molecules start forming micelles in the vicinity of the polymer chain. Following the bound surfactant, the concentration of the counterions will also move into the gel interior due to electroneutrality. The increase of the gel volume is due to the change of the counterion concentration in the gel, which increases the osmotic pressure in the interior of gel. For even higher SDS concentrations, a slight decrease in the gel volume was observed. When the surfactant concentration is higher than CMC, the formation of free micelles acts as a simple salt, and the net effect of

this is to reduce the difference between the interior of the gel and the outside of gel. Balancing the osmotic pressure causes the deswelling of the gel volume. As this result has been thoroughly explained by Piculell *et al.*, further discussion is not necessary.^{19,20}

DISCUSSION

The dynamic behavior of polymer chains in gel systems has been thoroughly explained by Tanaka's model.⁸ Only one relaxation mode was predicted in the model, which is termed cooperative relaxation. In many experiments, however, two relaxation modes have been observed.²¹ In cooperative diffusion, the motion of the polymer chain is balanced by a restoring force and the friction between the polymer chain and the solvent; the physical origin of the slow mode is unclear. In this study, we investigated the changes of the cooperative diffusion caused by the interaction between SDS and HEC or HMHEC gel. The method used for analyzing the ensemble-averaged ICFs separates all the relaxation modes on the measured time scale. The results clearly

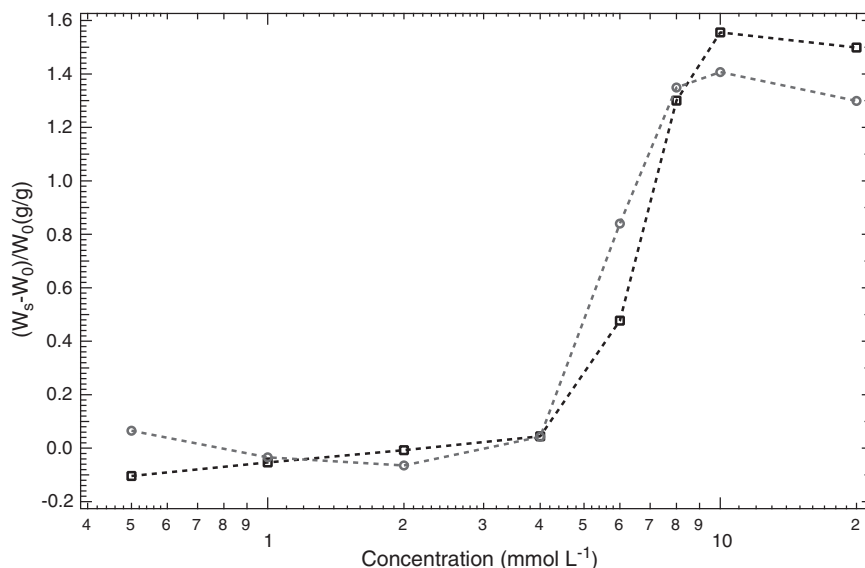


Figure 7 The change of volume of the gels is shown after the interaction with SDS in different concentrations. W_s represents the gel weight after the interaction and W_0 represents the original gel weight. As the density of the gel is approximately equal to the density of the media, the weight ratio is used to represent the same ratio of the volume. HEC (\square); HMHEC (\circ). A full color version of this figure is available at *Polymer Journal* online.

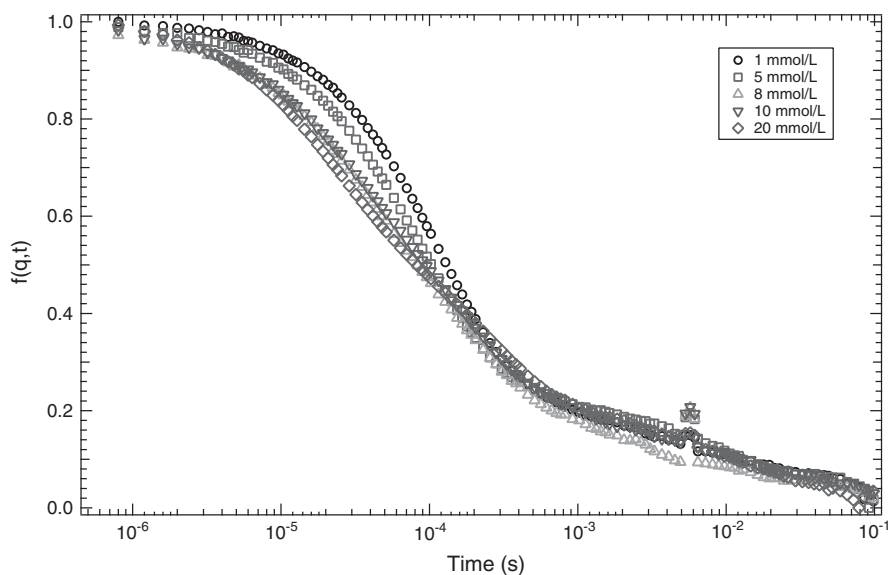


Figure 8 The dynamic structure factors for all concentrations of SDS with HEC by using an arbitrary chosen baseline at $f(1.87 \times 10^7, 0.1)$ in Figure 2 and subsequent normalization. A full color version of this figure is available at *Polymer Journal* online.

show two diffusion processes for the sample with SDS concentrations lower than the CMC. At higher SDS concentrations for both polymer systems, an inter relaxation mode appears, which we believe originates from the diffusion of free micelles of SDS into the gel matrix. Hence, in this section, we would like to discuss both the effect on the cooperative diffusion caused by adding SDS to the hydrogel and the diffusion of the free micelles in the hydrogel matrix.

The influence of SDS on the diffusion modes

In shear viscoelastic measurements, it has been shown that semidilute polymer solutions behave like an elastic gel at short times and a viscous fluid at longer times.²² A characteristic time that separated these two time regimes was observed, and the long-time relaxation was attributed to the lifetime of contact points between the polymers.

From the measurements shown in Figures 2 and 5, two relaxation modes can be determined, and the gelation process suppressed the long-time relaxation. This is commonly described as a freeze-in fact. As many studies have shown, this relaxation is similar to the α -relaxation of a glass material, which may be described by a stretched-exponential function.²³ We would not expect any effect on the long-time relaxation of the hydrogel due to interaction with SDS. However, this is not clearly observable from Figures 2 and 4, due to the differences in the static scattering of the gels (the saturation of the correlation function at long times), even though they were prepared under the same conditions. However, it is possible to reduce this difference by arbitrarily choosing a baseline (the value of B) and normalizing the ICFs. If a value of $B = f(q, 0.1)$ as a baseline is chosen for the ICFs shown in Figure 3a, and we subsequently normalize the

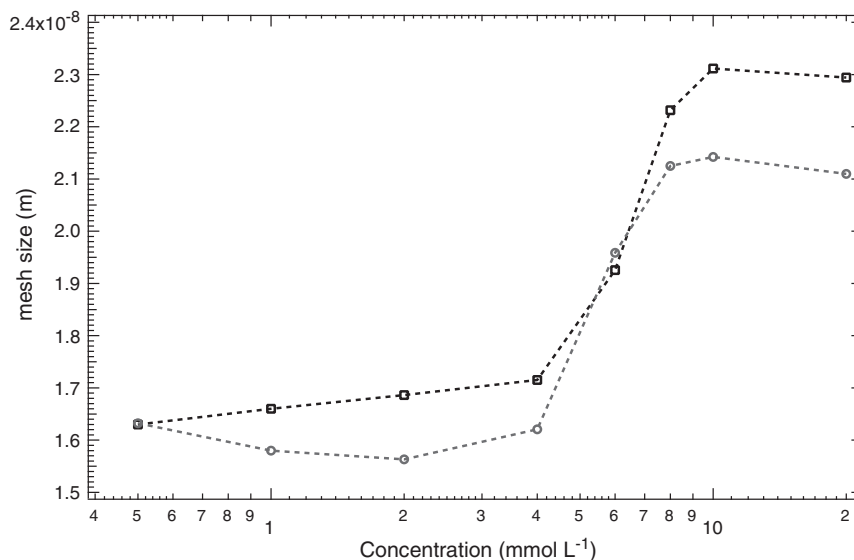


Figure 9 The mesh size calculated based on the volume change of the hydrogels. HEC (\square); HMHEC (\circ). A full color version of this figure is available at *Polymer Journal* online.

ICFs for all concentrations, the results are shown in Figure 8. Please note that this treatment of the data is used only for comparison between the data obtained from different SDS concentrations, as unacceptable errors would be introduced if used in a quantitative analysis.

In Figure 8, the stretched exponential decays overlap for all concentrations of SDS. It is therefore clear that the effect of interaction with SDS on the dynamics is only manifested on cooperative diffusion at a time scale $<10^{-3}$ s. It is also rather clear that the decay in the ICFs moved to shorter times with increasing SDS concentrations. This observation is consistent with what is shown in Table 1, namely that the cooperative diffusion coefficient increases with increasing SDS concentration. The same trend was found for HMHEC. As $D \sim (\eta\xi)^{-1}$ and the local viscosity should be constant or increase slightly within the concentration region, the increase of the diffusion coefficient would indicate a decrease of the correlation length.

However, this result is seemingly contradicted by the fact that the volumes of the hydrogels have increased by addition of SDS, as mentioned above. As shown in Figure 7, the gel volume starts increasing when the SDS concentration exceeds 5 mmol l^{-1} . The relation between volume fraction and correlation length has been described as follows: $\xi = \varphi^{-1/3} \langle r_0^2 \rangle^{1/2}$, where $\langle r_0^2 \rangle$ is the average end-to-end distance of the polymer in the solvent free state. As $\langle r_0^2 \rangle$ is constant in our experiments, the correlation length is only dependent on the volume fraction. In Figure 9, ξ may be calculated from the cooperative diffusion coefficient of the hydrogels without the addition of SDS. This value was obtained from a previous publication,²⁴ and then employed to calculate the corresponding mesh size for all the concentrations. This calculation is only based on the change of the volume fraction of the polymers without considering the increasing of the volume fraction caused by incorporating SDS in the hydrogels. As expected, the mesh size of the hydrogels increases with increasing SDS concentration, as shown in Figure 9.

The results of DLS suggest that the correlation length decreases with increasing SDS concentration in the hydrogel. The essential reason of the decrease of the correlation length is the association of the surfactant, and this process could be described by the degree of binding (β), where $\beta = (\text{bound surfactant concentration})/(\text{polymer}$

equivalent concentration). Thus, the volume fraction of the gel and surfactant (φ) can be given as $\varphi = (1+\beta)\varphi_p$. The interaction between polymer and surfactant can be generally treated as a micellization process. In our case, we can simplify the discussion by applying the Langmuir isotherm to describe the binding process. Therefore, the degree of binding (β) can be given as $\beta \sim \frac{kc_s}{1+kc_s}$ where k is the binding constant and c_s is the SDS concentration. With increasing SDS concentration, the polymer backbone will gradually become charged. As for neutral polymer chains, a blob analysis maybe used such that on a distance scale exceeding ξ , the chains are Gaussian. Within a blob, the chain behavior will relate to the concentration-dependent electrostatic persistence length (b). The electrostatic persistence length may be expressed by the charge number (p) derived by Odijk²⁵ as $b = Qp^2 / (4\kappa^2 l^2)$ where κ^{-1} is the screening length, l is the contour length of the polymer and Q is the Bjerrum length, which should be independent of SDS concentration. The correlation length (ξ) can be given as a function of b according to $\xi = b^{-1/2}(c_p a)^{-3/4}$, where c_p is the concentration of monomeric units and a is the characteristic dimension of the statistical unit.^{9,26} With increasing SDS concentration in the hydrogel, the polymer chain will gradually become charged due to the bound surfactant on the polymer chain. Hence, there exists a linear relationship between the number of charges (p) and the bound surfactant (β). On the basis of this relationship, the linewidth can be described as the following equation:

$$\Gamma \sim \xi^{-1} \sim \frac{2\kappa l}{Q^2(c_p a)^{3/4}} \frac{kc_s}{1+kc_s}$$

By using this equation, we fitted the data presented in Figure 4 for HEC and HMHEC systems, treating c_p as a constant. The regression shows a good match with the experimental data, which may indicate that the essential cause of the change of correlation length is the bound surfactant.

The change of polymer configuration will lead to a slow diffusion at high surfactant concentrations. This has previously been observed for oppositely charged surfactant-hydrogel systems and was interpreted thermodynamically by Hansson.²⁷ For an oppositely charged polymer-surfactant system, charge neutralization may lead to a decrease in

correlation length by a reduction in the electrostatic repulsion. In that case, measurement of the correlation length and gel volume would lead to a reduced diffusion coefficient. In the next section, we would like to discuss the diffusion coefficient of SDS micelles in non-charged hydrogels.

The diffusion of free micelles at the highest SDS concentration

For both polymer systems at the highest SDS concentration, an inter mode on the ensemble-averaged ICFs was detected. This mode was attributed to the diffusion of free SDS micelles, as the concentration of SDS was above the CMC. The results of the fitting showed that the mutual diffusion coefficients were $\sim 1.2 \times 10^{-11}$ and $0.81 \times 10^{-11} \text{ m}^2 \text{ s}^{-1}$ for the HEC and HMHEC systems, respectively.

For hydrogels with relatively stiff polymer chains, a model of the microstructure proposed by Ogston may be constructed based on a randomly oriented array of straight, cylindrical fibers of a certain radius and volume fraction.²⁸ For a particle with radius r_s , the diffusivities of the particle in a gel (D) and in free solution (D_0) can be related by the equation: $D = D_0 * \exp(-\frac{r_s}{\lambda})$.²⁹ The diffusion coefficients of free SDS micelles may be estimated using the correlation length obtained from the analysis of the ICFs. Although the volume fraction is related to the correlation length, this relation is neglected in the present evaluation. The hydrodynamic radius of SDS micelles is $\sim 21 \text{ \AA}$, and by applying the Stokes-Einstein formula the diffusion coefficients for SDS micelles may be calculated using the correlation length obtained from the cooperative diffusion modes for the respective polymers. The diffusion coefficients obtained for the SDS micelles in the gels for HEC and HMHEC systems were 1.18×10^{-11} and $1.57 \times 10^{-11} \text{ m}^2 \text{ s}^{-1}$, respectively. Compared with the diffusion coefficient of SDS micelles at 17 mmol l^{-1} (see the data cited here), the values have decreased by nearly 50%.³⁰ The values for the highest SDS concentration fall in the same order of magnitude as the values obtained by analyzing the inter diffusion mode, thereby supporting the assignment of the third diffusion mode to the micellar diffusion.

CONCLUSION

The interaction of SDS with HEC and HMHEC hydrogels was studied by means of dynamic light scattering. At low concentrations, two diffusion modes were identified, while at the highest concentration, an inter diffusion mode appears in both polymer systems. The latter may be assigned to the diffusion of free micelles in the hydrogels. It was found that the cooperative diffusion coefficients increase with increased SDS concentrations. This result is opposite to that which we obtained from the gel swelling results. We attribute the change of the correlation length to the quantity of bound surfactant. Retarded diffusion of free SDS micelles in the hydrogels was found by analyzing the inter diffusion mode, providing a theoretical foundation for the application in the controlled release of drugs and bio-macromolecules dissolved in a surfactant-hydrogel system.

ACKNOWLEDGEMENTS

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Supplementary Information accompanies the paper on Polymer Journal website (<http://www.nature.com/pj>)

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