Water-Catalyzed Hydrolysis of 1-Acyl-1,2,4-triazoles in the Presence of Surfactant–Polymer Mixed Micelles. Substrate Dependence of the Effect of Polymer on the Micellar Inhibition

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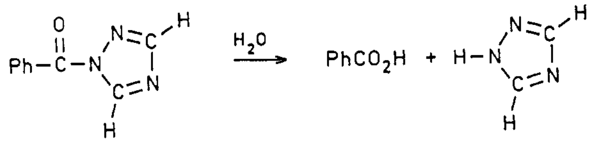
The water-catalyzed hydrolysis of 1-benzoyl-1,2,4-triazole (1) is inhibited by SDS micelles. Addition of poly(vinyl alcohol)–poly(vinyl acetate) copolymers (17% and 26% acetate, respectively) leads to a decreased inhibition. As supported by conductivity measurements, the rate effects are attributed to the formation of SDS–copolymer mixed micelles. Ultrafiltration experiments indicate increased binding of the substrate to the mixed micelles. Therefore the copolymer-induced rate accelerations can be best reconciled with an increase in the micropolarity at the substrate binding sites in the mixed micelles relative to unperturbed SDS micelles. With the aid of a computer, all kinetic data can be fitted into a kinetic scheme assuming hydrolysis of 1 in bulk water and in SDS and SDS–copolymer micellar pseudophases. Hydrolysis in SDS–poly(*N*-vinylpyrrolidone) (PVP) mixed micelles at low SDS concentrations (3–10 mM) was studied with the more hydrophobic substrate 3-phenyl-1-benzoyl-1,2,4-triazole (3). Now the SDS-induced inhibition is further increased by the polymer. Kinetic analysis shows that 3 is less strongly bound to mixed SDS–PVP micelles than to SDS micelles but that the rate constants in both micellar pseudophases are rather similar. It is argued that the different behavior of 1 and 3 in the mixed micelles primarily reflects the large propensity of 3 for stabilization by hydrophobic interactions.

It is now generally agreed that complexes may be formed between surfactant molecules and nonionic, water-soluble polymers in aqueous solution.[1] However, the morphology of these complexes is still an enigma.[2] Apart from their use in cosmetic and toiletry products, the complexes have recently found application in tertiary oil recovery processes.[3] In addition, the interactions between surfactants and proteins and those between surfactants and water-soluble polymers appear to be governed by similar forces.[1] Therefore an understanding of the structure of the surfactant–polymer complexes and of the effects of these complexes on chemical reactions is of considerable biological importance.

In a previous communication[4] we have reported that the inhibitive effect of micelles of sodium dodecyl sulfate (SDS) on the neutral (i.e., pH-independent) hydrolysis of 1-benzoyl-1,2,4-triazole (1, an activated amide) decreases on addition of atactic (at) poly(*N*-vinylpyrrolidone) (PVP). Herein we compare the effect of PVP with that of two poly(vinyl alcohol)–poly(vinyl acetate) copolymers (Mowiol 3-83, acetate content 17% and Mowiol 10-74, acetate content 26%) by using the same substrate 1. We also report the different effect of PVP on the micellar inhibition of the neutral hydrolysis of 3-phenyl-1-benzoyl-1,2,4-triazole (3), a substrate more hydrophobic than 1.



Results and Discussion

Conductivity Measurements. Figures 1 and 5 (supplementary material) show the specific conductivities (κ) of solutions containing varying concentrations of SDS at fixed concentrations of the copolymers Mowiol 3-83 and 10-74. The shapes of these plots are quite similar and are also similar to those found previously for the SDS–PVP system.[4] A typical plot (Figure 1) reveals the presence of three breaks and four regions. In region A, κ increases linearly with increasing SDS concentrations. In these solutions containing free surfactant monomers, the presence of the copolymers hardly affects the slope of the plots. A first break (labeled x) appears around 3.4 mM SDS and reflects the onset of a cooperative binding between SDS and the copolymer to form mixed micelles. The break point x is almost independent of copolymer concentration. Upon further increasing the SDS concentration (region B) the conductivity increases linearly with [SDS] but the slope of the plot is smaller than in region A. The degree of ionization of the mixed micelles (α, ratio of the slope in region B to that in region A)[5] is 0.74 ± 0.01 for both copolymers and is independent of copolymer concentration. After a second break (y), the plot loses its linearity in region C. This is due to the formation of unperturbed micelles of SDS in competition with the mixed micelles.[6] When all the binding sites on the polymer are saturated, a third break (z) appears and subsequently (region D) the plot becomes linear again. In this region $\alpha = 0.36 \pm 0.01$, independent of copolymer concentration and equal to that observed for unperturbed SDS micelles. Apparently in region D only normal SDS micelles are formed. As was found for the SDS–PVP system,[4] the concentration of SDS at which the break points y and z occur increase with increasing concentration of the copolymers.

The strong resemblance between the conductivity plots for the two SDS–copolymer systems and for SDS–PVP[4] is not a priori expected and suggests a strong similarity of the interactions involved in the complex formation between SDS and the macromolecules.

Effect of the Copolymers on the Micellar Rate Effects. The neutral hydrolysis of 1-acyl-1,2,4-triazoles occurs via water-catalyzed nucleophilic attack of water on the substrate carbonyl group.[7a] In the case of substrate

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[1] Breuer, M. M.; Robb, I. D. *Chem. Ind. (London)* **1972**, *13*, 530.

[2] (a) Fishman, M. L.; Eirich, F. R. *J. Phys. Chem.* **1975**, *79*, 2740. (b) Cabane, B. *J. Phys. Chem.* **1977**, *81*, 1639 and references cited therein.

[3] "Surface Phenomena in Enhanced Oil Recovery"; Shah, D. O., Ed.; Plenum Press: New York, 1981.

[4] Fadnavis, N. W.; Engberts, J. B. F. N. *J. Am. Chem. Soc.* **1984**, *106*, 2636.

[5] Zana, R.; Lang, J.; Lianos, P. *Polym. Prepr. Am. Chem. Soc. Div. Polym. Chem.* **1982**, *23*, 39.

[6] In this region unfolding of the polymer coil may occur as a result of electrostatic repulsions between polymer-bound surfactant molecules.[2a]

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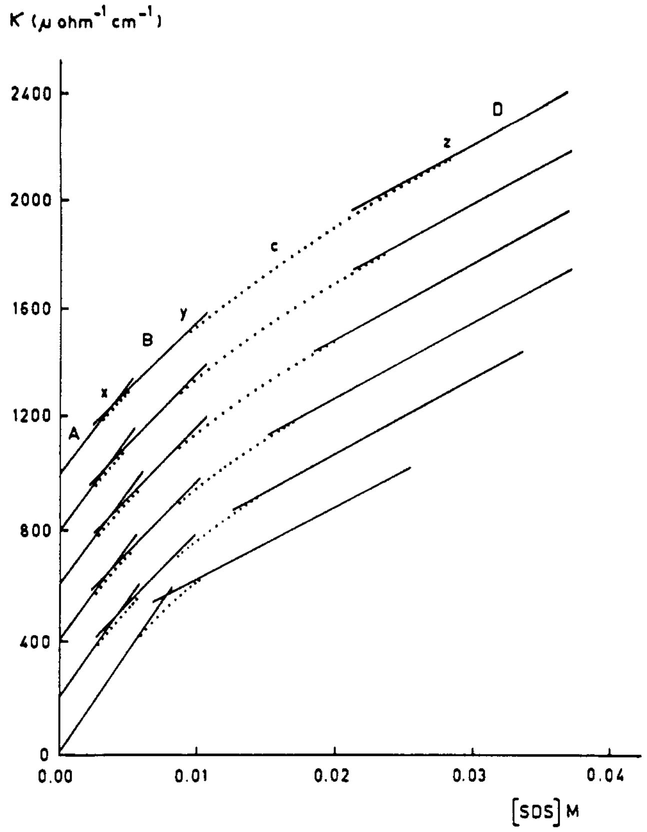


Figure 1. Plot of the specific conductivity vs. concentration of SDS at fixed concentrations of Mowiol 3-83; from top to bottom 0.5, 0.4, 0.3, 0.2, 0.1, and 0.0 g dL^{-1}. The curves have been displaced upwards starting relative to the bottom curve by 1-, 2-, 3-, and 4-scale units (100 μohm^{-1} cm^{-1}), respectively.

Table I. Pseudo-First-Order Rate Constants ($10^4 k_{\text{obsd}}$, s^{-1}) for the Neutral Hydrolysis of 1 in Aqueous Solutions Containing SDS and Mowiol 3-83 at 25 °C

	[Mowiol 3-83], g dL^{-1}				
[SDS], M	0.00	0.20	0.30	0.40	0.50
0.000	21.0	21.0	21.1	20.9	21.0
0.010	19.6	19.9	19.6	19.6	19.5
0.019	14.0	16.5	16.5	17.0	16.7
0.030	10.8	12.6	13.6	13.9	14.0
0.040	8.98	10.3	10.9	11.5	11.9
0.050	7.75	8.73	9.34	9.93	10.5
0.060	6.86	7.56	8.04	8.46	8.97
0.081	5.65	6.11	6.65	6.65	7.04
0.106	4.78	5.09	5.43	5.43	5.69

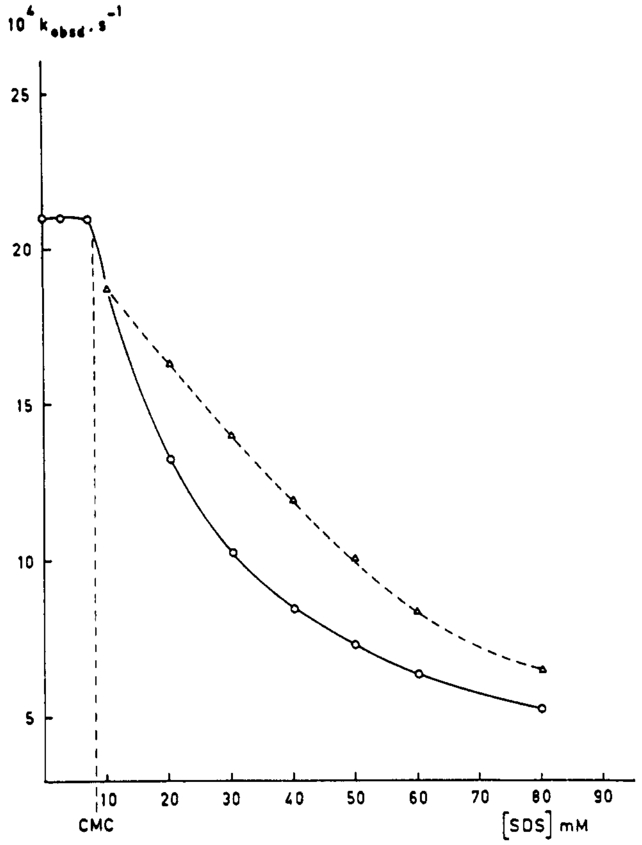
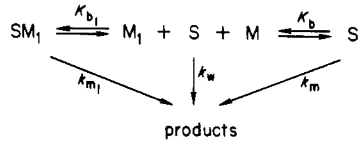


Figure 2. Pseudo-first-order rate constants for the neutral hydrolysis of 1 at 25 °C: ○, at varying concentrations of SDS; △, at varying concentrations of SDS in the presence of 0.5 g dL^{-1} of Mowiol 10-74.

Table II. Pseudo-First-Order Rate Constants ($10^4 k_{\text{obsd}}$, s^{-1}) for the Neutral Hydrolysis of 1 in Aqueous Solutions Containing SDS and Mowiol 10-74 at 25 °C

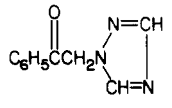
	[Mowiol 10-74], g dL^{-1}				
[SDS], M	0.00	0.20	0.30	0.40	0.50
0.000	21.0	21.3	21.5	21.7	21.3
0.010	18.8	18.9	19.1	18.9	18.6
0.020	13.2	16.0	16.4	16.3	16.3
0.030	10.3	12.1	13.3	13.9	14.0
0.040	8.50	9.82	10.6	11.4	11.9
0.050	7.34	8.20	8.95	9.42	10.1
0.060	6.39	7.09	7.49	7.87	8.42
0.080	5.27	5.72	5.96	6.20	6.47
0.100	4.52	4.79	4.97	5.09	5.36

Scheme I



1, the copolymers Mowiol 3-83 and 10-74 had no effect on the pseudo-first-order rate constants (k_{obsd}, pH ca. 4.1) at least up to 0.5 g dL^{-1}. In micellar SDS solutions k_{obsd} is decreased because of binding of 1 at the micellar Stern region where the local polarity is lower than that in bulk water.[7b] Addition of the copolymers to the SDS solutions *reduces* the micellar inhibition and k_{obsd} increases compared to that found in the solutions containing only SDS (Tables I and II, see also Figure 2). At low SDS concentrations (≤30 mM) k_{obsd} initially increases with added copolymer and then becomes constant. However, in these plateau regions, k_{obsd} is still considerably smaller than that in water. At high SDS concentrations (>30 mM), the k_{obsd} values continue to increase with increasing copolymer concentration.

The copolymer effect on the micellar inhibition could be the result of competitive binding of 1 and the copolymer to binding sites at the Stern region. Binding of the copolymer would then result in an increased concentration of substrate in the bulk aqueous phase and a concomitant increase of k_{obsd}. Ultrafiltration experiments, using a structurally closely related model substrate 2, show that this interpretation does not apply. At [SDS] = 0.04 M, in the absence of copolymers, the fraction of 2 in the



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(7) (a) Karzijn, W.; Engberts, J. B. F. N. *Tetrahedron Lett.* **1978**, 1787. (b) Fadnavis, N. W.; Engberts, J. B. F. N. *J. Org. Chem.* **1982**, *47*, 152.

aqueous pseudophase (f_w) is 0.607, whereas addition of 0.3 g dL^{-1} of Mowiol 3-83 and Mowiol 10-74 reduces f_w to 0.576 and 0.595, respectively. Thus it appears that the most probable reason for the rate increments is an increase of the micropolarity at the substrate binding sites as a result of the interaction with the copolymers. This conclusion agrees with that reached previously for SDS–PVP mixed micelles.[4] We submit that the hydrolysis of 1 takes place in the presence of three pseudophases, i.e., bulk water, unperturbed SDS micelles, and SDS–copolymer mixed micelles (Scheme I). S represents the substrate, M and M_1 are the SDS micelles and SDS–copolymer mixed micelles, respectively, k_m and k_{m_1} are the respective micellar rate constants, k_w is the rate constant in bulk water, and K_b and K_{b_1} are the binding constants for binding of the substrate to the unperturbed and mixed micelles, respectively. A rapid distribution of the substrate takes place between the three pseudophases. The fraction of the substrate in bulk aqueous phase[4] is given by

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

in which m and m_1 are the aggregation numbers of SDS micelles and mixed micelles, respectively, c_1 is the concentration of SDS bound to the polymer, and c is the concentration of SDS forming unperturbed micelles and equals $c_0 - c_f - c_1$ where c_0 is the total SDS concentration and c_f is the monomer concentration of SDS. With $c^* = c_0 - c_f$, the rate constant for the overall reaction[4] is given by

$$k_{obsd} = K_b k_m c^* m^{-1} f_w + c_1 f_w (K_{b_1} k_{m_1} {m_1}^{-1} - K_b k_m m^{-1}) + k_w f_w \qquad (2)$$

For a critical test of the kinetic scheme, we employed the kinetic data in Tables I and II. Assuming that the properties of the unperturbed SDS micelles are not affected by the presence of the mixed micelles, k_{obsd} values were calculated by using eq 1 and 2. The values of $K_b m^{-1}$ and k_m were those obtained from hydrolysis in SDS solutions in the absence of the copolymers. The value of k_w refers to hydrolysis in pure water. Finally, c_f was taken as the concentration of SDS at which the first break occurs in the conductivity plots (Figures 1 and 5). We are then left with three unknowns, $K_{b_1}{m_1}^{-1}$, k_{m_1}, and c_1. But the results of the ultrafiltration experiments (vide supra) and the breaks in the conductivity plots provide insights into the upper and lower limits of these constants. A computer program was devised to assess reasonable estimates, starting from calculated k_{obsd} values (eq 1 and 2) obtained from each combination of $K_{b_1}{m_1}^{-1}$, k_{m_1}, and c_1 at a fixed polymer concentration. A converging set of values was obtained upon minimizing the difference between the experimental and calculated k_{obsd} values. Similar sets were obtained for the other copolymer concentrations, the best values for $K_{b_1}{m_1}^{-1}$ and k_{m_1} were selected and the corresponding values for c_1 were obtained for each polymer concentration. The kinetic data for the SDS–PVP system[4] were also processed in this manner and the results are recorded in Table III.[8] The agreement between the calculated and experimental rate constants (±4%) is excellent in view of the assumptions made in the calculations. For all three surfactant–polymer mixed micelles, k_{m_1} is considerably larger than k_m, indicating that the microenvironment at the binding sites of the mixed micelles is more polar or water penetrated than that at the binding sites of normal SDS micelles. Fluorescence studies on the SDS–PVP system have led to a similar conclusion.[5,9]

Table III. Parameters of the Neutral Hydrolysis of 1 in the Presence of SDS–Polymer Mixed Micelles at 25 °C

	[polymer], g dL^{-1}					
	0.20	0.30	0.40	0.50	$K_{b_1}{m_1}^{-1}$,[a]	
polymer	c_1 (±0.5), mM[c]				M^{-1}	$10^3 k_{m_1}$,[b] s^{-1}
PVP	10.0	11.5	13.5	15.5	26 ± 1	1.10 ± 0.1
Mowiol 3-83	12.0	16.5	18.0	21.0	32 ± 1	1.0 ± 0.1
Mowiol 10-74	15.0	20.0	24.0	28.0	26 ± 1	0.5 ± 0.02

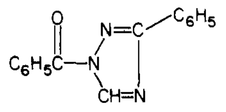
[a] For SDS, $K_b m^{-1}$ = 52 M^{-1}. [b] For SDS, $10^3 k_m$ = 0.168 s^{-1}. [c] The c_1 values are those for "saturation" of the polymer with SDS (usually $c_0 \geq 0.03$ M).

Table IV. Pseudo-First-Order Rate Constants ($10^4 k_{obsd}$, s^{-1}) for the Neutral Hydrolysis of 3 in Aqueous Solutions Containing SDS and PVP at 25 °C

	[PVP], g dL^{-1}				
[SDS], mM	0.00	0.20	0.30	0.40	0.50
0.00	12.4	12.4	12.4	12.4	12.4
1.0	12.4	12.4	12.4	12.4	12.4
2.0	12.4	12.4	12.5	12.3	12.4
3.0	12.3	6.13	5.86	5.66	5.64
4.0	12.4	6.01	5.44	5.34	5.24
5.0	12.3	4.60	4.09	4.06	3.95
6.4	12.4	3.30	3.03	2.99	2.88
8.0	5.91	2.64	2.49	2.36	2.34
10.0	2.94	2.05	1.90	1.90	1.85
15.0	1.65	1.44	1.38	1.37	1.32
20.0	1.24	1.14	1.15	1.09	1.08
25.1	1.02	0.994	0.972	0.955	0.956
30.0	0.905	0.866	0.855	0.858	0.850
35.0	0.842	0.808	0.816	0.799	0.813
40.0	0.804	0.790	0.789	0.770	0.774
50.0	0.733	0.736	0.730	0.715	0.696

We contend that our kinetic treatment based on Scheme I adequately describes the effect of the added polymers on the SDS-inhibited neutral hydrolysis of 1. However, because of the not too strong binding of 1 to SDS micelles, it was impossible to study the effect of the polymers at SDS concentrations below the cmc (8 mM), where mixed micelles are predominantly present. Therefore we have chosen 3-phenyl-1-benzoyl-1,2,4-triazole (3) as a second substrate for detailed studies. It binds to SDS micelles very efficiently at low SDS concentrations[7] and hydrolizes via the same mechanism as 1.[7a,10]

Effect of PVP on the SDS Micellar Inhibition of the Neutral Hydrolysis of 3. Table IV lists pseudo-first-order rate constants (k_{obsd}) for the neutral hydrolysis of 3 in aqueous solutions of SDS containing varying concentrations of at-PVP. The reaction rate in water is not affected by the addition of PVP at least up to 0.5 g dL^{-1}. For the same reasons as for 1, the reaction is inhibited in SDS solutions. As shown in Table IV, the reaction is



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[8] The previous data for the SDS–PVP system were analyzed by using only one polymer concentration. The present computer calculations give a better fit to the overall data. Although $K_{b_1}{m_1}^{-1}$ (26 M^{-1}) differs from the value reported previously (40 M^{-1}),[4] the conclusions are not affected.

[9] Bloor, D. M.; Wyn-Jones, E. J. Chem. Soc., Faraday Trans. 2 1982, 78, 657.

[10] (a) Karzijn, W. Ph.D. thesis, Groningen, 1979. (b) Karzijn, W.; Engberts, J. B. F. N. Recl. Trav. Chim. Pays-Bas 1983, 102, 513.

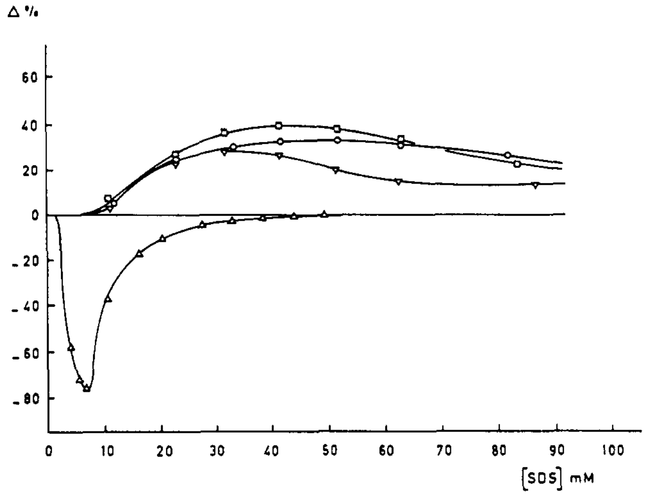

Figure 3. Effect of polymers on the SDS-inhibited neutral hydrolysis of 1 and 3. Polymer-induced change in k_{obsd} is defined as $\Delta = (k_{(SDS-polymer)} - k_{(SDS)})(k_{SDS})^{-1} \times 10^2$. Substrate 1: ▽, 0.5 g dL^{-1} PVP; ○, 0.5 g dL^{-1} Mowiol 3-83; □, 0.5 g dL^{-1} Mowiol 10-74. Substrate 3: △, 0.5 g dL^{-1} PVP.

inhibited further by addition of PVP to SDS solutions.[11] This is in remarkable contrast to the previous observations for the neutral hydrolysis for 1 in SDS–PVP mixtures (Figure 3). In the presence of PVP there occurs an abrupt decrease in k_{obsd} at 3 mM SDS (well below the cmc of 8 mM), lending further support to the idea that the first break point, x, in the conductivity plot corresponds to mixed micelle formation. In the concentration region between 3 mM and 10 mM SDS, k_{obsd} decreases further upon increasing PVP concentrations at a fixed SDS concentration and finally reaches a constant value. These effects gradually vanish at higher SDS concentrations. The polymer effect on the micellar inhibition also decreases gradually and at high SDS concentrations (40–50 mM) the effect is negligible. These findings can be rationalized as follows. At low SDS (≤10 mM) and PVP (≤0.2 g dL^{-1}) concentrations there is an equilibrium between the polymer, SDS monomers, and mixed micelles. At high polymer concentration (≥0.4 g dL^{-1}) all the SDS monomers (above the critical concentration of 3 mM) are bound to the polymer to form mixed micelles. The concentration of mixed micelle will not change on further addition of PVP. This explains why k_{obsd} ultimately attains a constant value. These arguments are in keeping with the thermodynamics of surfactant–polymer interactions.[12] When the SDS concentration is made high enough to form unperturbed micelles in competition with mixed micelles (region C in the conductivity plots) the polymer effect will gradually vanish and in the presence of a large excess of SDS only the normal SDS inhibition is observed.

In the region of low SDS (3–10 mM) and high PVP (≥0.5 g dL^{-1}) concentrations only mixed micelles are present together with SDS monomers (c_f ca. 3 mM). Now Scheme I will reduce to the simple scheme of the pseudophase model for micellar catalysis[13] and the kinetic data can be described by

$$(k_w - k_{obsd})^{-1} = (k_w - k_{m_1})^{-1} + [(k_w - k_{m_1})^{-1}(K_{b_1}m_1{}^{-1})^{-1}(c_0 - c_f)^{-1}] \quad (3)$$

Figure 4 shows the linear plot[14] of $(k_w - k_{obsd})^{-1}$ against $(c_0 - c_f)^{-1}$. The plot is linear up to an SDS concentration of about 20 mM and then deviates from linearity because now a significant part of the substrate will react in unperturbed micelles. Values for k_{m_1} and $K_{b_1}m_1{}^{-1}$ were calculated from the intercept and slope of the linear plot, respectively. By using these parameters and values for k_m, K_bm^{-1}, and k_w obtained from the hydrolysis in SDS solutions and water, k_{obsd} values were calculated from eq 1 and 2 for other SDS–PVP solutions. Values for c_1 were taken from Table III. Again the maximum deviation of the calculated rate constants from the experimental k_{obsd} values was 4%. We find $K_bm^{-1} = 1380 \pm 50$ M^{-1}, $K_{b_1}m_1{}^{-1} = 950 \pm 50$ M^{-1}, $k_m = (5.30 \pm 0.2) \times 10^{-5}$ s^{-1}, and $k_{m_1} = (4.7 \pm 0.2) \times 10^{-5}$ s^{-1}. The similarity of the k_m and k_{m_1} values indicates that the microenvironment experienced by 3 in SDS micelles and SDS–PVP mixed micelles is hardly different. This is apparently in conflict with the conclusions drawn from the kinetic studies with 1 which implied more polar microenvironments at the binding sites of the SDS–polymer complexes.[4] It is tempting to rationalize these differences in terms of the following two effects. First, it may be assumed that 3, which is more hydrophobic[10] than 1, binds at relatively "dry" regions of the mixed micellar surface while 1 binds at more aqueous regions. A second possibility involves a difference in substrate orientation, i.e., 3 is oriented at the mixed micellar surface in such a way that the attack of water at the amide carbonyl is more hindered than in the case of 1. Unfortunately there is at present neither adequate information about orientational effects in micellar-phase reactions nor any realistic method to determine the exact location of a substrate in the Stern region, particularly at low concentrations (10^{-5} M) of the substrate. It has been observed repeatedly that the information obtained about the micropolarity of the binding sites in the micellar pseudophase is rather dependent upon the nature of the probe molecule.[15] We found previously that the neutral hydrolysis of 3 is much more inhibited by SDS micelles than that of 1 (3, $k_w/k_m = 24$, 1, $k_w/k_m = 12.5$).[7b] Comparison of the rates of hydrolysis of 1 and 3 in 1,4-dioxane–water mixtures as a function of dielectric constant (Table V) shows that the effect is about the same for both substrates. However, in aqueous mixtures containing a *hydrophobic* cosolvent (i.e., in t-BuOH–H_2O),[10] the effect of a change in the reaction medium is much larger for 3 than for 1. Thus it is likely that the more pronounced inhibition of the hydrolysis of 3 by SDS mi-

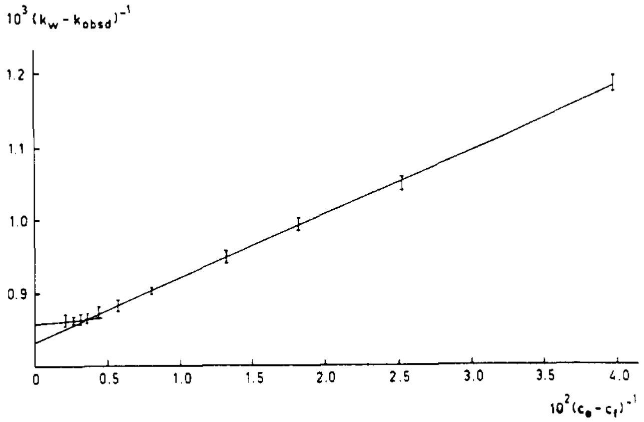

Figure 4. Plot of $(k_w - k_{obsd})^{-1}$ vs. $(c_0 - c_f)$ for the neutral hydrolysis of 3 at 25 °C in SDS solutions containing 0.5 g dL^{-1} PVP.

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[11] Preliminary measurements with the two Mowiol copolymers also indicated an enhanced inhibition.,

[12] Nagarajan, R. *Polym. Prepr. Am. Chem. Soc. Div. Polym. Chem.* **1981**, *22*, 33.

[13] Menger, F. M.; Portnoy, C. A. *J. Am. Chem. Soc.* **1967**, *89*, 4968.

[14] The free monomer concentration (c_f) was taken as 2.5 mM instead of 3 mM to get the best fit. It can be described as a "kinetic" c_f.

[15] Otruba, J. P.; Whitten, D. G. *J. Am. Chem. Soc.* **1983**, *105*, 6503 and references cited therein.

Table V. Neutral Hydrolysis of 1 and 3 in 1,4-Dioxane-H_2O and t-BuOH-H_2O at 25 °C

compd	solvent	n_{H_2O}	ϵ	k_w/k_{obsd}
1	H_2O	1.00	78.6	1
1	1,4-dioxane-H_2O	0.95	60.8	2.54
1	1,4-dioxane-H_2O	0.92	52	5.13
3	1,4-dioxane-H_2O	0.95	60.8	2.54
3	1,4-dioxane-H_2O	0.92	52	4.92
1	*t*-BuOH-H_2O	0.95	65.4	2.36
1	*t*-BuOH-H_2O	0.92	58.1	4.35
1	*t*-BuOH-H_2O	0.90	53.5	5.69
3	*t*-BuOH-H_2O	0.95	65.4	3.67
3	*t*-BuOH-H_2O	0.92	58.1	7.52
3	*t*-BuOH-H_2O	0.90	53.5	13.60

Table VI. Pseudo-First-Order Rate Constants ($10^4 k_{obsd}$, s^{-1}) for the Neutral Hydrolysis of 3 in Aqueous Solutions Containing SDS and *N*-Isopropylpyrrolidone at 25 °C

	[*N*-*i*-PP], M				
SDS, M	0.00	0.02	0.03	0.04	0.05
0.010	2.94	2.99	3.02	3.06	3.13
0.015	1.59	1.70	1.83	1.88	1.92
0.020	1.22	1.33	1.44	1.49	1.54

celles is caused by a larger initial-state stabilization effect as a result of stronger hydrophobic interactions. This explanation holds even if both substrates are bound at the same binding sites in the (mixed) micelles. Therefore, we emphasize that the different inhibition observed for 1 and 3 does not necessarily imply different binding sites or different orientational effects.

Addition of *N*-isopropylpyrrolidone (*N*-*i*-PP, the model monomer unit of PVP) to SDS solutions causes an increase in k_{obsd} for hydrolysis of 3 compared to the k_{obsd} values in the corresponding SDS solutions (Table VI). As shown by previous ultrafiltration measurements,[4] competition in binding between *N*-*i*-PP and 3 to the micelle will lead to transfer of 3 from the micellar pseudophase to the bulk aqueous phase and a concomitant increase in rate. In this respect the kinetic effect of the monomer is fundamentally different from that of the polymer.

Experimental Section

Materials. 1-Benzoyl-1,2,4-triazole (1, mp 72.1–72.5 °C (lit.[10a] mp 71.8–72.4 °C)), 1-phenacyl-1,2,4-triazole (2, mp 114.4–115.0 °C (lit.[10a] mp 114.0–115.2 °C)), and 3-phenyl-1-benzoyl-1,2,4-triazole (3, mp 79.1–79.5 °C (lit.[10a] mp 78.6–79.9 °C)) were prepared by literature methods.[10] SDS was purified by a standard method.[16] *N*-Isopropylpyrrolidone (GAF corporation, New York) was distilled twice under reduced pressure (bp 59 °C (0.001 mm)). The purification of poly(*N*-vinylpyrrolidone) (Kolloidon-90, BASF) has been described previously.[4] The copolymers poly(vinyl acetate)-poly(vinyl alcohol) Mowiol 3-83 (17% acetate) and Mowiol 10-74 (26% acetate) (both from Hoechst) were first fractionated from DMF-ether. Aqueous solutions (5%, w/w) of these materials were deionized by passing through cationic (Dowex-50w) and anionic (Dowex-1) ion exchange columns till the specific conductivities of the solutions were less than 20 μohm^{-1} cm^{-1}. The deionized solutions were dialized against demineralized water in cellulose acetate tubes for 24 h. Then the solutions were freeze dried and the copolymers were finally dried over P_2O_5 in vacuo. Weight averaged molecular weights were 1.79 × 10^4 D for Mowiol 3-83 and 6.04 × 10^4 D for Mowiol 10-74.

Measurements. The kinetic, conductivity, and ultrafiltration measurements have been carried out as described previously.[4,7,10] Generally, the k_{obsd} values were reproducible to within 2%.

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Registry No. 1, 60718-51-6; 3, 79746-00-2; SDS, 151-21-3; PVP (homopolymer), 9003-39-8; Mowiol 3-83, 9002-89-5; Mowiol 10-74, 9002-89-5.

Supplementary Material Available: Figure 5, showing a plot of the specific conductivity of SDS at a series of fixed concentrations of Mowiol 10-74 (1 page). Ordering information is given on any current masthead page.

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Photoinduced Electron-Transfer-Initiated Aromatic Cyclization

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Photochemical reaction of substituted 1,4-naphthoquinones with 1,1-diarylethylenes led primarily to benz[*a*]anthracene-7,12-dione derivatives. Evidence was obtained that the photoreaction proceeded via a photoinduced electron-transfer process. Extension of the reaction provided regioselective syntheses of other polycyclic aromatic quinones.

Polycyclic aromatic compounds have attracted much attention because of their physicochemical and biochemical properties.[1] However, investigations of polycyclic aromatic compounds have been hampered by lack of general and facile regioselective synthetic routes to them.[2] A facile route to A ring substituted benz[*a*]anthracene-7,12-diones was recently reported[3a] using the Diels–Alder reaction of 1,4-naphthoquinone with styrene derivatives. However, several weeks are required to complete the Diels–Alder

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