Interactions between Poly(N-vinylformamide) and Sodium Dodecyl Sulfate As Studied by Fluorescence and Two-Dimensional NOE NMR Spectroscopy
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The interactions between water-soluble polymers and surfactants have been extensively studied for more than four decades. The mixed polymer/surfactant systems are of interest not only because of many prevalent and hopeful applications such as pharmaceutical formulation, food products, detergency, paints and inks, improved oil recovery, etc., but also because of the nature of interaction between the polymer and surfactant, especially the issue concerned about the concentration far below the regular critical micelle concentration (cmc) of surfactant.

N-vinylformamide (NVF) has been able to commercially produced lately. The NVF-based polymers have been considered as possible substitutes for the polymers, which are made from the acrylamide (AA) that is now widely known as a possible carcinogen. Besides, NVF is easily polymerizable and copolymerizable with other acrylic monomers by means of conventional free radical polymerization. Additionally, poly (vinylamine) can be simply prepared through acidic or basic hydrolysis of PNVF. NVF-based materials have been proved applicable for some industrial fields to be taken in many applications, such as inorganic oxide hybrid materials, papermaking, coating slips, petroleum recovery, hair care, and the drag reducing polymers. Moreover, fundamental researches about NVF are of interest recently. However, no study about the interactions between PNVF and anionic surfactant SDS has been reported.

In the present study, we investigate the interaction between water-soluble and uncharged PNVF and the anionic surfactant SDS in terms of pyrene fluorescence and the 2D NOESY experiments. In addition, the correlation between the bulk solution properties obtained from pyrene fluorescence and the cooperative association behavior of surfactant to the polymer chain, which could be obtained using the 2D NOESY, is the main purpose of this study. As seen in figure 1, the cmc of SDS is about 8 mM in the absence of PNVF. Above the cmc of SDS, the $I_E/I_M$ values are between 1.1 and 1.2 which are consistent with the reported literature. The location and distribution of pyrene molecules in the solution can be obtained from the $I_E/I_M$ ratios. For the pure SDS solution in figure 1b, as [SDS] are lower than the cmc of SDS, the $I_E/I_M$ ratios maintain a value ($\approx 0.011$) and do not change with [SDS]. As the [SDS] just higher than the
cmc of SDS, pyrene molecules are solubilized into the SDS micelles. At the same concentrations, the $I_E/I_M$ ratio reaches the peak value as observed ($= 0.025$). After that, the number of SDS micelles drastically increases as SDS is continuously added into solution, but the total pyrene concentration in the solution remains the same ([pyrene] = $1.0 \times 10^{-6}$ M). Therefore, the pyrene molecules are averagely dispersed in a large number of micelles, leading to that the $I_E/I_M$ ratios drop to the low values again.

![Graph showing correlation between $I_1/I_3$ and $I_E/I_M$ of pyrene solubilized in water, 3 g/L PNVF, and 5 g/L PNVF aqueous solutions and concentration of SDS.](image)

Fig 1. Correlation pictures between (a) $I_1/I_3$ and (b) $I_E/I_M$ of pyrene solubilized in water (◇), 3 g/L PNVF (△), and 5 g/L PNVF (●) aqueous solutions and concentration of SDS. The cac of SDS (ca. 3 mM) in the presence of PNVF is taken as the onset of the plateau in region II.

The correlation plots between the $I_1/I_3$ ratios of PNVF/SDS and [SDS] could be divided into three regions. In region 1, the $I_1/I_3$ ratios are independent of [SDS] and maintain a low value about 1.7. As [SDS] higher than 0.4 mM, $I_1/I_3$ ratios begin decreasing slowly. Obviously, the $I_1/I_3$ ratios of 5 g/L PNVF solution which are between 0.075 and 0.095 are larger than the ones of 3 g/L PNVF solution (= 0.050). Besides, the PNVF/SDS solutions have higher $I_E/I_M$ ratios but lower $I_1/I_3$ ratios than the pure SDS.
solution. It indicates that dissolved PNVF chains form the microdomains which are less polar than the bulk water phase. Further, the $I_E/I_M$ ratios of the PNVF/SDS solutions are larger than the ones for pure SDS solution at the cmc of SDS. It indicates that more pyrene molecules can be solubilized into the polymer coils than into the polymer-free SDS micelles.

Figure 2. $^1$H-$^1$H 2D NOESY spectra for the PNVF/SDS/D$_2$O solutions at 1 mM (a), 6 mM (b), and 10 mM (c) of SDS. The mixing time is 800 ms, and the contour levels in the spectra are linearly spaced. The cross-peaks are in phase with the diagonal peaks. (d) The cross section taken at S3~11 along the $\omega_2$ from each 2D spectrum. The cross-peaks shown in the 2D spectra and 1D cross sections clearly indicate that alkyl protons of SDS are in close contact (<0.5 nm) with polymer chains.

According to the figure 2a, there is no cross-peak between PNVF and SDS, showing that at [SDS] = 1 mM which is the midpoint of the first $I_1/I_3$ reduction in region I, the SDS molecules don’t approach (within 0.5 nm) the polymer chains closely. At the same time, SDS molecules probably start to form aggregates, but it is not necessarily that PNVF-SDS aggregates form at the low [SDS]. The results are similar to the PVP/SDS system, in which the reduction of the $I_1/I_3$ ratio starta at [SDS] below the accepted cac. Up to now, there is no proper explanation.
Figure 3. (a) An illustration of the complex structure of PNVF-induced SDS aggregate. (b) An illustration of the structure of a spherical SDS micelle. (c) Visualization of the possible structure (right) of surfactant molecules in the vicinity of the PNVF as deduced from the cross-relaxation effects in the 2D NOESY spectra (left). The 1D spectrum above the 2D spectrum is the cross section at S12 in the $\theta_2$ dimension. The cross-peak between S12 and S1 is due to the intermolecular interaction of the SDS molecules.

In figure 3a, we propose the structure of SDS aggregates bound on the PNVF chains as a result of the cross-relaxation obtained by the 2D NOESY experiments. First, the SDS alkyl chain in the PNVF-SDS aggregates is more curly than in the pure SDS micelle in figure 3b. The sulfate group is away from the polymer chain because no correlation between S1 and polymer protons is seen in the 2D NOESY spectra. Because of the curled alkyl chain of SDS and perturbational polymer chain, the curled alkyl chain of SDS is partially associated with polymer chain. We except the sulfate head groups are not closely packed and not forming a spherical surface, which is like that of the pure SDS micelle. The PNVF-induced SDS aggregate has a ragged surface with water. In other words, some SDS molecules protrude into the bulk water phase and some with curly alkyl chains are closer to the polymer chain. As showed in figure 3c, the supramolecular structure of PNVF-SDS complex, the folded conformation of SDS leads to the intermolecular cross relaxation between S12 and S1, which is observed in the 2D NOESY spectra ([SDS] = 6 and 10 mM).