Treatment of either of the above compounds with potassium hydroxide in methanol (or tetrahydrofuran) afforded cyclopropane **31** as the exclusive product.

Preparation of Methyl *cis*- and *trans*-2,2-Dimethyl-1-(*p*-tolylsulfonyl)-3-(phenylthio)cyclopropanecarboxylate (39 and 40). To a stirred solution containing 1.0 g of *trans*-2,2-dimethyl-3-(*p*-tolylsulfonyl)cyclopropyl phenyl sulfide (**31**) in 50 mL of dry tetrahydrofuran at 0 °C was added 2.2 mL of a 1.43 M solution of *n*-butyllithium in hexane. The yellow solution was stirred for an additional 15 min followed by the addition of 0.22 mL of methyl chloroformate. The resulting solution was stirred for an additional 30 min at 0 °C, then warmed to 25 °C, and stirred for 12 h. The reaction was quenched with a saturated ammonium chloride solution, diluted with ether, washed several times with water, dried over magnesium sulfate, and evaporated to give 1.38 g of a yellow oil. This material was chromatographed on a 4-mm chromatatron plate by using a 5% acetone–hexane mixture as the eluent. The first fraction contained 880 mg (91%) of an oil which crystallized on standing and was identified as methyl *trans*-2,2-dimethyl-1-(*p*-tolylsulfonyl)-3-(phenylthio)cyclopropanecarboxylate (**40**) on the basis of its spectral data: mp 104–105 °C; IR (KBr) 3010, 3000, 2970, 1750, 1600, 1590, 1305, 1250, 750, 660, and 600 cm^{-1}; ^{1}H NMR (CCl_4, 90 MHz) δ 1.20 (s, 3 H), 1.68 (s, 3 H), 2.40 (s, 3 H), 3.50 (s, 4 H), 7.0–7.39 (m, 7 H), and 7.68 (d, 2 H, J = 9.0 Hz); UV (95% ethanol) 230 nm (ϵ 19 000) and 248 (11 000). Anal. Calcd for $C_{20}H_{22}O_4S_2$: C, 61.51; H, 5.68; S, 16.42. Found: C, 61.59; H, 5.73; S, 16.46.

The second fraction contained 90 mg (9%) of a white solid whose structure was assigned as methyl *cis*-2,2-dimethyl-1-(*p*-tolylsulfonyl)-3-(phenylthio)cyclopropanecarboxylate (**39**) on the basis of its characteristic spectral properties: mp 122–123 °C; IR (KBr) 3020, 2970, 1735, 1600, 1590, 1350, 1250, 820, 670, and 615 cm^{-1}; ^{1}H NMR (CCl_4, 90 MHz) δ 1.25 (s, 3 H), 1.70 (s, 3 H), 2.35 (s, 3 H), 3.11 (s, 1 H), 3.48 (s, 3 H), 7.10–7.35 (m, 7 H), and 7.70 (d, 2 H, J = 9.0 Hz); UV (95% ethanol) 228 nm (ϵ 18 000) and 250 (9600). Anal. Calcd for $C_{20}H_{22}O_4S_2$: C, 61.51; H, 5.68; S, 16.42. Found: C, 61.67; H, 5.72; S, 16.36.

Preparation of Methyl *trans*-2,2-Dimethyl-3-(phenylsulfonyl)-1-(*p*-tolylsulfonyl)cyclopropanecarboxylate (41). To a stirred solution containing 350 mg of cyclopropane **40** in 25 mL of chloroform was added 0.33 g of *m*-chloroperoxybenzoic acid in 25 mL of chloroform at −10 °C under a nitrogen atmosphere. The resulting mixture was slowly warmed to 25 °C and was stirred for an additional 12 h. At the end of this time, the solution was washed with a saturated solution of sodium bicarbonate. The organic layer was dried over magnesium sulfate and concentrated to give a brown oil. This material was crystallized from a dichloromethane–petroleum ether mixture to give 200 mg (52% yield) of a white solid whose structure was assigned as methyl *trans*-2,2-dimethyl-3-(phenylsulfonyl)-1-(*p*-tolylsulfonyl)cyclopropanecarboxylate (**41**) on the basis of its spectral data: mp 121–122 °C; IR (KBr) 3040, 3000, 2980, 1740, 1600, 1590, 1320, 1150, 1080, 660, and 610 cm^{-1}; ^{1}H NMR ($CDCl_3$, 360 MHz) δ 1.64 (s, 3 H), 1.67 (s, 3 H), 2.44 (s, 3 H), 3.56 (s, 1 H), 3.58 (s, 3 H), 7.20 (d, 2 H, J = 9.0 Hz), 7.45–7.80 (m, 5 H), and 8.01 (d, 2 H, J = 9.0 Hz); UV (95% ethanol) 222 nm (ϵ 21 000) and 265 (1800). Anal. Calcd for $C_{20}H_{22}O_6S_2$: C, 56.85; H, 5.25. Found: C, 56.95; H, 5.29.

A 75-mg sample of **41** was treated with 1 equiv of LDA at −78 °C and the mixture was allowed to warm to −20 °C and was then quenched with methanol. Normal workup resulted in a clear oil whose NMR spectrum showed it to consist of a 1:1 mixture of **41** and **42**. NMR ($CDCl_3$, 360 MHz) of **42**: δ 1.65 (s, 3 H), 1.68 (s, 3 H), 2.46 (s, 3 H), 3.43 (s, 1 H), 3.62 (s, 3 H), 7.21 (d, 2 H, J = 9.0 Hz), 7.45–7.80 (m, 5 H), and 8.02 (d, 2 H, J = 9.0 Hz).

Acknowledgment. We are grateful to the National Science Foundation for financial support of this work.

Perturbation of SDS and CTAB Micelles by Complexation with Poly(ethylene oxide) and Poly(propylene oxide)

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Pseudo-first-order rate constants have been determined for the neutral hydrolysis of 1-benzoyl-3-phenyl-1,2,4-triazole in aqueous solutions in the presence of SDS and CTAB micelles and SDS–PEO, SDS–PPO, and CTAB–PPO mixed micelles. The micellar rate inhibition of the hydrolysis is clearly modified as a result of micelle–polymer complexation, the effects being rather specific for the nature of the surfactant and the polymer. The kinetic data were analyzed by a simple pseudophase model. The results revealed stabilization of the micelles by interaction with the polymer and polymer-induced microenvironmental changes at the micellar binding sites of the substrate. Results from conductivity measurements facilitated the interpretation of the kinetic data.

There is considerable recent interest in the complexes formed between micelles and uncharged water-soluble polymers.[1-4] However, neither the morphology of these polymer-complexed micelles ("mixed micelles") nor the interactions governing the complex formation have been clearly established. In the present study we compare micelle–polymer complexes formed from an anionic surfactant (sodium dodecyl sulfate, SDS) and a cationic surfactant (cetyltrimethylammonium bromide, CTAB) and two structurally related water-soluble polymers, poly(ethylene oxide) (PEO) and poly(propylene oxide) (PPO). Emphasis is placed on a comparison of the inhibitory effects of these complexes on a water-catalyzed hydrolysis reaction.[5] The interpretation of the kinetic data is facilitated by results from conductivity studies.

Results and Discussion

Conductivity Measurements. Figures 1 and 2 show specific conductivities (κ) as a function of the SDS concentration in aqueous solution in the presence of fixed concentrations of PEO (weight-averaged MW 10 000) or PPO (weight-averaged MW 1000, relatively low in order to ensure water solubility). For both polymers there is an initial linear increase of κ with increasing SDS concentration up to the first break at a well-defined SDS con-

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(1) For an authoriative review, see: Goddard, E. D. *Colloids Surf.* **1986**, *19*, 255.

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(5) For previous studies, see: (a) Fadnavis, N. W.; Engberts, J. B. F. N. *J. Am. Chem. Soc.* **1984**, *106*, 2636. (b) Fadnavis, N. W.; Van de Berg, H.; Engberts, J. B. F. N. *J. Org. Chem.* **1985**, *50*, 48.

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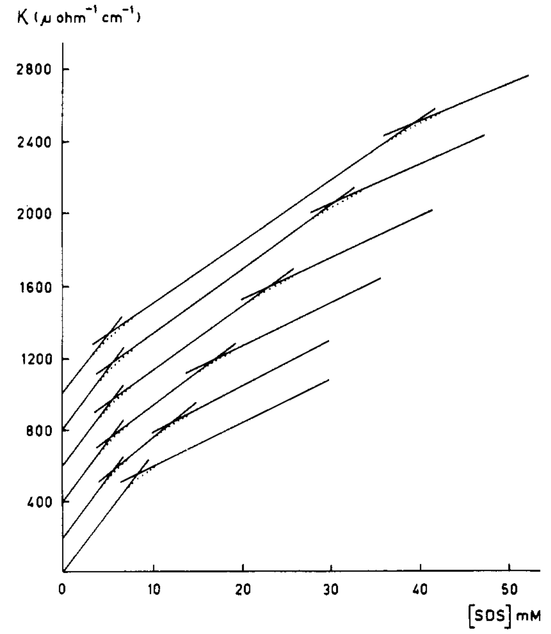

Figure 1. Plots of the specific conductivity (κ) vs concentration of SDS at fixed concentrations of PEO. Top to bottom: 0.5, 0.4, 0.3, 0.2, 0.1, and 0.0 g·dL^{-1}. The curves have been displaced upward, starting relative to the bottom curve, by 1–5 scale units (200 μΩ^{-1}.cm^{-1}), respectively.

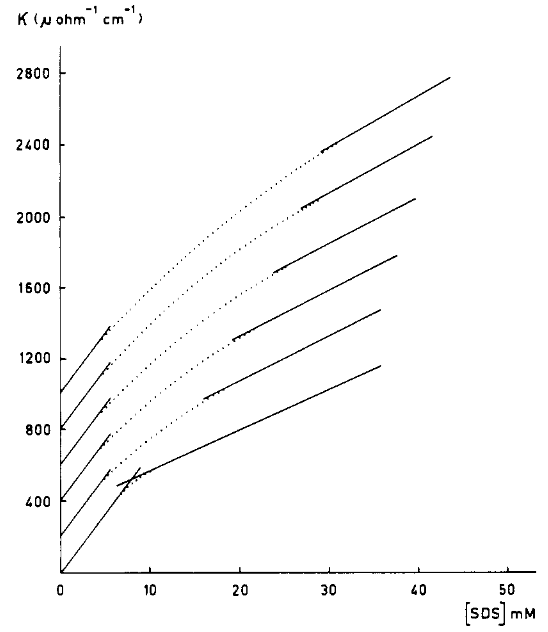

Figure 2. Plots of the specific conductivity (κ) vs concentration of SDS at fixed concentrations of PPO. Top to bottom: 0.5, 0.4, 0.3, 0.2, 0.1, and 0.0 g·dL^{-1}. The curves have been displaced upward, starting relative to the bottom curve, by 1–5 scale units (200 μΩ^{-1}.cm^{-1}), respectively.

Table I. Results of Conductivity Measurements at 25 °C

	c_f,[a] mM	c_1,[b] mM	α[c]
SDS[d]	8.3 ± 0.2		0.37 ± 0.02
SDS–PEO[e]	5.6 ± 0.2	40	0.58 ± 0.02
SDS–PPO[e]	4.0 ± 0.2	30	0.82 ± 0.04[f]
CTAB[g]	0.95 ± 0.03		0.24 ± 0.02
CTAB–PPO[e]	0.75 ± 0.03	ca. 20	0.80 ± 0.04[f]

[a] Premicellar breakpoint, see text. [b] Postmicellar breakpoint, see text. [c] See text. [d] Aggregation number 62. [e] Polymer concentration 0.5 g·dL^{-1}. [f] Calculated on the basis of the tangent of the line through the first six to eight data points after the first breakpoint and the slope below c_f. [g] Aggregation number 80.

centration (c_f), well below the critical micelle concentration (cmc) of pure SDS. Apparently the premicellar breakpoint at c_f reflects a cooperative association process akin to micellization in which surfactant molecules are bound to the polymer in the form of micellelike aggregates.[3,6,7] In the solutions containing PEO, κ increases again linearly after the break but with a smaller slope. Now complexed micelles are being formed that possess a smaller aggregation number ("minimicelles") as compared with unperturbed SDS micelles.[8,9] Table I shows the value of α, defined as the ratio of the slope in the second region of the conductivity plot to that in the first region up to c_f. The larger value of α for the complexed micelles is indicative of an increased degree of ionic dissociation as a result of interactions with the polymer.[8] Finally, a second break occurs at the SDS concentration (c_1) where the polymer becomes saturated with micelles.[10] At still higher SDS concentrations only unperturbed SDS micelles are being formed as supported by the magnitude of α, which is equal to that of SDS solutions in the absence of polymer and which is independent of the polymer concentration. Interestingly, the conductivity plot of the SDS–PPO solutions in the second region from c_f to c_1 is not linear. This could be explained by assuming that in this region complexed and regular SDS micelles are formed simultaneously.[11] However, since c_f is lower for PPO than for PEO (Table I), the complexed micelles are more stabilized by PPO. This makes the assumption that above c_f only complexed micelles are formed in PEO solutions, and both complexed and noncomplexed micelles in PPO solutions, less likely. The first micelles that bind to PPO will have a smaller aggregation number and a larger value of α than those binding to PEO, and we submit that the curvature in the plot of κ vs [SDS] is caused by an increase of the aggregation number and/or gradual uncoiling[12] of PPO, both with increasing concentration of SDS.

It is clear, however, that because of the substantial difference in molecular weight between PEO and PPO, the maximum number of complexed micelles per polymer chain will be much higher for PEO than for PPO. In fact, the data indicate that less than one micelle binds to each PPO chain, and the possibility that more than one polymer chain interacts with one micelle must not be discarded.[8] However, the number of monomer segments interacting with the micellar surface at surfactant concentrations of about c_1 will be approximately the same for both polymers.

The stronger binding of SDS micelles to PPO than to PEO may be the result of the higher hydrophobicity of PPO, leading to an enhanced contribution of hydrophobic interactions[13] in the polymer–surfactant complexation process. However, since the PPO backbone expands upon

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(6) Cabane, B.; Duplessix, R. *Colloids Surf.* **1985**, *13*, 19.

(7) Francois, J.; Dayantis, J.; Sabbadin, J. *Eur. Polym. J.* **1985**, *21*, 165.

(8) (a) Zana, R.; Lang, J.; Lianos, P. *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* **1982**, *23* (No. 1), 39. (b) Zana, R.; Lang, J.; Lianos, P. In *Microdomains in Polymer Solutions*; Dubin, P., Ed.; Plenum: New York, 1985; p 357.

(9) Lissi, E. A.; Abuin, E. *J. Colloid Interface Sci.* **1985**, *105*, 1.

(10) The values of c_f and c_1 are in good agreement with those reported by Francois et al.[7] These authors reported that c_f and c_1 are independent of the molecular weight of the polymer in the range of 6,000–200,000.

(11) Similar nonlinear plots were found previously for the SDS–PVP and SDS–Mowiol systems.[5b]

(12) In aqueous solution, PPO has a compact structure (coiled disk) with most of the methyl groups in the center of the coil: Sandell, L. S.; Goring, D. A. I. *Macromolecules* **1970**, *3*, 50.

(13) (a) Tanford, C. *Physical Chemistry of Macromolecules*; Wiley: New York, 1961; Chapter 7. (b) Nagarajan, R.; Kalpacki, B. *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* **1982**, *23*, (No. 1), 41.

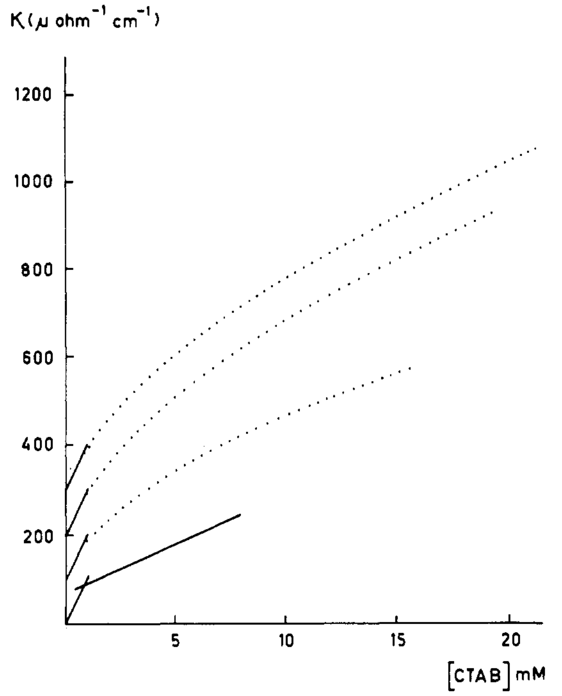


Figure 3. Plots of the specific conductivity (κ) vs concentration of CTAB at fixed concentrations of PPO. Top to bottom: 0.5, 0.3, 0.1, and 0.0 g·dL^{-1}. The curves have been displaced upward, starting relative to the bottom curve, by 1–3 scale units (100 $\mu\Omega^{-1}$.s^{-1}), respectively.

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

	[PEO], g·dL^{-1}			
[SDS], mM	0.00	0.20	0.30	0.50
0.0	12.8	12.7	12.6	12.6
4.0	12.4	12.1	12.1	11.9
6.0	12.0	6.33	6.19	6.12
8.0	9.97	4.36	4.30	4.27
10.0	5.06	3.12	2.95	2.96
15.0	3.11	2.15	2.01	1.97
20.0	2.51	1.89	1.70	1.60
30.0	1.89	1.69	1.40	1.36
40.0	1.69	1.56	1.45	1.23
50.0	1.52	1.40	1.25	1.15
70.0	1.48	1.39	1.32	1.22

complexation, a larger increase of the polymer conformational entropy[13a] in the case of PPO upon binding of SDS may also contribute to the difference.[14] The considerably higher α value for SDS–PPO than for SDS–PEO (Table I) indicates that the upper Stern region of the SDS micelles is more disturbed by interaction with PPO and less counterions are involved in the stabilization of the PPO-complexed micelles.

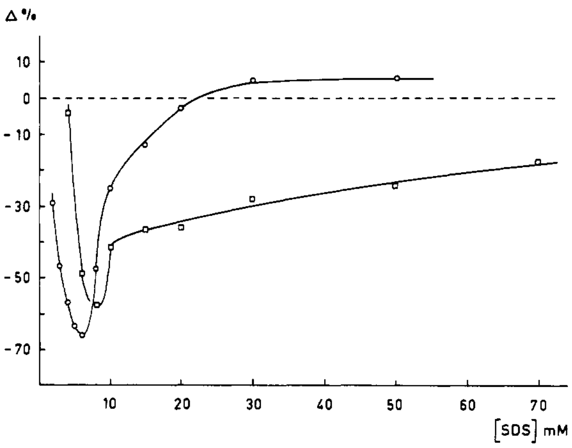


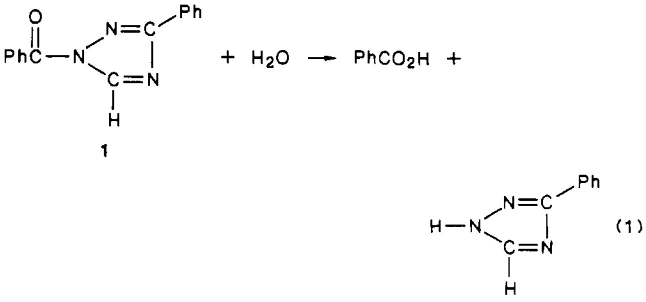
Figure 4. Effects of polymers on the SDS-inhibited neutral hydrolysis of 1. For the definition of Δ, see the text. Key: □, 0.5 g·dL^{-1} PEO; ○, 0.5 g·dL^{-1} PPO.

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

	[PPO], g·dL^{-1}			
[SDS], mM	0.00	0.20	0.30	0.50
0.0	12.8	11.9	11.7	11.3
2.0	12.4	10.6	9.96	8.77
3.0	12.3	8.23	7.49	6.58
4.0	12.2	6.35	5.78	5.27
5.0	12.0	5.32	4.96	4.42
6.0	11.4	4.59	4.28	3.87
8.0	5.98	3.63	3.41	3.15
10.0	3.65	3.14	2.95	2.73
14.9	2.44	2.31	2.22	2.12
20.0	1.91	1.99	1.91	1.85
30.0	1.43	1.49	1.51	1.50
50.0	1.11	1.13	1.15	1.17

Since CTAB interacts only very weakly with PEO, specific conductivities were only determined for CTAB–PPO (Figure 3).[15] The behavior of κ as a function of the surfactant concentration is rather similar to that for the SDS–PPO system (decrease of the cmc, curved plot beyond c_f, large increase of α; see Table I), but the measurements have not been extended to CTAB concentrations well beyond c_1 (ca. 20 mM) in order to avoid complications as a result of a change in micellar size and shape. Further comparison of the systems SDS–PPO and CTAB–PPO reveals that the PPO-induced reduction of the cmc is somewhat larger for SDS, whereas the ratio c_1/c_f is much smaller for SDS. Both observations support the conclusion that the anionic surfactant shows the greatest propensity for binding to the polymer.

Effect of PEO and PPO on Micellar Rate Effects. The model reaction we have chosen for study is the pH-independent hydrolysis of 1-benzoyl-3-phenyl-1,2,4-triazole (1; eq 1). This water-catalyzed reaction is highly medium dependent and proceeds via water-catalyzed nucleophilic attack of water on the carbonyl moiety.[16,17] The hydrolysis is inhibited by both SDS and CTAB micelles, largely as a result of the reduced micropolarity at the substrate binding sites in the Stern region of the micelle.[18]



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(14) Electrostatic forces also seem to contribute to the micelle–polymer interactions. See: Reference 1 and Schwuger, M. J. *J. Colloid Interface Sci.* **1973**, *43*, 491.

(15) The observation that cationic surfactants interact with water-soluble polymers more weakly than anionic surfactants seems to be quite general: Saito, S.; Mizuta, Y. *J. Colloid Interface Sci.* **1967**, *23*, 604. Compare also ref 1.

(16) Karzijn. W.; Engberts, J. B. F. N. *Tetrahedron Lett.* **1978**, 1787.

(17) Karzijn. W.; Engberts, J. B. F. N. *Recl.: J. R. Neth. Chem. Soc.* **1983**, *102*, 513.

(18) Fadnavis, N. W.; Engberts, J. B. F. N. *J. Org. Chem.* **1982**, *47*, 152.

Table IV. Pseudo-First-Order Rate Constants (10^4k_{obsd}, s^{-1}) for the Neutral Hydrolysis of 1 in Aqueous Solutions Containing 0.5 g•dL^{-1} of PEO or PPO, 0.4 M NaBr, and Varying Concentrations of SDS (25 °C)

	medium		
[SDS], mM	SDS	SDS–PEO	SDS–PPO
0.0	10.9	10.8	7.89
0.5	9.47	9.24	6.88
1.0	6.06	6.96	6.09
1.5	4.04	5.21	5.00
3.0	2.18	3.11	3.52
4.0	1.69	2.48	2.99
6.0	1.29	1.87	2.37
10.0	0.892	1.27	1.71
15.0	0.735	0.980	1.34
20.0	0.615	0.809	1.13
30.0	0.506	0.638	0.893
40.0	0.455	0.558	0.747
50.0	0.446	0.506	0.652
70.0	0.400	0.441	0.521

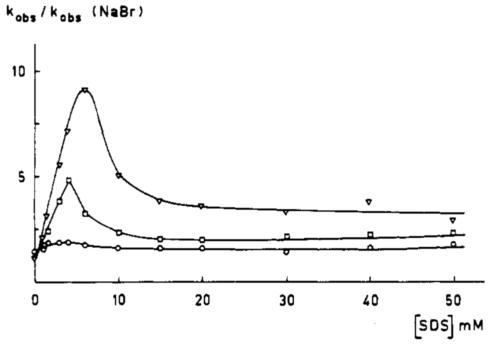

Figure 5. Effect of NaBr (0.4 M) on the neutral hydrolysis of 1 in aqueous solutions of SDS and SDS–polymer complexes. Key: ▽, SDS; □, SDS–PEO (0.5 g·dL^{-1}); ○, SDS–PPO (0.5 g·dL^{-1}).

Table V. Pseudo-First-Order Rate Constants for the Neutral Hydrolysis of 1 in Aqueous Solutions Containing CTAB and PPO (0.5 g•dL^{-1}) at 25 °C

	10^4k_{obsd}, s^{-1}			10^4k_{obsd}, s^{-1}	
[CTAB], mM	CTAB	CTAB–PPO	[CTAB], mM	CTAB	CTAB–PPO
0.0	12.9	11.6	6.00	2.02	2.99
0.5	12.9	10.4	6.99	1.88	2.75
0.99	10.3	8.22	8.00	1.77	2.55
1.50	5.77	6.60	9.00	1.66	2.39
1.96	4.21	5.65	10.00	1.61	2.25
3.00	3.00	4.47	12.00	1.47	2.06
4.00	2.51	3.78	14.00	1.37	1.91
5.00	2.22	3.33	16.00	1.29	1.80

Pseudo-first-order rate constants (k_{obsd}) for the neutral hydrolysis of 1 at 25 °C in aqueous solutions of SDS containing varying concentrations of PEO and PPO are listed in Tables II and III, respectively. The data show that the polymers alone have only a very small effect on k_{obsd}. In the solutions containing both polymer and surfactant, the rate inhibition starts already well below the cmc of regular micelles, consistent with the stabilization of the micelles by interaction with the polymers. In Figure 4, the effects of PEO and PPO are compared at a constant concentration of the polymer (0.5 g·dL^{-1}). In these plots, Δ represents the polymer-induced change of k_{obsd} (in percent) at different surfactant (surf) concentrations.

$$\Delta = [(k_{surf\text{-}pol} - k_{surf})/k_{surf}] \times 10^2$$

The decrease in k_{obsd} occurs at a lower SDS concentration in the solution containing PPO, as expected on the basis of the low c_f for PPO in comparison with that of PEO (Table I). The maximum inhibition found for SDS–PPO solutions ($\Delta \sim 67\%$) is higher than that for SDS–PEO solutions ($\Delta \sim 57\%$). This demonstrates again that the SDS micellar surface is slightly more perturbed by PPO than by PEO, in accordance with the conclusion drawn from the conductivity measurements. In the SDS–PPO solutions above 6 mM of SDS there is a rapid increase of Δ until a small and almost constant value of Δ is reached at the saturation concentration c_1 (~30 mM). The increase of Δ may be accounted for in terms of an increase of the aggregation number of the mixed micelles and the fact that at high SDS concentrations ($\geq c_1$) only regular SDS micelles will be formed. A similar behavior was found previously for the system SDS–poly(*N*-vinylpyrrolidone).[5b] By contrast, in the SDS–PEO system, Δ is still about 20% at 70 mM of SDS. This could be the result of the rather high c_1 for SDS–PEO (Table I) in combination with the small aggregation number ($m_1 = 36$)[9] compared with that of normal SDS micelles ($m = 62$). This situation ensures that even at 70 mM of SDS the number of unperturbed micelles is small compared with that of PEO-complexed micelles and that still a significant fraction of the substrate reacts in the SDS–PPO mixed micelles.

Cabane and Duplessix[6] found that the number of SDS micelles that binds to PEO is greatly increased in the presence of 0.4 M NaBr. Therefore, we have briefly examined the consequences of this salt effect for the neutral hydrolysis of 1 in aqueous solutions of SDS, SDS–PEO, and SDS–PPO (Table IV). It is well established that SDS micelles are stabilized in the presence of NaBr as revealed by a decrease of the cmc and an increase of the aggregation number.[19] Relative rate effects are plotted as a function of the SDS concentration in Figure 5, where k_{obsd} and k_{obsd}(NaBr) are the rate constants in the absence and presence of 0.4 M NaBr, respectively. For normal SDS micelles, k_{obsd} is decreased by the presence of the salt, which reflects the lowered micropolarity at the substrate binding sites as caused by the more compact packing of the surfactant molecules.[20] The rate constants in Table IV show that above 1 mM SDS (+0.4 M NaBr) the k_{obsd} values are higher in the presence of the polymers. However, the salt effect is appreciably depressed by the polymers, this being more pronounced for PPO than for PEO (Figure 5). In fact, the effect of NaBr is almost negligible in the presence of PPO. We submit that stabilization of SDS micelles by interaction with PEO and PPO apparently outweighs the stabilization by increased counterion binding in the presence of 0.4 M NaBr. As shown by the α values in Table I, counterion binding is lower in SDS–PEO and SDS–PPO micelles than in normal SDS micelles, and this situation is accompanied by a reduced propensity for further stabilization by added sodium ions.

Rate constants for neutral hydrolysis of 1 in aqueous solutions of CTAB and CTAB + 0.5 g·dL^{-1} PPO are listed in Table V. In the presence of the polymer, the rate inhibition again starts below the cmc of normal CTAB micelles but, in contrast to the SDS–PPO systems, rate constants beyond the normal cmc are larger in the presence of the complexed micelles than in solutions of normal CTAB micelles. The different behavior of SDS–PPO and CTAB–PPO systems, as expressed in plots of Δ vs surfactant concentration, is illustrated in Figure 6. As in the case of the conductivity measurements (vide supra), the CTAB–PPO system was only examined up to [CTAB] =

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(19) Lindman, B.; Wennerstrom, H. In *Topics in Current Chemistry*; Boschke, F. L., Ed.; Springer: New York, 1980; Vol. 87, p 1.

(20) Compare: (a) Sudhölter, E. J. R.; Engberts, J. B. F. N. *J. Phys. Chem.* **1979**, *83*, 1854. (b) Rupert, L. A. M.; Engberts, J. B. F. N. *J. Org. Chem.* **1982**, *47*, 5015.

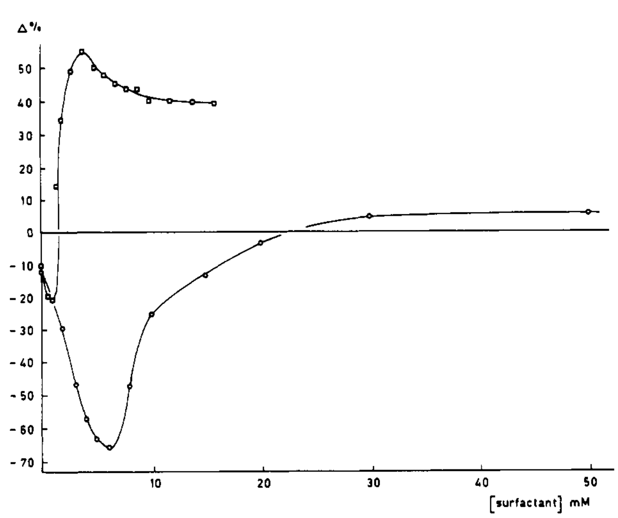

Figure 6. Comparison of the effect of PPO (0.5 g·dL^{-1}) on the SDS- (○) and CTAB- (□) inhibited neutral hydrolysis of 1. For the definition of Δ, see the text.

20 mM. It is evident, however, that the Δ parameter drops more rapidly to about zero in the case of SDS–PPO.

In previous papers[5] we have shown that kinetic data for the hydrolysis reaction in the presence of micelle–polymer complexes can be analyzed in terms of a three-phase model. But if the substrate is sufficiently hydrophobic and binds efficiently to the polymer-complexed micelles, the data can also be treated by using the more simple pseudophase model[21] for micellar catalysis and inhibition, provided that the surfactant concentration is well below c_1. These conditions hold for the systems used in the present study; thus

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

in which k_w is the rate constant in bulk water, k_{m_1} the rate constant in the polymer-complexed micelles, K_{b_1} the binding constant for binding of the substrate to the mixed micelles, m_1 the aggregation number of the mixed micelles, c_0 the total surfactant concentration, and c_f the monomer concentration of the surfactant. Indeed, plots of $(k_w - k_{obsd})^{-1}$ vs $(c_0 - c_f)^{-1}$ are linear up to [SDS] = 20 and 30 mM for PPO- and PEO-complexed micelles, respectively, deviations from linearity at higher concentrations being caused by formation of normal micelles. For CTAB the plot is linear to at least 16 mM. Values for k_{m_1} and $K_{b_1}m_1^{-1}$, obtained from the intercept and slope of the linear plots, respectively, are listed in Table VI.

Rate constants, binding constants, and aggregation numbers for the normal micelles are designated by k_m, K_b, and m, respectively. The data in Table VI nicely illustrate the subtlety of the polymer-induced modification of the micellar rate inhibition. A few salient points are the following:

(a) Rate retardations already start below the cmc of normal micelles, in accord with the stabilization of the "minimicelles" by interaction with the polymer.

Table VI. Kinetic Data for the Neutral Hydrolysis of 1 in Aqueous Solutions Containing Micelles and Micelle-Polymer Complexes (25 °C)

	10^5k_m, s^{-1}	$10^5k_{m_1}$, s^{-1}	K_bm^{-1}, M^{-1}	$K_{b_1}m_1^{-1}$, M^{-1}
SDS	5.3[a]		1380	
SDS–PEO		6.5		890
SDS–PPO		9.2		1080
CTAB	9.7		1960	
CTAB–PPO		10.0		870

[a] Reference 5b.

(b) Comparison of the k_{m_1} values for SDS–PEO and SDS–PPO complexed micelles shows that the larger value is found for the SDS–PPO system, in accordance with a more "open" structure of the mixed micelle and stronger binding to the polymer.[8,22] For CTAB, the k_m and k_{m_1} (PPO) values are rather similar, despite the large increase of α (Table I) upon binding of the micelles to PPO. Apparently, the kinetic probe responds much more weakly to a change in structure of the cationic micelle.

(c) Binding constants for micelles and complexed micelles cannot be compared quantitatively in the absence of accurate values for m_1. However, the small value of $K_{b_1}m_1^{-1}$ for CTAB–PPO mixed micelles compared with K_bm^{-1} may well contribute to (vide supra) the large positive value of Δ (Figure 6) for this system.

(d) The overall rate effects, as expressed in k_{obsd}, are largely determined by the decrease of the normal cmc in the presence of the polymer and by the presence of *more* micelles around the normal cmc as a result of the smaller aggregation number of complexed micelles relative to normal micelles.

Conclusion

We have shown that a relatively small variation in the structure of a polymer (PEO vs PPO) already exerts a clear influence on the formation and properties of micelle–polymer complexes. The polymer-induced changes in the properties of the mixed micelle also depend on the charge type of the surfactant. Micellar rate effects observed in aqueous solutions of mixed micelles reveal the stabilization of the micelles upon binding to the polymer and also reflect minor changes in the Stern region relative to unperturbed micelles.

Experimental Section

Materials. The preparation of 1-benzoyl-3-phenyl-1,2,4-triazole (1) has been described previously.[5a] SDS (BDH, especially pure, cmc in accord with literature data[1,7]) was used as received. Anal. Calcd for $C_{12}H_{25}NaO_4S$: C, 49.97; H, 8.76; S, 11.12; Na, 7.98. Found: C, 49.95; H, 8.83; S, 10.98; Na, 7.87. A shallow minimum in the surface tension plot as a function of [SDS] is indicative of the presence of a small amount of a surface-active impurity, which is very difficult to remove completely. A likely candidate is *n*-dodecanol. Therefore, k_{obsd} values were measured for the hydrolysis of 1 in SDS (15 mM) and in SDS (15 mM) + PEO (0.5 g·dL^{-1}) solutions in both the absence and presence of added *n*-dodecanol (0.5%, w/w, relative to SDS). The k_{obsd} values were equal within 3%, which suggests that the presence of the long-chain alcohol has no significant effect on the kinetic analysis. CTAB (Merck) was purified as described by Duynstee and Grunwald.[23] The aggregation numbers of SDS[24] and CTAB[25] (Table I) are literature values. PEO (Fluka, weight-averaged MW 10 000) was purified as described previously.[26] PPO (Janssen, weight-averaged MW 1000) was used as received.

Measurements. The conductivity and kinetic measurements were performed as described previously.[5a,b] α values obtained from

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the conductivity plots have previously been shown to be in excellent agreement with those based upon emf measurements using ion-selective electrodes.[27] Furthermore, SDS behaves as a typical 1:1 electrolyte below its cmc.[28]

Pseudo-first-order rate constants (k_{obsd}) for the neutral hydrolysis of 1 were reproducible to within 2%. The rate constants reported in Tables II–V have been determined for each series with the same surfactant stock solution to which varying amounts of polymer and/or salt were added. This procedure was employed to avoid ambiguities that may result from factors such as aging of the surfactant solution. Several control experiments were run using SDS–PEO and SDS–PPO solutions prepared from the same SDS stock solution. The latter data showed the same trends in k_{obsd} as found previously.

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Registry No. SDS, 151-21-3; CTAB, 57-09-0; PEO, 25322-68-3; PPO, 25322-69-4; 1-benzoyl-3-phenyl-1,2,4-triazole, 79746-00-2.

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Specifically Deuteriated Bicyclo[3.2.0]hepta-2,6-dienes

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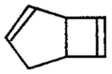
An efficient synthetic route from the dichloroketene/cyclopentadiene adduct to bicyclo[3.2.0]hepta-2,6-diene has been developed and adapted to prepare deuteriated analogues of this diene labeled specifically at C1–C5, C6, or C7, or any combination of these possibilities.

Bicyclo[3.2.0]hepta-2,6-diene (1) and specifically deuteriated analogues such as 2–8 were required in fair quantities for studies of several stereochemical and mechanistic problems. A perusal of the literature provided little encouragement that established synthetic routes could be exploited.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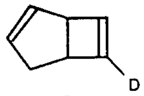

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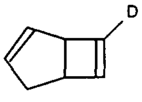

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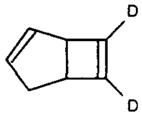

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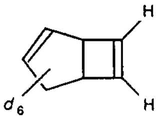

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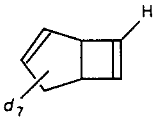

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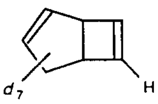

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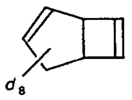
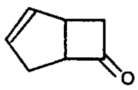


8

Relatively small quantities of the unlabled diene 1 may be secured through photochemical isomerization of cyclohepta-1,3,5-triene,[1–4] but the conversion lacks efficiency, does not lend itself to convenient scale-up, and cannot be adapted to secure specifically deuteriated variants. Synthesis of diene 1 from bicyclo[3.2.0]hept-2-en-6-one (9), an intermediate readily accessible through the cycloaddition of cyclopentadiene with ketene[5] or dichloroketene,[6–8] has attracted attention for more than 30 years, yet the overall conversion of 9 → 1 has been achieved only in disappointing yields.



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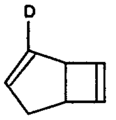

10

Hofmann degradation of the trimethylammonium hydroxide derived from 9 by way of the oxime and the 6-amino bicyclic olefin achieved the first synthesis of 1, in very low yield.[9] Reduction of ketone 9 gives predominantly the endo alcohol; mesylate, tosylate, and methyl xanthate derivatives of the alcohol react solvolytically or thermally to give mostly cyclohepta-1,3,5-triene.[10–12] Assisted ionization of these derivatives with cleavage of the C1–C5 bond appears stereoelectronically favorable.[13] A synthesis of 2 from 9 by $LiAlD_4$ reduction and pyrolysis of the mixture of xanthates did give the specifically labeled product, but after isolation and purification by preparative gas chromatography, the overall yield for 9 → 2 was only

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