example, benzeneselenol deaminates secondary alkylamines, resulting in alkylbenzyl selenide.[17] In conclusion, we have demonstrated the first known catalytic role for selenocysteine in an enzyme.

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Polymer-Induced Breakdown of Rodlike Micelles. A Striking Transition of a Non-Newtonian to a Newtonian Fluid

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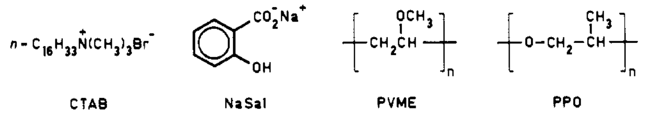
Cetyltrimethylammonium salicylate (CTASal) is the archetype of a cationic surfactant that forms rodlike micelles even in dilute ($\sim 10^{-4}$ M) solutions.[1-5] At higher concentrations, the viscous, gel-like solution of CTASal shows all the peculiarities of a viscoelastic, non-Newtonian fluid.[6] Herein we report that addition of small quantities of the weakly hydrophobic but *water-soluble* poly(vinyl methyl ether) (PVME) or poly(propylene oxide) (PPO)



completely eliminates the viscoelasticity and transforms the solution into a normal Newtonian liquid of water-like viscosity.[7] This novel extension of the scope of polymer-micelle interactions[8] may have industrial importance, for example, in soap dispersion. Poly(ethylene oxide) (PEO) and poly(vinylpyrrolidone) (PVP), which are definitely more hydrophilic than PVME and PPO as well as the low molecular weight additives EtOH and *t*-BuOH, do not perturb the CTASal rods.

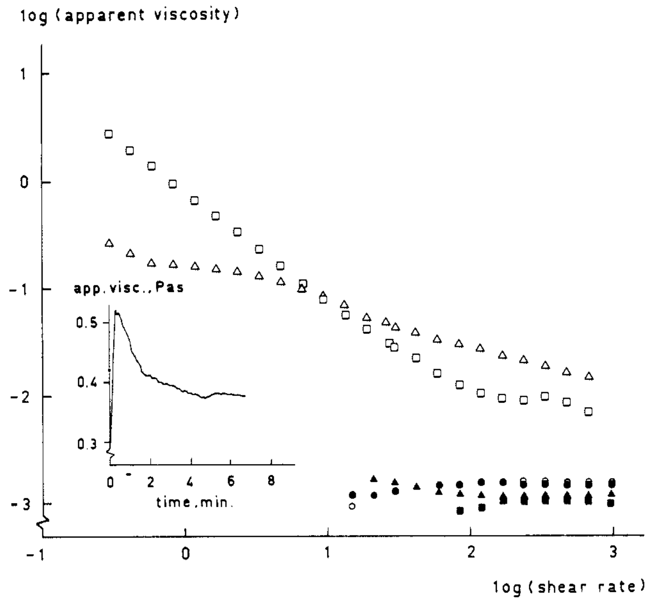


Figure 1. Double logarithmic plot of apparent viscosity vs shear rate for the following aqueous solutions of CTAB (25 mM): ■, no additives; ▲, +PEO (0.5 g dL^{-1}); ●, +PVME (0.5 g dL^{-1}); □, +NaSal (15 mM); △, +NaSal (15 mM) + PEO (0.5 g dL^{-1}); ○, +NaSal (15 mM) + PVME (0.5 g dL^{-1}). Inset: thixotropic behavior of CTAB (25 mM)/NaSal (15 mM)/PEO (0.5 g dL^{-1}). At t = 0 min, the shear rate is switched from 1.19 to 2.38 s^{-1}. Temperature = 25 °C.

Table I. The Effect of Sodium Salicylate and Several Monomeric and Polymeric Additives on the Viscosity of a Micellar CTAB Solution

[CTAB], mM	[NaSal], mM	additive[a]	viscosity, cP
25			1.08 ± 0.02
25		PVME	1.510 ± 0.0006
25		PEO	1.26 ± 0.02
25	15		2771,^{b} 8.8^{c}
25	15	PVME	1.630 ± 0.006
25	15	PPO	1.08 ± 0.006
25	15	PEO	274,^{b} 16.9^{c}
25	15	PVP	2817,^{b} 15.4^{c}
25	15	EtOH	3055,^{b} 8.1^{c}
25	15	*t*-BuOH	2213,^{b} 8.9^{c}

[a] [Additive] = 0.5 g dL^{-1}. [b] Shear rate = 0.2985 s^{-1}. [c] Shear rate = 477.6 s^{-1}.

Although the change in the properties of the CTASal aggregates induced by PVME or PPO strikes the eye, rheological measurements[9] were performed to quantify the effect. Apparent viscosities as a function of shear rate (cylindrical geometry) are depicted in Figure 1. As recommended by Hoffmann et al.,[4] mixtures of equal volumes of CTAB (50 mM) and sodium salicylate (NaSal; 30 mM) were used to obtain pronounced viscoelastic and gel-like properties. These CTAB/NaSal (whether or not in the presence of PVP) and, to a lesser extent, the CTAB/NaSal/PEO solutions exhibit genuine non-Newtonian behavior (Table I), that is, the apparent viscosities vary dramatically with changing shear rate. The enormous drop in viscosity with increasing shear rate may be attributed to shear-induced aligning and/or breakdown of the rodlike micelles.[13] By contrast, the apparent viscosities of the CTAB/NaSal/PVME and CTAB/NaSal/PPO solutions and the CTAB solutions in the absence of NaSal are independent of shear

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(9) Brabender Rheotron rheometer, equipped with a normal F-sensor, which allows the measurement of first normal stress differences. PVME (Aldrich, mw 27 000, purified[10]) and PEO (Sigma, mw 20 000, purified[11]), PPO (Janssen, mw 1000), and PVP (Kollodion-90, BASF, purified[12]) were used.

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(13) (a) Whether the decrease of the viscosity (Figure 1; power law index n = 0) is due to a uniform structural change or a structural change only near the wall of the vessel ("effective slip at the wall")[14] has yet to be determined. Similar behavior, though in a different range of shear rates, has recently been reported; see: Strivens, T. A. *Colloid Polym. Sci.* **1989**, *267*, 269. (b) The CTAB/NaSal, CTAB/NaSal/PVP, and CTAB/NaSal/PEO solutions exhibit marked thixotropy[6] (Figure 1, inset) and rheopexy,[6] which also originates from shear-induced changes in the internal structure of the liquid. Similar effects are found for the CTAB/NaSal solutions containing EtOH or *t*-BuOH.

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rate (Table I, entries 1-3, 5, and 6, and Figure 1),[6] indicative of Newtonian behavior.

The addition of PVME or PPO (both in 0.5 g dL^{-1} concentrations) completely changes the solution characteristics of the CTAB/NaSal solution. The viscosity is reduced by several orders of magnitude to a water-like value, and no viscoelasticity can be observed either visually or rheometrically. These data suggest a complete transition from rodlike to spherical micellar aggregates.[7] Presumably, this morphological transition is driven by the tendency of sufficiently hydrophobic polymers to wrap around the surface of surfactant aggregates, thereby reducing the unfavorable core-water contact at the surface of the assembly.[8,10,15] Since the surface/volume ratio is larger for spherical micelles than for rods, the presence of PVME or PPO leads to preferred sphere formation.[15] No such effect is found for PEO or PVP (Figure 1, Table I). The viscoelasticity of the CTAB/NaSal solution in the presence of PEO at shear rates ranging from 0.119 to 3808 s^{-1} is slightly increased as indicated by the first normal stress difference (cone-and-plate geometry). This is probably related to the enhanced viscosity of the CTAB/NaSal/PEO system in this range of shear rates. Thus the presence of PEO does not greatly affect the rodlike structures, although modest effects on the exact rheological properties are revealed. The same conclusion holds for PVP.

In summary, the present results show that micelle-polymer interactions can have a dramatic effect on the morphology of the surfactant assembly and can completely change the rheological behavior of the solution. Further studies in this field are in progress.

Acknowledgment. We are much indebted to Prof. L. P. B. M. Janssen and Dr. J. P. Sek for their help with the rheological measurements and for stimulating discussions.

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(15) Brackman, J. C.; van Os, N. M.; Engberts, J. B. F. N. *Langmuir* **1988**, *4*, 1266. Binding of PVME or PPO to spherical CTAB micelles[10] is driven both by a reduction of the unfavorable core-water contact and by a favorable Gibbs energy for transfer of polymer segments from the aqueous to the micellar environment. See also: Ruckenstein, E.; Huber, G.; Hoffmann, H. *Langmuir* **1987**, *3*, 382.

A Body-Diagonal Bond in Cubane: Can It Be Introduced?

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1,4-Dihalogenated norbornanes and bicyclo[2.1.1]hexanes react with alkali metal vapors[2] to yield [2.2.1]propellane[3] and [2.1.1]propellane.[4] Can a body-diagonal bond be introduced into cubane? Like [1.1.1]propellane,[5] **1** might lead to staff-like oligomers[6-9] and polymers.[6,8,10]

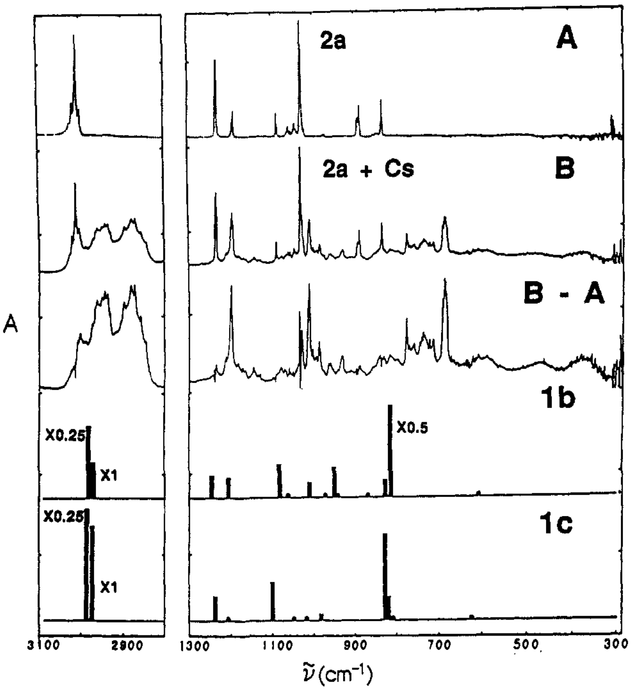
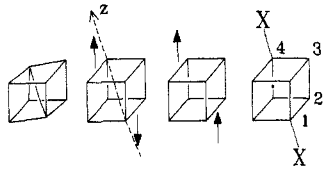


Figure 1. IR spectra in Ar at 12 K (top) and calculated, scaled by 10% (bottom). No significant IR absorption was observed outside the region shown.

Scheme I



1a 1b 1c 2 a X=I b X=Br

Codeposition of argon with 1,4-diiodocubane (**2a**)[11] to yield **1** (Scheme I) and K or Cs vapor, or 1,4-dibromocubane (**2b**)[12] and Cs vapor, on a cold CsI window yielded matrices colored by excess metal. IR showed much unreacted **2** and a series of bands (Figure 1) whose relative intensities and frequencies agreed (±5 cm^{-1}) in the three sets of experiments, suggesting that they belong to a single species **X**, different from authentic samples of cubane,[13] iodocubane,[14] and bromocubane[15] and containing neither a halogen nor a metal atom. The low C-H stretching frequencies fit expectations for hyperconjugating H-C-C$^{\bullet}$[16] or H-C-C$^-$.[17]

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