

# Anomalous Surfactant Diffusion in a Gel of Chemically Cross-Linked Ethyl(hydroxyethyl) Cellulose

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The interactions of sodium dodecyl sulfate (SDS) with chemically cross-linked gels of ethyl(hydroxyethyl) cellulose (EHEC) were studied. Above the so-called critical association concentration (cac), binding of SDS gives rise to an increased swelling of the EHEC gels. The binding of SDS to the gels was measured with flame emission analysis of the sodium ion. The self-diffusion of the surfactant ion (DS) in the gels was studied by the NMR pulsed field gradient spin–echo technique. Both experiments were performed on gels swollen to equilibrium in SDS solutions of varying concentrations. Comparisons with the DS diffusion in a solution of non-crosslinked EHEC were also made. In the EHEC solutions the observed spin–echo decays for DS were always describable in terms of a single surfactant diffusion coefficient (Gaussian diffusion). In contrast, the DS diffusion in the gels above the cac (SDS) was clearly non-Gaussian, or anomalous. The echo decays in the gels could be fitted to a log-normal distribution of diffusion coefficients. When the time during which the diffusion was measured was increased, the width of the distribution increased, while the average diffusion coefficient remained constant. An increase in the width of distribution was also seen when the SDS concentration was increased. The anomalous diffusion is ascribed to inhomogeneities in the gel.

## Introduction

Associating aqueous mixtures of polymer and surfactant are widely studied and utilized.<sup>1,2</sup> Recently, a number of studies have pointed to the possibilities for use of polymer-binding surfactants to manipulate the properties of nonionic polymer gels.<sup>3–18</sup> In this context, a surfactant may also serve as a model for substances that might be interesting in applications, such as drug delivery. Most studies on surfactants in gels so far have dealt with the swelling or collapse of the gels when immersed in aqueous solutions of the surfactant. Only a few studies deal with the transport of the surfactant molecules inside the gels<sup>19,20</sup>—a topic of obvious relevance both for the surfactant-induced volume transition and for applications. In polymer solutions, on the other hand, the diffusion of binding surfactants has been studied in a few cases, and useful dynamic and static information (such as surfactant binding isotherms) could be obtained.<sup>15,21,22</sup>

The purpose of the present study is to study and compare the self-diffusion of a binding surfactant both in a chemically cross-linked polymer gel, at its equilibrium swelling in a surrounding bath of surfactant solution, and in the corresponding polymer solution. We have chosen to work with a well-studied system, the polymer ethyl(hydroxyethyl) cellulose (EHEC) and the surfactant SDS. The association of SDS with EHEC in solution has been studied by a number of methods,<sup>22–26</sup> including the diffusion of the surfactant ion,<sup>22</sup> and recently the temperature-dependent swelling of covalently cross-linked EHEC in SDS solutions has also been studied.<sup>12,14</sup>

## Experimental Section

**Materials.** EHEC was supplied by Akzo Nobel Surface Chemistry AB, Stenungsund, Sweden. The degree of substitution of hydroxy(ethyl) and ethyl groups was  $MS_{EO} = 1.8$  and  $DS_{ethyl} = 0.6–0.7$ , respectively, referring to the average numbers of substituents per sugar unit of the polymer. The molecular weight of the polymer was approximately 100 kDa. NaOH (analytical grade from Eka Nobel) and divinyl sulfone (DVS; from Sigma) were used in the cross-linking of EHEC.<sup>12,14</sup> SDS and NaCl (BDH) were used as obtained without further purification. Suprapure  $H_2SO_4$  (Merck) was used for breaking the EHEC gels in the sodium analysis.  $D_2O$  for the NMR experiments was obtained from Dr. Glaser AG, Basel. The purity of  $D_2O$  was 99.8% (0.2%  $H_2O$ ). MilliQ filtered water was used for the sodium analysis.

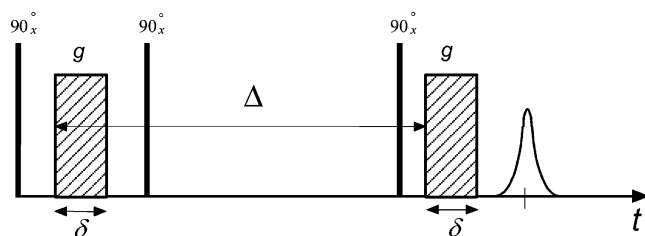
**Preparation of Gels for NMR.** Heavy water ( $D_2O$ ) was used throughout. A 2% EHEC solution was mixed with the same volume of a 40 mM NaOH solution. DVS was added in the same amount as the weight of the dry polymer. The solution was poured into sample tubes (6.5 mm i.d.) where the cross-linking reaction was allowed to proceed for 24 h. Sulfur analysis of similar gels indicated a molar ratio of 0.4 DVS units per glucose unit in the gel.<sup>12</sup> This figure does not correspond to the cross-link density, however, since DVS not only cross-links but also polymerizes. The gels thus obtained were then immersed for two weeks in  $D_2O$ , with several changes, to wash out any residual chemicals from the cross-linking reaction. After that the gels were immersed for 1 month in the appropriate SDS solutions in  $D_2O$ , with changes of solution once a week, to obtain an equilibrium concentration of SDS in the gel, as well as an equilibrium swelling. The gels were then punched into 5 mm NMR sample tubes open in both ends, whereafter the ends of the tubes were sealed. All sample preparation steps were carried out at ambient temperature (ca. 20 °C).

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**Figure 1.** Stimulated echo pulse sequence used in the NMR self-diffusion experiment.

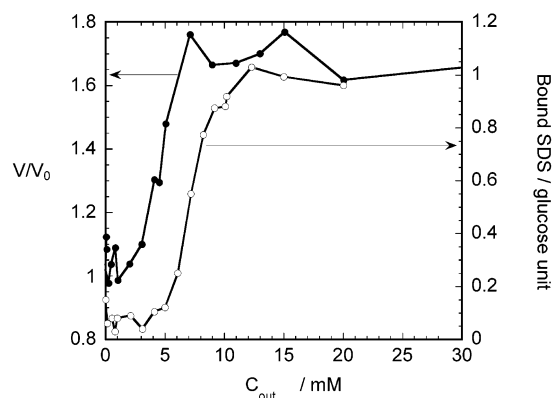
**Sodium Analysis.** Gels were made according to the same procedure as for the NMR samples except that normal water and thinner glass tubes (0.36 mm i.d.) were used. After swelling in the SDS solutions the gels were removed, weighed, and put in volumetric flasks of volumes 25, 50, or 100 mL depending on the SDS concentration in the gels. Approximately 1 mL of super clean sulfuric acid was added to each flask which dissolved the gel in approximately 1 h. Then the sample was diluted to the exact volume of the flask with MilliQ water. One blank sample and four different standard solutions (from NaCl) all containing  $\text{H}_2\text{SO}_4$  were prepared. A GBC 932 AA atomic absorbance spectrometer was used. The experiment was performed as a flame emission experiment at a detection wavelength of 589 nm and a band-pass of 0.5 nm.

**NMR Measurements.** The NMR spectrometer used for the diffusion measurements was a Bruker DMX 200. The stimulated echo pulse sequence (see Figure 1) was used since the surfactant displayed a transversal relaxation ( $T_2$ ) that was much shorter than the longitudinal ( $T_1$ ) relaxation time. For that reason the measurements were performed by varying the gradient strength ( $g$ ) and by keeping the length of the gradient pulse as short as possible, typically between 0.5 and 3 ms. The time between the first two  $90^\circ$  pulses in the stimulated pulse sequence was thus kept as short as possible in order to minimize the  $T_2$ -dependent time. The time between the second and the third  $90^\circ$  pulses was longer and varied between 9 ms and 1 s. All NMR measurements were performed at  $25^\circ\text{C}$ .

### Theoretical Background

The NMR self-diffusion technique measures, in a component resolved manner, the true self-diffusion of molecules.<sup>27</sup> It is thus a very powerful technique for the study of transport properties in complex systems. The theoretical treatment is straightforward for normal diffusion behavior, i.e., when the diffusion is unrestricted and when the exchange between different sites is fast compared to the experimental diffusion time. However, when the diffusion becomes restricted and thus deviates from free diffusion, the evaluation is more complex.

In this paper we encounter the problem of an apparent non-Gaussian self-diffusion. This is manifested in the fact that the echo decay for the surfactant is nonlinear when plotted against the relevant experimental parameters (a so-called Stejskal-Tanner plot where the diffusion coefficient is given by the slope of the curve; cf. Figure 3 below). A general complication is the fact that different diffusion mechanisms can give the same effect in the echo decay; hence the elucidation of the true diffusion mechanism can be difficult. For example, a polymer solution always gives a nonlinear echo decay for the polymer component simply because of its polydispersity and, hence, distribution in polymer diffusion coefficients.<sup>28</sup> Another case where a nonlinear echo decay is obtained is exemplified by the self-diffusion of water trapped inside emulsion droplets.<sup>29</sup> When the experimental diffusion time is such that the mean square displacement of the



**Figure 2.** Swelling isotherm for EHEC gels (left axis) and binding isotherm for SDS to EHEC gels (right axis) versus the outside SDS concentration in gel swelling experiments.

water molecules is much smaller than the radius of the emulsion sphere the echo decay is linear in a Stejskal-Tanner plot. However, if the experimental diffusion time is increased so that the mean square displacement of the water molecules is comparable to the radius of the sphere, the echo decay will show a nonlinear behavior.

In this work it is noted here that by assuming a simple log-normal distribution in diffusion constants we were able to account for the experimental results in terms of a mean diffusion coefficient and the width in diffusion coefficient as obtained from a nonlinear least-squares fit of eq 1 to the data:

$$E(q, \Delta) = \frac{\int_0^\infty P(D) \exp(-4\pi^2 q^2 D \Delta) dD}{\int_0^\infty P(D) dD} \quad (1)$$

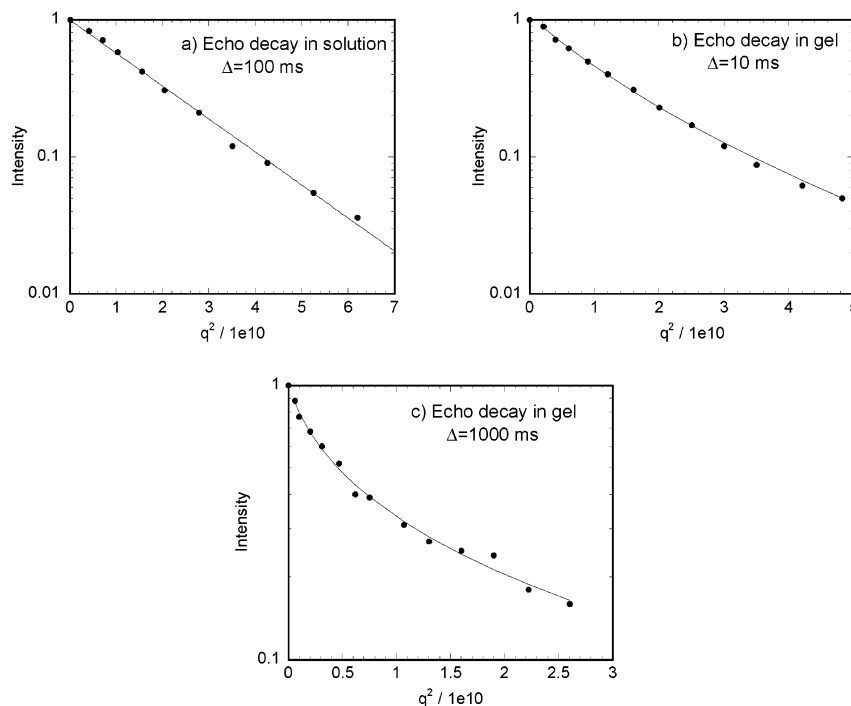
where  $q^2 = (\gamma \delta g)^2$  and  $g$  and  $\delta$  are the strength and length of the field gradient pulses and  $\gamma$  is the magnetogyric constant for  $^1\text{H}$ .  $D$  is the self-diffusion constant and  $\Delta$  the time separation between the gradient pulses (see also Figure 1).  $P(D)$  is represented by the log-normal distribution:

$$P(D) = \frac{1}{D\sigma\sqrt{2\pi}} \exp\left[-\left(\frac{\log(D) - \log(D_m)}{\sqrt{2}\sigma}\right)^2\right] \quad (2)$$

Here  $D_m$  is the mass weighted median diffusion coefficient and  $\sigma$  is the standard deviation of the logarithm of the diffusion coefficient.

### Results

**Surfactant Binding and Gel Swelling.** The variation of the equilibrium swelling of an EHEC gel when immersed in SDS solutions of increasing concentration has been reported previously,<sup>12,14</sup> and the results are reproduced in Figure 2. The swelling is given as  $V/V_0$ , where  $V$  is the equilibrium swollen volume and  $V_0$  is the reference volume of the gel in the reaction bath after the cross-linking reaction. A pronounced swelling of the gel sets in when the outside surfactant concentration,  $c_{\text{out}}$ , is equal to the so-called critical association concentration (cac) of SDS, where polymer-bound micelles are formed. The value of the cac agrees well with that found independently in solution studies of the same batch of EHEC.<sup>22</sup> The increased swelling is due to the additional osmotic pressure exerted by the counterions of the bound surfactant ions.<sup>30</sup> The swelling continues until the concentration in the outside solution reaches the critical micellar concentration (cmc) of SDS. At this point "free" surfactant micelles are formed, and the binding of

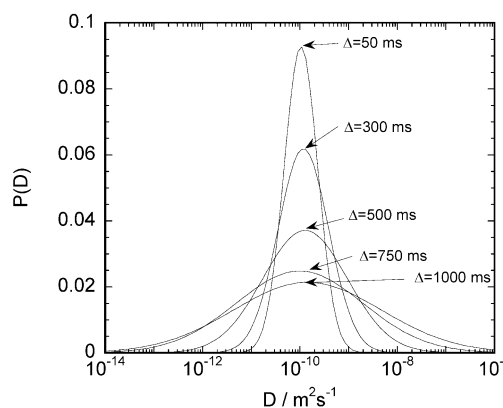


**Figure 3.** Intensity decrease (echo decay) of the signal from the DS ion plotted against  $q^2$  (Stejskal-Tanner plot). (a) 1% EHEC solution at  $\Delta = 100$  ms, (b) EHEC gel at  $\Delta = 10$  ms, and (c) EHEC gel at  $\Delta = 1000$  ms. The errors in  $D_m$  and  $\sigma$  were estimated to less than 30 and 15%, respectively (cf. text).

surfactant to the EHEC polymer levels off. This behavior has been found also for other combinations of binding ionic surfactant and nonionic polymer.<sup>11–16</sup>

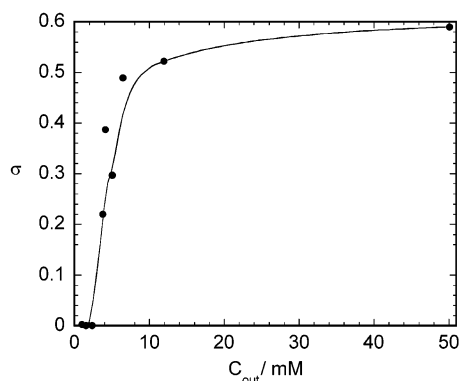
Measurements of the binding of SDS to the gels (Figure 2) confirm the essential correctness of the molecular picture given above. The data were obtained from atomic flame emission measurements of the sodium ion (cf. the Experimental Section); since no other electrolyte was present, the concentration of the dodecyl sulfate and sodium ions inside the gel must be equal. The binding is expressed in terms of the excess concentration of bound SDS inside the gel,  $c_b$ , obtained as the difference between the measured sodium concentration inside the gel,  $c_{in}$ , and the known concentration of surfactant in the external solution,  $c_{out}$ . The qualitative features of the binding isotherm are the same as those of the swelling isotherm: A cooperative binding, due to the micellization of the surfactant on the polymer chains, sets in at a surfactant concentration below the cmc, and the binding levels off around the cmc of the surfactant. The two isotherms are slightly shifted with respect to each other along the surfactant concentration axis. At this stage, we cannot say whether this shift is significant, or if it may be ascribed to experimental uncertainties. One possible source of the discrepancies is that the binding and swelling experiments were performed on different gel batches (although the parent batch of EHEC was the same).

**Anomalous Surfactant Diffusion.** After equilibration of the gels in surfactant solutions of varying concentrations as described in the Experimental Section, the diffusion of surfactant ions in the gels were measured by NMR. Similar measurements were also performed on SDS dissolved in 1% solutions (in  $D_2O$ ) of EHEC. Measurements on SDS and the same batch of linear EHEC have been performed previously by Thuresson et al.,<sup>12</sup> but owing to the improved instrumentation we did not encounter the same problems as the former authors with overlapping signals from the polymer and the surfactant. A well-resolved surfactant peak was noted and used for the evaluation of the SDS self-diffusion measurements.

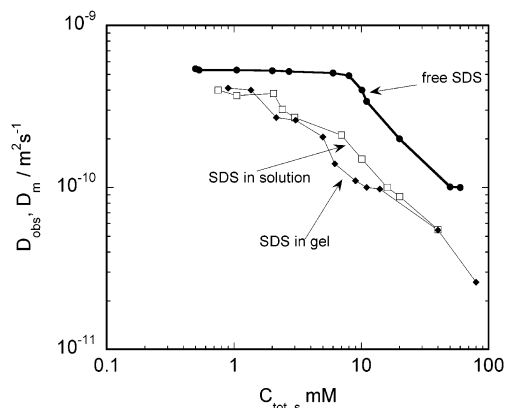


**Figure 4.** Illustration of the distribution of diffusion coefficients for the DS ion at 6.27 mM in an EHEC gel at different  $\Delta$ .

In the EHEC solutions, the observed spin-echo decays for DS were always describable in terms of a single surfactant diffusion coefficient owing to the fast exchange between different surfactant surroundings. This was not found, however, for the DS diffusion in the gels above the cac, as shown in Figure 3 for three different diffusion times ( $\Delta$ ). Diffusion of DS was clearly non-Gaussian, or anomalous. To describe the anomalous gel data mathematically, we chose to fit the echo decays to a log-normal distribution of diffusion coefficients, as described by eq 2 above. Although the physical significance of this procedure is unclear, Figure 3 shows that it provides a good description of the data. From Monte Carlo simulations the errors in  $D_m$  and  $\sigma$  were estimated to less than 30 and 15%, respectively, as evaluated at one standard deviation in width. Surprisingly, the apparent width,  $\sigma$ , of the distribution increased with increasing  $\Delta$ , while the average diffusion coefficient  $D_m$ , defined through eq 2, remained unchanged. This trend is illustrated in Figure 4 for a particular surfactant concentration; however, the patterns were the same for all surfactant concentrations above the cac.



**Figure 5.** The apparent width of the distribution of DS diffusion coefficients (at  $\Delta = 300$  ms) in an EHEC gel as a function of the outside surfactant concentration.



**Figure 6.** Diffusion coefficient for the DS ion versus the total SDS concentration in a pure surfactants solution, in a 1wt % EHEC solution, and in an EHEC gel.

At very low surfactant concentrations, the diffusion was Gaussian within the accuracy of the measurements. Figure 5 shows how the apparent width of the distribution in  $D$  (at  $\Delta = 300$  ms) varies with  $c_{\text{out}}$ . A value of  $\sigma = 0$  in the figure corresponds to an echo decay that may be described by single diffusion coefficient within the experimental accuracy and thus gives a straight line in a Stejskal-Tanner plot. Figure 5 displays a striking similarity with the binding/swelling isotherms in Figure 2; a steep increase around the cac is followed by a leveling off around cmc. It thus seems clear that the anomalous diffusion is related to the binding of the surfactant the polymer gel.

As expected, no anomalous diffusion, nor any significant lowering of the self-diffusion coefficient, was found for the diffusion of  $\text{D}_2\text{O}$  in the gels ( $D = 1.7 \times 10^{-9} \text{ m}^2/\text{s}$  at  $25^\circ\text{C}$  for  $c_{\text{out}} = 4 \text{ mM}$ ). In contrast, the diffusion of a nonionic surfactant, octyl tetraethyleneglycol ( $\text{C}_8\text{E}_4$ ) in a gel, was both decidedly non-Gaussian for  $\Delta < 300$  ms and significantly retarded compared to the diffusion in pure water ( $D_{\text{m}} = 3.4 \times 10^{-10} \text{ m}^2/\text{s}$  in the gel compared to  $D = 4.3 \times 10^{-10} \text{ m}^2/\text{s}$  in pure  $\text{D}_2\text{O}$ ). This was surprising, since this surfactant has a high cmc and is not expected to bind to EHEC. Again,  $D_{\text{m}}$  was insensitive to  $\Delta$ , but in this case  $\sigma$  decreased with increasing  $\Delta$ , so that a Gaussian diffusion was observed for  $\Delta > 300$  ms.

**Gels versus Solutions.** Since  $D_{\text{m}}$  was found to be independent of  $\Delta$  for the surfactant diffusing in the gel, it seemed relevant to compare with SDS solutions, with and without EHEC present. This is done in Figure 6. Note that the concentration axis in this case gives the total concentration of SDS ( $c_{\text{s}}$ ) in the samples. For the gels,  $c_{\text{s}}$  was obtained from  $c_{\text{out}}$  with the help of the

binding isotherm in Figure 2. The top curve in Figure 6, for SDS in pure  $\text{D}_2\text{O}$ , shows the well-known behavior for a micelle-forming surfactant in water:<sup>31</sup>  $D$  is constant until  $c_{\text{s}} = \text{cmc}$  where a decrease is seen, owing to the much slower diffusion of micelles compared to that of the monomeric surfactant. The observed diffusion coefficient is a population weighted average over monomeric and micellized surfactant molecules, and since the fraction of monomeric surfactant decreases above  $c_{\text{s}} = \text{cmc}$ , the observed diffusion coefficient decreases. The data are in excellent agreement with the established cmc value of  $8 \text{ mM}$  for SDS at  $25^\circ\text{C}$ .<sup>32</sup> The diffusion coefficient for monomeric DS was found to decrease with increasing concentration, e.g., from  $5.7 \times 10^{-10} \text{ m}^2/\text{s}$  at  $0.5 \text{ mM}$  to  $4.9 \times 10^{-10} \text{ m}^2/\text{s}$  at  $8 \text{ mM}$ .

The diffusion coefficients obtained for SDS in 1% EHEC solutions (Figure 6) are in excellent agreement with the data previously obtained by Thuresson et al.<sup>22</sup> except at low concentrations, where the data of the former authors—because of the poorer instrumentation—showed more scatter. Moreover, and for the same reason, their measurements did not extend to concentrations below  $2.5 \text{ mM}$  of SDS. In this low-concentration region, our measurements show a plateau in the observed self-diffusion, similar to the plateau observed for SDS alone. The break-point at  $2\text{--}3 \text{ mM}$  of surfactant agrees well with the estimated cac of SDS in this type of EHEC.<sup>22</sup>

The average diffusion coefficients for DS in the gels, finally, are quite similar to the diffusion coefficients in the EHEC solutions at the same overall concentrations of surfactant. The decay in  $D_{\text{m}}$  for  $c_{\text{s}} > \text{cac}$  seems more gradual in the gels than in the solutions. However, this may be due to the fact that the concentration of EHEC in the gels decreases with increasing surfactant concentration above cac. From the swelling isotherm in Figure 2, it can be seen that the volume of the swollen gel may be up to a factor of 1.7 larger than that of the initial 1% gel.

## Discussion

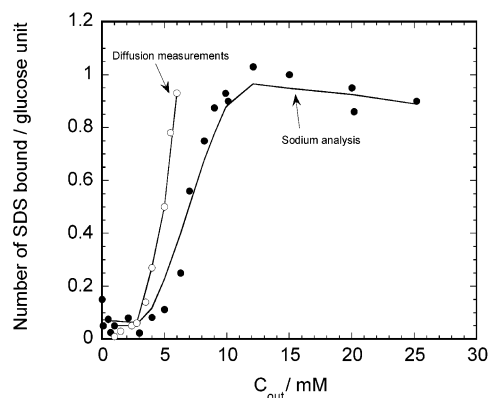
**Saturation Binding.** The plateau level of SDS binding in Figure 2 gives an estimate of the saturation binding of SDS to the EHEC gel. A plateau level of  $1.0 \text{ mol}$  of SDS per glucose unit in EHEC corresponds to  $3.9 \text{ mmol}$  of SDS per gram of EHEC. This compares excellently to the value  $4.0 \text{ mmol}$  of SDS per gram of EHEC obtained from measurements of the binding of SDS to the same batch of EHEC in solution.<sup>22</sup> Moreover, the latter agreement means that it is unlikely that the surfactant binding in our case is restricted to the surface of the gel, as was recently reported for the binding of sodium dodecylbenzenesulfonate (NaDBS) to gels of poly(*N*-isopropylacrylamide).<sup>6,7</sup> We suggest that the inhomogeneous distribution in the latter gels may be related to the much lower cmc (and, presumably, cac) of NaDBS ( $1.2 \text{ mM}$ )<sup>6</sup> or that it is an effect of the higher Krafft temperature of NaDBS, as compared to SDS. The latter effect should give rise to a much slower diffusive transport of NaDBS into the gel.

**Binding Isotherms from Diffusion.** For the EHEC/SDS solutions, surfactant diffusion displays an averaged diffusion coefficient,  $D_{\text{obs}}$ , that simply is the population weighted average of the diffusion coefficients of bound and free surfactant ions:

$$D_{\text{obs}} = p_{\text{b}} D_{\text{b}} + (1 - p_{\text{b}}) D_{\text{f}} \quad (3)$$

where  $p_{\text{b}}$  is the fraction of polymer-bound surfactant, and  $D_{\text{b}}$  and  $D_{\text{f}}$  are the diffusion coefficients for bound and free surfactant, respectively.  $D_{\text{f}}$  should be equal to the diffusion





**Figure 7.** Comparisons between the binding isotherms for SDS in an EHEC gel obtained from NMR self-diffusion measurements and sodium analysis.

coefficient for monomeric  $D_s$ , since the reported data all pertain to concentrations below saturation, where no free SDS micelles should exist.  $D_b$ , on the other hand, is expected to be equal to the diffusion coefficient of the polymer molecules,  $D_p$ . We measured  $D_p$  (data not shown) and found it to be sufficiently slow that the contribution to  $D_{obs}$  (from the term  $p_b D_b$ ) was negligible. Thus, eq 3 may be simplified to

$$D_{obs} = (1 - p_b)D_f \quad (4)$$

Figure 6 shows that the average diffusion coefficients of DS in the gels were quite similar to the diffusion coefficients in the EHEC solutions. This suggests that, to a good approximation, eq 4 should hold also in the gels, with  $D_m$  replacing  $D_{obs}$ . (For the chemically cross-linked EHEC in the gels,  $D_p$  vanishes completely). This implies that the average diffusion coefficients in the gels report on the global fraction of bound DS in the gels, so that  $D_m$  can be used to construct binding isotherms as has been done previously.<sup>15,22</sup> Figure 7 compares the binding isotherm thus obtained from eq 4 (with  $p_b = c_b/c_s$  and  $D_f$  equal to the measured diffusion coefficient for DS in pure  $D_2O$  at the relevant concentration) with the one obtained from the sodium analysis (Figure 2). Although there are quantitative discrepancies between the two isotherms, they clearly show the same trends. Note also that the binding isotherm obtained from the diffusion experiments agrees better with the swelling isotherm in Figure 2.

The diffusion of monomeric surfactant was significantly lower in the gels and EHEC solutions than in the pure surfactant solution, both for DS and for  $C_8E_4$ . The effect is too large to be a simple obstruction effect, caused by the tortuosity of the diffusion paths in a polymer network. Significant obstruction effects are only expected either for much larger diffusing molecules or surfactant micelles.<sup>19,33,34</sup> A possible artifact could be if the diffusion measurements of SDS in pure water were affected by convective flow in the NMR tubes, an effect that effectively enhances the measured mean square displacement and thus gives a higher apparent diffusion coefficient.<sup>27</sup> A third possibility is that there exist some very hydrophobic environments on the irregularly substituted EHEC molecules, with the capacity to bind individual surfactant ions prior to the cooperative binding of micellized SDS. Other studies have pointed to a weak surfactant binding to EHEC prior to the cac.<sup>22,35</sup> We note that the concentration of such "early bound" surfactant molecules is still very small; binding isotherms obtained from the diffusion coefficients (cf. Figure 7) yield  $c_b < 1$  mM at the cac of SDS. This low concentration would escape unnoticed in

many measurements, such as the sodium measurements (Figure 2), since it is of the order of the experimental uncertainty.

**Anomalous Diffusion.** The most novel observation in this work is undoubtedly the distribution in diffusion coefficients of surfactant molecules in the chemically cross-linked gel. In a polymer solution, the diffusion of the polymer molecules becomes slower at concentrations well above the overlap concentration and, more importantly, since all polymers are more or less polydisperse, the diffusion coefficient depends more strongly on the molecular weight of the polymer.<sup>33,36</sup> Normally,  $D = KM^{-\nu}$ , where  $K$  is a constant and  $\nu$  can vary between 0.5 and 2 depending on the concentration and/or molecular weight. For a distribution in molecular weights it is not surprising that a wide distribution in diffusion coefficients is obtained, because of the strong molecular weight dependence.

Nonlinear echo decays have been found also in solutions of strongly associating water-soluble polymers of the hydrophobically modified type. The deviation from linearity is strongly dependent on the concentration of the polymer. This effect has been demonstrated both for polydisperse systems<sup>37</sup> and for model polymers with a low polydispersity index.<sup>38</sup> Although the exact nature of this phenomenon is unresolved, the results indicate that it is related to the fact that the solution shows a network-like character due to the strong intermolecular interactions leading to polymer association.

To our knowledge, anomalous diffusion has not previously been observed for surfactants diffusing in polymer networks. Previous NMR self-diffusion studies of surfactant diffusion in mixed solutions of associating polymer/surfactant pairs have all shown normal Gaussian behavior,<sup>21,22,38,39</sup> as was indeed found also in the present study for the non-crosslinked EHEC. The simplest explanation of the anomalous diffusion is that the chemical cross-linking induces inhomogeneities in the polymer network on a length scale that is at least comparable to the mean displacement of the surfactant molecules during the NMR experiment. The correlation between the surfactant binding isotherm and the spread in diffusion coefficients is interesting; it indicates that significant binding of the surfactant is necessary for the non-Gaussian behavior to occur. One may imagine a direct effect of surfactant binding (such as an inhomogeneous distribution of bound surfactant molecules in the gel), but also an indirect effect; surfactant binding induces a swelling of the gel (Figure 2), and a chemical gel has been shown to be more inhomogeneous when swollen than at the volume where the cross-linking reaction was performed.<sup>40,41</sup>

For an estimate of the size of the inhomogeneities, we may assume that the mean square displacement of DS molecules in the gel is given simply by  $\langle z^2 \rangle = 2D\Delta$  as would be the case for Gaussian diffusion. The median DS diffusion in the gel was  $10^{-10}$  m<sup>2</sup>/s, and the longest diffusion time used in the experiments was 1000 ms. That is, the longest root-mean-square displacement travelled by the surfactants is of the order of 10  $\mu$ m. On the other hand, the gels were quite transparent, giving no indication of heterogeneities on this length scale. One should, however, bear in mind that even the average concentration of polymer is quite low in the swollen gels.

At this stage we should remark that our analysis in terms of a log-normal distribution has a simple physical interpretation only for a system that really consists of a distribution of domains, each characterized by a different but Gaussian DS diffusion, between which the surfactant exchange is slow on the time scale of the experiment. A simple example would be domains differing in polymer concentration, and thus in  $p_b$  (cf. eq 3). We doubt, however, that this is a realistic description of

our system. One obvious problem is the rapid "tail" in the apparent distribution of diffusion coefficients (cf. Figure 4, especially for the large values of  $\Delta$ ). Domains where the diffusion is faster than that of monomeric DS, i.e.,  $5 \times 10^{-10}$  m<sup>2</sup>/s, are hard to account for, and at this stage we cannot exclude the possibility that the rapid tail is simply an artifact of the assumed functional form of the distribution in diffusion coefficients. However, we note that computer simulations and theory development both have shown that so-called super diffusion can occur in systems with fractal dimensions.<sup>42</sup> Interestingly, super diffusion arises as a consequence of a tail of fast-moving components in a distribution.

A second problem concerns the observation that the width of the distribution in diffusion increases with increasing  $\Delta$  while  $D_m$  remains invariant. At present, we have no model that can predict this behavior. Clearly, at sufficiently long time scales, the diffusion has to become Gaussian. This means that the variation of  $\sigma$  with  $\Delta$ —if  $\Delta$  could be made sufficiently long—would have to be nonmonotonic.

Finally, we should consider the possibility of artifacts due to the way in which the samples were prepared, i.e., by letting surfactant molecules diffuse into the gels from an outside reservoir. A too short soaking time would result in a nonhomogeneous distribution of surfactant into the gel, and the remaining macroscopic concentration gradients would give rise to a net flow of surfactant in the gel. However, several arguments independently make this explanation unlikely. First and foremost, our experience on the time required to reach swelling equilibrium for these particular gels, as well as independent estimates of the surfactant transport, indicate that the soaking time should be sufficient, certainly for the lower concentrations. For instance, calculations for the sample displayed in Figure 4, using the relevant expressions for diffusion into a cylinder with  $D = D_m$  in the gel,<sup>43</sup> indicate that 4 days of soaking in an unstirred solution would be sufficient to yield a homogeneous surfactant concentration to within 0.1% accuracy in the gel. Second, if there were any concentration gradients, these would be expected to be essentially radial. The NMR experiment is insensitive to radial flow, since the axial displacement is measured. Third, it is difficult to reconcile the observation that  $D_m$  is independent of  $\Delta$  with a flow-term in the diffusion.

## Conclusions

Both in EHEC gels and in EHEC solutions a decreased diffusion of a binding surfactant occurs above the cac, reflecting the formation of polymer-bound surfactant micelles. The main difference between the gels and the solutions is that above cac, the surfactant diffusion in the gel is non-Gaussian on the time scale of the NMR diffusion experiment, most probably as a result of inhomogeneities in the gel on long length scales. A detailed interpretation of the observed behavior cannot be made at this stage. Similar experiments on simpler gels, based on surfactant-binding homopolymers (such as poly(*N*-isopropylacrylamide)), might shed additional light on our observations.

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