(acetophenone), is 873.

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Supplementary Material Available: Tables of the effect of sodium bromide, sodium acetate, perchloric acid, and temperature on the rate of reaction of 2,4,6-trimethylacetophenone and bromine (4 pages). Ordering information is given on any current masthead page.

Surfactant–Polymer Interactions and Their Effects on the Micellar Inhibition of the Neutral Hydrolysis of 1-Benzoyl-1,2,4-triazole

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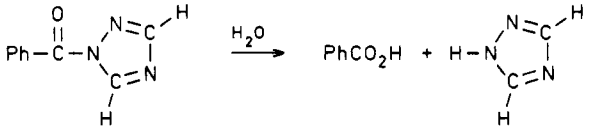
Abstract: Binding of sodium dodecyl sulfate (SDS) to atactic poly(*N*-vinylpyrrolidone) (PVP) has been studied by conductivity measurements. It is proposed that in addition to normal micelles of SDS an additional pseudophase of mixed micelles of PVP and SDS is present in solution. The effect of polymer–surfactant binding on the catalytic/inhibitive activity of SDS micelles has been investigated by studying the rates of the pH-independent hydrolysis of 1-benzoyl-1,2,4-triazole (**1**). Though the polymer itself has no effect on the hydrolysis reaction in water, addition of PVP to SDS solutions decreases the micellar inhibition, and pseudo-first-order rate constants (k_{obsd}) are higher than those in the absence of PVP. Ultrafiltration experiments using a model substrate indicate increased solubility of the substrate in the micellar pseudophase upon addition of PVP. On the basis of the enzyme model of micellar catalysis, a kinetic scheme is presented to explain the observed rate effects. It is argued that the microenvironment at the binding sites of the mixed micelles of SDS and PVP is more polar than that at the binding sites of unperturbed micelles. Comparative studies with *N*-isopropylpyrrolidone (*N*-iPP) reveal the basic differences in the interaction of micelles with a macromolecule and with a polar additive of low molecular weight.

The formation of complexes between surfactants and nonionic, water-soluble polymers has already been recognized more than two decades ago.[1] These mixed systems find application in tertiary oil recovery[2] and also serve as model systems to understand the interactions between a biomacromolecule (such as protein) and a biological membrane. Measurements of a physical property such as conductivity[3a-d] or surface tension[3a,c,e] of the surfactant–polymer mixture in solution indicate that the surfactant binds to the polymer forming a polymer–surfactant complex. This binding is cooperative. It increases with increasing hydrophobicity of the polymer[4a] and the surfactant molecule.[3c,4b] However, the charge on the head group[4b] and the nature of the counterion of the surfactant molecule[4c,d] also affect the binding process significantly. Viscosity measurements[3a,b] suggest that these complexes behave as polyelectrolytes in aqueous medium. Attempts have been made to study the molecular structure of these complexes by NMR[5a,b] and ultrasonic relaxation spectroscopy,[6] light scattering,[7] and pressure-jump relaxation kinetics.[8] These studies have led to the idea that the complexes are formed by incorporation of micelles along the polymer chain, and they have been described as micellar clusters or mixed micelles. The thermodynamics of these mixed micelles have been discussed by Nagarajan[9a] and by Gilanyi and Wolfram.[9b] In spite of all these efforts, a well-defined picture of the structure of the polymer–surfactant complexes and the nature of the interactions involved in complex formation is yet to emerge. Also, no studies have been reported on the effect of the polymer on the catalytic/inhibitive activity of the micelles. This is surprising in view of the worldwide interest in micellar effects on chemical reactions. Herein we report a first example of the effect of a water-soluble polymer (atactic poly(*N*-vinylpyrrolidone), PVP) on the inhibition of a reaction by micelles of sodium dodecyl sulfate (SDS).

The reaction chosen is the neutral hydrolysis of 1-benzoyl-1,2,4-triazole (**1**) in water. The reaction is pH independent in the range pH ~3–5 and involves water-catalyzed nucleophilic attack of water at the amide carbonyl.[10]



This reaction is sensitive to the polarity of the reaction medium and hence is useful to probe the local microenvironment at the binding sites of the micelles[11] and of the surfactant–polymer complexes.

Before presenting the kinetic results, we will demonstrate the presence of SDS/PVP complexes in aqueous solution as revealed by conductivity measurements.[12]

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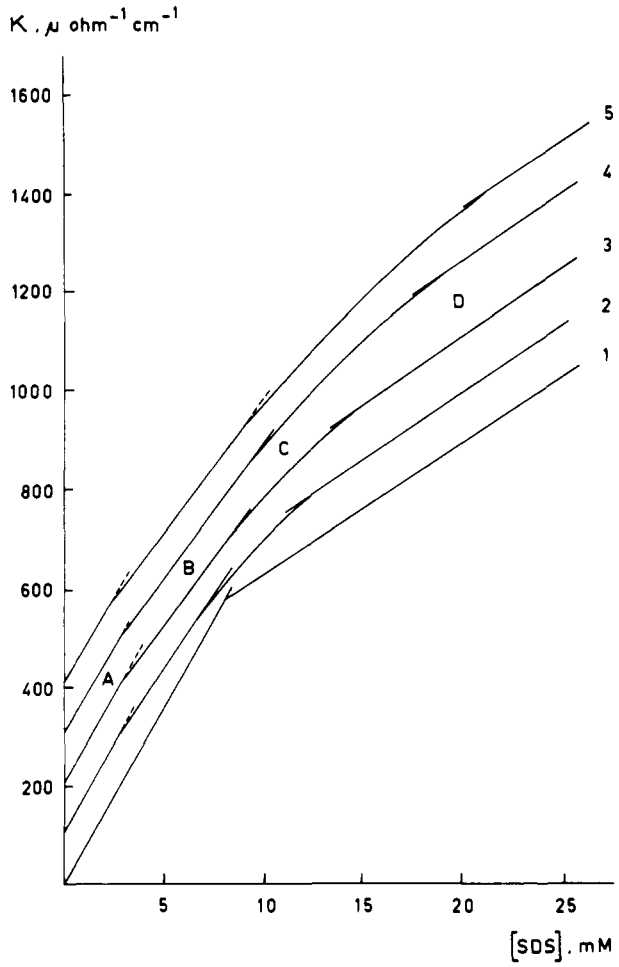

Figure 1. Plot of the specific conductivity vs. concentrations of SDS at fixed concentrations of PVP: (1) 0.0 g dL^{-1}; (2) 0.1 g dL^{-1}; (3) 0.3 g dL^{-1}; (4) 0.5 g dL^{-1}; (5) 0.6 g dL^{-1}. Curves 2–5 have been displaced upward relative to curve 1 by 1, 2, 3, and 4 scale units (100 $\mu\Omega^{-1}$ cm^{-1}), respectively.

Results and Discussion

Conductivity Measurements. Figure 1 shows the changes in specific conductivity (κ) of the solution as a function of SDS concentration at various fixed concentrations of PVP. Although at a first glance the plots exhibit the presence of two breaks or three regions, as has been reported previously by Fishman and Eirich,[3b] a closer look reveals the presence of three breaks or four regions. A typical plot (Figure 1) shows an initial linear increase in κ with increasing SDS concentration up to 3 mM SDS (region A). After a break at this concentration, the conductance increases linearly with SDS concentration (region B) but with a smaller slope than that in region A. The linearity of the plot in the region B is lost in region C. Upon a further increase in the SDS concentration the plot becomes linear again in the region D. The amount of SDS required to reach the regions C and D depends on the PVP concentration. It is observed that the conductance of the solution decreases in region B and increases in region D on increasing the concentration of PVP at a fixed SDS concentration. However, the values of the slopes do not vary appreciably. The value of α or the approximate degree of ionization, which is given by the ratio of the slope in region B or D to that in region A[13] (0.74 ± 0.02 for region B and 0.36 ± 0.01 for region D), is practically independent of polymer concentration. Also, the α value for region D is practically the same as that observed for a solution containing solely SDS.

The above observations can be rationalized in the following way. Region A consists of free surfactant monomers that are completely dissociated. The constancy of the first break at 3 mM, independent of PVP concentration (up to 0.5 g dL^{-1}), as well as a constant value of α in region B indicates a process similar to micellization. We propose that the formation of SDS–PVP complexes takes place in this region. The high value of α (0.74) compared to that for pure SDS (0.36) may be taken as evidence that the SDS aggregation number of these mixed micelles is smaller than that of the unperturbed micelles, as suggested previously.[9b,13]

Following Gilanyi and Wolfram,[9b] the formation of mixed micelles may be described by the association constant

$$K_{M_1} = \frac{[M_1]}{[P][DS^-]^{m_1}[Na^+]^{n_1}} \quad (1)$$

where $[M_1]$ is the concentration of mixed micelles, $[P]$ is the concentration of binding sites on the polymer, m_1 is the aggregation number of the mixed micelles, and n_1 is the number of bound Na^+ counterions.

According to eq 1 an increase in polymer concentration at a fixed SDS concentration will cause a decrease in the concentration of free ions in the solution. This would then explain the lowering of the conductivities with increasing polymer content in region B.

The second break represents the onset of the formation of unperturbed micelles of SDS in competition with the mixed micelles of PVP and SDS (region C). The formation of normal micelles is described by the association constant of micellization:

$$K_M = \frac{[M]}{[DS^-]^m[Na^+]^n} \quad (2)$$

where M represents the normal micelles, m is the aggregation number, and n is the number of bound counterions.

When all the binding sites on the polymer are saturated with the surfactant, a third break appears and a further increase in SDS concentration now only increases the concentration of unperturbed micelles (region D). Since the mixed micelles are also present in the solution and the α value for mixed micelles is higher than that for unperturbed micelles, the concentration of free counterions will be higher in the presence of PVP than in its absence. Since the concentration of mixed micelles increases with the amount of PVP in solution, the conductance of the solution in the region D will increase with polymer concentration at a fixed concentration of SDS. Thus the detailed dependence of the specific conductivity upon SDS concentration will depend on the equilibrium concentrations of various species present in the solution.

N-Isopropylpyrrolidone (*N*-iPP, a model for a monomeric unit in PVP) and SDS show quite different interactions from those between PVP and SDS. Figure 2 shows the changes in specific conductivity (κ) as a function of SDS concentration in the presence of *N*-iPP. The addition of *N*-iPP causes a decrease of the cmc and an increase of α, and these effects increase with increasing concentration of *N*-iPP. The effect of *N*-iPP on the micelles of SDS is similar to that caused by addition of small polar molecules like alcohols.[14] Quite generally, adsorption of a small molecule like *N*-iPP near the head groups of the micelle causes a decrease in head group repulsions, leading to a decrease of the cmc. As anticipated,[14] the plot of cmc vs. concentration of *N*-iPP is linear (Figure 3). Since the addition of *N*-iPP will cause a decrease in surface charge density of the micelle, the increase of α can be readily rationalized.

Effect of PVP on the Micellar Rate Effects. In view of the results discussed in the previous section, one could expect that the interactions between the SDS micelles and PVP would modify the catalytic/inhibitive effects of the micelles. This was borne out in practice by using the neutral hydrolysis of 1-benzoyl-1,2,4-triazole as a model reaction (vide supra). At the outset, it

(12) The SDS–PVP system has been studied previously by conductometry (see ref 3b). In view of our kinetic results and the large difference in the molecular weight of the polymer used in the previous study and by us, we have reinvestigated the system.

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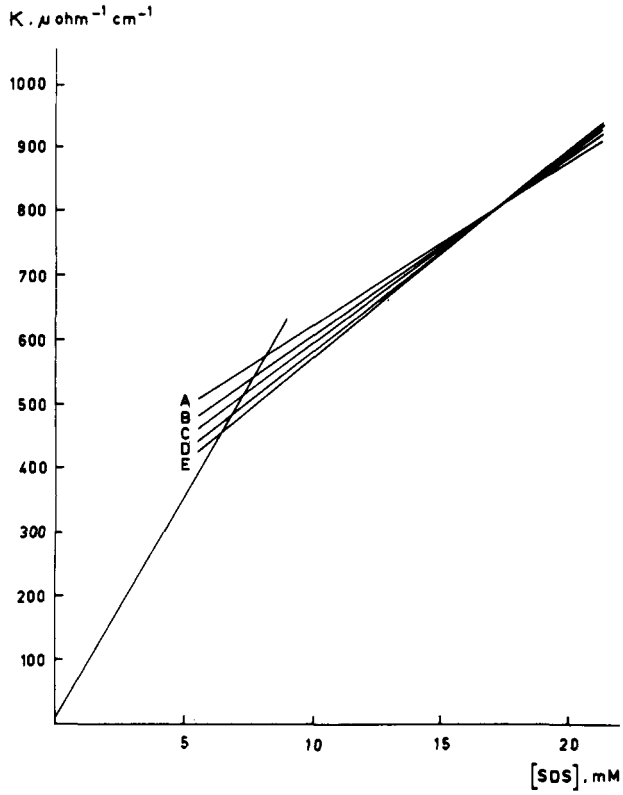


Figure 2. Plot of the specific conductivity vs. concentrations of SDS at fixed concentrations of *N*-iPP: A, 0 mM; B, 10 mM; C, 20 mM; D, 30 mM; E, 40 mM.

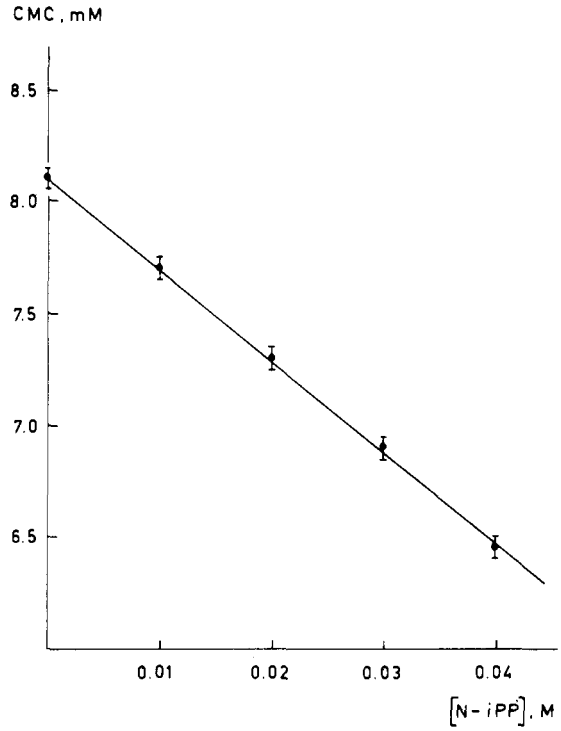


Figure 3. Plot of the cmc of SDS vs. concentration of *N*-iPP.

was observed that the pseudo-first-order rate constants (k_{obsd}) for the reaction in water were not affected by the addition of PVP at least up to 1 g dL^{-1}. In SDS solutions the reaction is inhibited because of binding of the substrate at the micellar Stern region where the local micropolarity is lower than that of bulk water.[11] Addition of PVP to the surfactant solution induces a significant effect on the micellar inhibition. The observed rate increases compared to that in pure SDS solution, clearly the polymer inhibits micellar inhibition.

Table I. Pseudo-First-Order Rate Constants ($10^4 k_{obsd}$, s^{-1}) for the Neutral Hydrolysis of **1** in Aqueous Mixtures Containing SDS and PVP at 25 °C

[SDS], M	[PVP], g dL^{-1}					
	0.0	0.1	0.2	0.3	0.4	0.5
0	20.9	20.9	20.9	20.9	20.9	20.9
0.011	18.5	19.2	19.4	19.1	18.9	18.9
0.020	13.6	14.5	15.6	16.4	16.7	16.7
0.030	10.6	11.1	11.7	12.2	12.8	13.6
0.041	8.77	9.35	9.68	10.1	10.5	11.2
0.050	7.65	7.92	8.34	8.60	8.91	9.08
0.060	6.73	6.96	7.09	7.42	7.61	8.04
0.086	5.49	5.52	5.63	5.75	5.95	6.32
0.110	4.78	4.91	5.04	5.13	5.21	5.31

Table II. Binding of 1-Phenacyl-1,2,4-triazole (**2**) to SDS Micelles in the Absence and Presence of PVP and *N*-iPP at 25 °C

[SDS], M	f_w,[a] SDS	f_w,[a] SDS + 0.1 g dL^{-1} PVP	f_w,[a] SDS + 0.03 M *N*-iPP
0.04	0.497	0.353	0.548
0.05	0.428	0.326	0.504
0.06	0.372	0.300	0.436
0.08	0.305	0.255	0.379
0.10	0.253	0.226	0.319

[a] Fraction of **2** in the aqueous pseudophase as determined by ultrafiltration experiments.

The polymer effect on k_{obsd} was found to depend on the polymer concentration. At low concentration of SDS ($\leq 2 \times 10^{-2}$ M) the rate first increases with added PVP and then reaches a limiting value, which is still lower than that in bulk water. At higher SDS concentration ($\geq 3 \times 10^{-2}$ M) the rate continues to increase with increasing polymer concentration (Table I).

For low SDS concentration (region C in Figure 1) it has been suggested that individual SDS molecules bind along the polymer chain or a few SDS molecules form small clusters on the polymer chain, thereby converting the polymer into a polyelectrolyte.[3b] The rates would then respond to the presence of a polyelectrolyte in the solution, leading to a positive salt effect on the reaction. However, the rates are much lower than expected for electrolyte solutions of comparable concentrations.[10] Moreover, it has been observed that the presence of a polyelectrolyte such as highly dissociated polymethacrylic acid has very little effect on reactions of this type.[15] Thus the hydrolysis rates observed in this region lend support to our interpretation of the conductivity data (vide supra), namely, region C consists of polymer–surfactant complexes in equilibrium with normal micelles, the equilibrium shifting toward the formation of mixed micelles upon increasing polymer concentration.

Two major possibilities can be invoked to explain the observed effect of polymer on the micellar inhibition. First, the polymer may compete with the substrate for binding to the micelle. This would result in the transfer of the substrate from the micellar pseudophase into the aqueous phase and a concomitant overall increase in k_{obsd}. A second possibility is that the micropolarity at the substrate binding sites would be increased upon interaction of the micelles with the polymer.

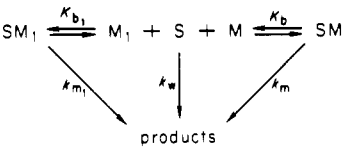
The first possibility for the rate enhancement can be ruled out on the basis of ultrafiltration experiments using a model substrate, 1-phenacyl-1,2,4-triazole (**2**), structurally closely related to **1** but not prone to hydrolysis under the employed reaction conditions. No binding of the model substrate to PVP was observed in the absence of SDS. The results listed in Table II clearly indicate that the solubility of the substrate in the micellar pseudophase *increases* upon the addition of PVP. These results are consistent with previous observations on the solubilization of hydrophobic substrates in surfactant–polymer mixtures.[16a,b] Thus it appears

(15) Jager, J.; Engberts, J. B. F. N., to be published.

Table III. Pseudo-First-Order Rate Constants ($10^4 k_{obsd}$, s^{-1}) for the Neutral Hydrolysis of **1** in Aqueous Mixtures Containing SDS and *N*-iPP at 25 °C

[SDS], M	[*N*-iPP], M					
	0.00	0.01	0.02	0.03	0.04	0.05
0.000	20.9	20.9	20.9	20.9	20.9	20.9
0.030	10.8	11.2	11.5	11.8	11.9	12.1
0.040	8.74	9.39	9.79	10.1	10.2	10.4
0.050	7.51	8.14	8.52	8.82	8.95	9.26
0.060	6.76	7.22	7.63	7.90	8.10	8.17
0.086	5.49	5.90	6.25	6.39	6.57	6.93
0.110	4.67	4.96	5.21	5.40	5.62	5.87

Scheme I



that the micropolarity experienced by the substrate in the micellar pseudophase is increased upon binding of PVP.

For comparison the effect of *N*-iPP on the micellar inhibition has also been studied. It is found that addition of *N*-iPP to SDS solution also causes an increase in k_{obsd} (Table III). However, the effect of *N*-iPP on the micellar inhibition is qualitatively quite different from that of the polymer. In this case the ultrafiltration experiments with model substrate (**2**) in the presence of *N*-iPP reveal that the solubility of the model substrate in the micellar pseudophase is *decreased* in the presence of *N*-iPP (Table II). Thus the rate increments observed for this additive can be readily explained by assuming transfer of the substrate from the micellar pseudophase into the bulk aqueous phase. Similar qualitative and quantitative differences between the interactions of the surfactant with monomeric and polymeric molecules have been observed by Zana and co-workers[13] in their fluorescence studies on the SDS–PVP system.

By taking into account the results of the conductivity and ultrafiltration experiments a kinetic scheme (Scheme I) has been developed based on the enzyme model of micellar catalysis[17] to explain the inhibitive effect of PVP on the micellar inhibition of hydrolysis of **1**. Herein S represents the substrate, M and M_1 are the unperturbed and mixed micelles, respectively; k_m and k_{m_1} are the respective micellar rate constants and K_b and K_{b_1} are the corresponding binding constants for the binding of the substrate to the unperturbed and the mixed micelles, respectively.

We propose that the SDS–PVP micelles are present in the solution as a pseudophase different from that of unperturbed SDS micelles. The substrate will then be distributed between mixed micelles, unperturbed micelles, and water.

The fraction of substrate present in bulk aqueous phase (f_w) is given by

$$f_w = 1 - \frac{K_b c m^{-1} + K_{b_1} c_1 m_1^{-1}}{1 + K_b c m^{-1} + K_{b_1} c_1 m_1^{-1}} \quad (3)$$

and the ratio of the fraction of substrate bound to the micellar (unperturbed and mixed micelles) pseudophase (f_b) to f_w is given by

$$\frac{f_b}{f_w} = K_b c m^{-1} + K_{b_1} c_1 m_1^{-1} \quad (4)$$

where m_1, m, K_{b_1}, and K_b have the same meaning as in eq 1 and 2 and in Scheme 1, c_1 is the concentration of SDS bound to the polymer, c is the concentration of SDS forming the unperturbed micelles (and equals $c_o - c_f - c_1$ where c_o is the total SDS concentration and c_f is the monomer concentration of SDS).

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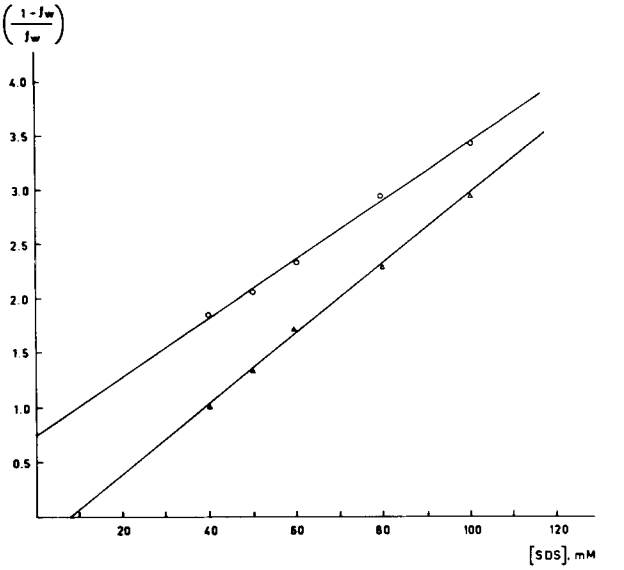

Figure 4. Plot of $(1 - f_w)f_w^{-1}$ vs. concentration of SDS: (△) pure SDS; (○) SDS solutions containing 0.1 g dL^{-1} of PVP.

Table IV. Experimental and Calculated Pseudo-First-Order Rate Constants for the Neutral Hydrolysis of **1** in Aqueous SDS Solutions Containing 0.5 g dL^{-1} of PVP

[SDS], M	c, M	c_1, M	f_b[a]	f_w[a]	$10^4 k_{obsd}$, s^{-1}, calcd[b]	$10^4 k_{obsd}$, s^{-1}, obsd
0.011	0.000	0.008	0.242	0.758	18.4	18.9
0.020	0.000	0.017	0.405	0.595	16.7	16.7
0.030	0.010	0.017	0.545	0.454	13.2	13.6
0.041	0.021	0.017	0.639	0.361	10.8	11.2
0.050	0.030	0.017	0.691	0.309	9.47	9.08
0.060	0.040	0.017	0.734	0.266	8.39	8.04
0.086	0.066	0.017	0.805	0.195	6.60	6.32
0.110	0.090	0.017	0.843	0.157	5.65	5.31

[a] Calculated by using eq 3, $K_{b_1} m_1^{-1} = 40$, $k_{m_1} = 1.05 \times 10^{-3}$ s^{-1}, $K_b m^{-1} = 52$, $k_m = 1.68 \times 10^{-4}$ s^{-1}, $c_f = 3.10^{-3}$ M. [b] Calculated by using eq 9.

In the range of SDS concentration where all the binding sites on PVP are saturated (region D in Figure 1) the factor $K_{b_1} c_1 m_1^{-1}$ in eq 4 will be constant. Equation 4 may then be written as

$$f_b/f_w = K_b(c_o - c_f - c_1)m^{-1} + C \quad (5)$$

In eq 5 the concentrations c_f and c_1 will also be constant. Thus, at a fixed PVP concentration, a plot of $f_b f_w^{-1}$ against c_o will be a straight line with a slope of $K_b m^{-1}$. Such a plot is shown in Figure 4. The data for substrate binding were obtained from ultrafiltration experiments using model substrate **2** at a fixed PVP concentration of 0.1 g dL^{-1}. The slope of the linear plot amounts to 27.5 M^{-1} and is close to that observed in the absence of PVP (32 M^{-1}). Apparently, the structure of SDS micelles is not greatly affected by the presence of mixed micelles in the same solution.

According to Scheme I, the distribution of the substrate will take place following eq 3 and 4 and the reaction will then occur in both pseudophases and in water with rate constants k_{m_1}, k_m, and k_w, respectively. The rate constant of the overall reaction (k_{obsd}) is given by

$$k_{obsd} = f_m k_m + f_{m_1} k_{m_1} + f_w k_w \quad (6)$$

where f_m and f_{m_1} represent the fraction of the substrate present in the unperturbed and in the mixed micelles, respectively. The fractions f_m and f_{m_1} can be obtained from

$$f_m = K_b f_w c m^{-1} \quad (7)$$

$$f_{m_1} = K_b f_w c_1 m_1^{-1} \quad (8)$$

Substituting the values for f_m and f_{m_1} in eq 6 and rearranging give

$$k_{obsd} = K_b k_m c^* m^{-1} f_w + c_1 f_w (K_{b_1} k_{m_1} m_1^{-1} - K_b k_m m^{-1}) + k_w f_w \quad (9)$$

where $c^* = c_o - c_f$.

Using the rate constants in the low SDS concentration region ([SDS] = 0.011 and 0.020 M; [PVP] = 0.5 g dL^{-1}) where the rates level off (Table I), and assuming that all SDS molecules above the cmc (3 mM) are bound to the polymer in this region, values for $K_{b_1}m_1^{-1}$ and k_{m_1} were estimated.[18] Taking the values for K_bm^{-1} and k_m from the rate data in the absence of PVP,[11] k_{obsd} values were calculated by using eq 9 and are listed in Table IV. The agreement between the calculated and observed rate constants is quite satisfactory and substantiates the validity of the kinetic analysis.[19]

Although a higher degree of binding of the hydrophobic substrates is observed in the presence of PVP, eq 3 and 4 and the estimated values of K_{b_1} and K_b indicate that the PVP–SDS complexes do not necessarily have a higher binding capacity than the unperturbed SDS micelles. The reason for increased solubility is that the addition of PVP causes a decrease of the cmc and an increase in overall concentration of micelles. This is in accord with the observation that the solubility effects are more marked at low SDS concentrations (Table II) than at high SDS concentration where the changes in cmc do not greatly affect the overall micellar concentration.

A comparison of micellar rate constants k_m and k_{m_1} indicates that the microenvironment at the binding sites of the SDS–PVP complexes is more polar or water penetrated than that at the binding sites of unperturbed micelles. These conclusions are consistent with those of Zana and co-workers.[13] Apparently, the presence of the polymer diminishes head group repulsions between the detergent molecules in the aggregate, thereby reducing the cmc. *This combination of a decrease in cmc with an increase in surface polarity is an interesting phenomenon, usually not attainable solely by variation of the structure of the surfactant.*

The above picture of PVP–SDS complexation contrasts with the description of poly(ethylene oxide)–SDS complexes given by Cabane.[5a] In his model the polymer segments wrap around the micelles (or adsorb near the head groups) to form mixed micelles. Such a wrapping process would render mixed micelles more hydrophobic instead of hydrophilic than normal micelles. Although an unambiguous distinction between both complexation modes cannot be made solely on the basis of our rate data,[20] it appears to us that the formation of PVP–SDS complexes occurs due to a combination of (i) hydrophobic interactions between the surfactant tails and hydrophobic domains in the polymer coils and (ii) electrostatic interactions between the polar amide function of the pyrrolidone ring and the charged surfactant head groups.

The difference between Cabane's and our model for polymer–surfactant complexation is probably due to differences in the binding modes which may occur because of the differences in the structure and hydrophobicities of the two polymers. Further studies are in progress to obtain a more detailed description of the structure and reactivity of surfactant–polymer complexes.

Experimental Section

Materials. 1-Benzoyl-1,2,4-triazole (**1**, mp 72.1–72.5 °C) and 1-phenacyl-1,2,4-triazole (**2**, mp 114.4–115 °C) were prepared by literature methods.[10] SDS was purified by a standard method.[22] *N*-Isopropylpyrrolidone (G.A.F. Corp., New York) was distilled twice under reduced pressure (bp 59 °C/0.001 mm). Poly(vinylpyrrolidone) (Kolloidon-90, BASF) was fractioned by dissolution in chloroform and precipitation in ether. A 5% solution of the fractionated material was deionized by passing through cationic (Dowex-50w) and anionic (Dowex-1) ion-exchange columns until the specific conductivity of the solution was close to 5 $\mu\ \Omega^{-1}\ cm^{-1}$. The deionized solution was dialyzed against demineralized water in cellulose acetate tubes for 3 days to remove any diffusible material. The solution was freeze-dried and then finally dried in vacuo at 60 °C for 24 h. The viscosity-averaged molecular weight ($\bar{M}_v$) of the purified material was 6.03×10^5.

Kinetic Measurements. The solutions were made in deionized double-distilled water acidified with dilute HCl to pH ca. 4.1 to prevent catalysis by OH^- ions. The reactions were followed in 1-cm quartz cuvettes which were placed in the thermostated cell holder of a Varian Cary 210 spectrophotometer. Under vigorous stirring, ca. 5 μL of a solution of **1** in acetonitrile was added to ca. 2.5 mL of the surfactant solution to give a final substrate concentration of ca. 2×10^{-5} M. The reactions were followed at 249.5 nm up to 10 half-lives. Good first-order kinetics were observed upto at least 3 half-lives. k_{obsd} values were reproducible to within 2%.

Ultrafiltration Measurements. The partitioning of the model substrate (**2**) into the micellar and aqueous pseudophases was studied by using a Thomapore Millipore filter.[23] A solution of **2** in acetonitrile (50 μL) was added to thermostated bulk solution (25 °C) of SDS or SDS containing PVP or *N*-iPP (250 mL) until the absorbance of the bulk solution at 250 nm was about 0.80. The solution was circulated through the Millipore filter at a rate of 300 mL h^{-1} and the filtrate was collected at a rate of 9 mL h^{-1}. The solute concentrations in the filtrate and the bulk filtrand were determined by measuring the absorbance at 250 nm.

Conductivity Measurements. Conductivity was measured by using a Wayne–Kerr Autobalance Universal Bridge B 642 with a constant frequency of 1592 Hz. A Philips PW 9512/01 electrode (cell constant c = 0.71 cm^{-1}) was used. The solutions were thermostated at 25 ± 0.1 °C for a least 30 min before the readings were taken. All the solutions were made in deionized double-distilled water that had a specific conductivity of 2 $\mu\Omega^{-1}\ cm^{-1}$ at 25 °C. The PVP solutions had specific conductivities between 4 and 10 $\mu\Omega^{-1}\ cm^{-1}$ which were substracted from the measurements.

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Registry No. 1, 60718-51-6; **2**, 58905-26-3; SDS, 151-21-3; PVP, 9003-39-8; *N*-iPP, 3772-26-7.

(18) Starting from a reasonable value for $K_{b_1}m_1^{-1}$ (52 M^{-1}, [SDS] = 0.011 M), f_w was calculated from

$$f_w = 1 - \frac{K_{b_1}m_1^{-1}c_1}{1 + K_{b_1}m_1^{-1}c_1}$$

This value of f_w was then introduced into the expression

$$k_{obsd} = f_{m_1}k_{m_1} + f_wk_w$$

and k_{m_1} was calculated using the experimental value of k_{obsd}. Then these $K_{b_1}m_1^{-1}$ and k_{m_1} values were employed for the calculation of the rate constant at [SDS] = 0.020 M. Excellent agreement between calculated and observed rate constants was finally found for $K_{b_1}m_1^{-1}$ = 40 M^{-1}.

(19) Preliminary results using poly(vinyl acetate) (83% hydrolyzed; $\bar{M}_v$ ca. 13000) instead of PVP show a similar reduction of the SDS-induced inhibition of the hydrolysis of 1-benzoyl-1,2,4-triazole. The data also fit our kinetic scheme (van de Berg, H. J.; Fadnavis, N.; and Engberts, J. B. F. N., submitted for publication).

(20) Recently, Bunton[21] has pointed out that even the spontaneous pH-independent water reactions can be affected by the charge on the micellar surface. Our conductivity data indicate that the counterion binding in the mixed micelles is considerably less, and hence these mixed micelles possess a relatively high net negative charge. It is possible that this might increase the nucleophilic activity of water molecules in the vicinity of the head groups. This would then explain the rate effects even in terms of Cabane's model. Although this possibility cannot be definitely excluded, we have observed that the micellar rate constants for hydrolysis of **1** in SDS and CTAB are not too different,[11] indicating that the charge on micellar surface is only of minor importance.

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