

Interactions of Aminoalkylcarbamoil Cellulosics and Sodium Dodecyl Sulfate. I. Surface Tension

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ABSTRACT: We have compared the interactions between Polyquaternium 10 and sodium dodecyl sulfate (SDS) with similar complexes of mono and diquaternary aminoalkylcarbamoil cellulose derivatives by measuring the surface tension of their aqueous solutions. The results indicate that reduction of surface tension of aqueous solutions occurs via the formation of highly surface active polymer-surfactant complexes. At approximately a 1 : 1 stoichiometric ratio of SDS to quaternary groups, a complex of low solubility forms which is more efficient at reducing surface tension than the surfactant alone. The ability of the polymer-surfactant complex to reduce surface tension appears to be independent of polymer architecture and dependent only upon adsorption of the surfactant species at the cationic polymer sites. © 1998 John Wiley & Sons, Inc. *J Appl Polym Sci* 68: 1091–1097, 1998

Key words: cellulose; quaternary ammonium; water soluble; sodium dodecyl sulfate; surface tension

INTRODUCTION

Water-soluble polymers and surfactants are commonly formulated together in cosmetic products. Polymer-surfactant systems are used in a variety of two-in-one products, such as shampoos and hand lotions, to condition hair and skin. These two components can interact to produce either highly desired attributes or unwanted problems affecting both emulsion formulation and stability. A critical factor in formulation is the surface tension resulting from the interactions which occur between water-soluble polymers and surfactants.

Goddard and coworkers have studied the system of Polyquaternium 10 (a cationic cellulosic polymer) and sodium dodecyl sulfate (SDS) extensively.^{1–10} The results of these studies show that the components form strong polymer surfac-

tant complexes which are highly surface-active, despite the fact that Polyquaternium 10 by itself is only slightly surface-active. From surface tension studies,^{1–4,10} it was determined that a cationic polymer and SDS, like many uncharged polymer-SDS mixtures, exhibit an interaction zone.^{11–14} However, the interaction zone for the cationic polymer and SDS was shifted to much lower surfactant concentrations than for uncharged polymers and SDS.³ From these studies, no interaction was detected between the parent (uncharged) polymer, hydroxyethyl cellulose, and SDS by surface tension method.^{1–3,10,15} The essential features of the surface tension plots of Polyquaternium 10 and SDS are (1) a synergistic lowering of the surface tension at very low concentrations of SDS, which implies the formation of a highly surface-active polymer-surfactant complex; (2) the persistence of a low surface tension even in the zone of high precipitation; and (3) coincidence with the surface-tension curve of SDS solution in the micellar region.^{1,2} Goddard and Ananthapadmanabhan² have explained this phe-

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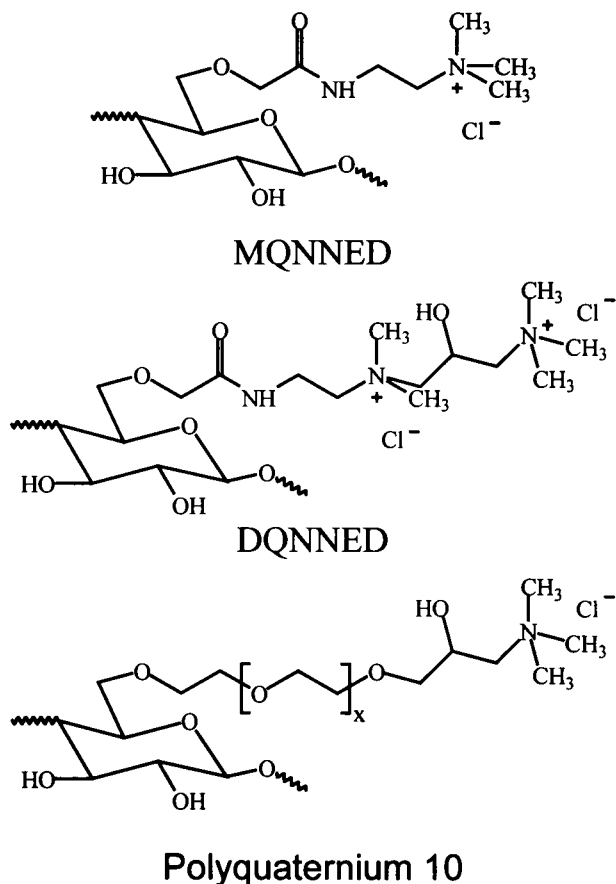


Figure 1 Structures of mono and diquaternary ammoniumalkylcarbamoyl cellulose derivatives and Polyquaternium 10.

nomenon as being the result of changes in surface-active species present at the interface due to the progressive uptake of the SDS by the polymer. An increase in foaming power of these solutions, which is a direct consequence of the increased surface activity of the Polyquaternium 10–SDS complex formed, was also observed.⁴

We have prepared new mono and diquaternary ammoniumalkylcarbamoyl cellulose derivatives (Fig. 1) with defined charge densities where the quaternary nitrogen is located at the sites of carboxymethylation of the starting polymer.^{16,17} The degree of substitution of the carboxymethylcellulose was 0.70 and the degree of substitution of the aminoamide derivative was 0.56.^{18,19} These model polymers have been used to determine the changes in surface tension resulting from complexation of the charged polymers with SDS. The effects of these polymer–SDS complexes on surface tension have been compared with the behavior of the Polyquaternium 10–SDS complex. Poly-

quaternium 10 (Fig. 1) is a quaternized hydroxyethyl cellulose derivative where the cationic moiety is attached to polyoxyethylene spacer groups that provide flexibility independent of the cellulose chain.²⁰ The results of these studies reveal the role of polymer charge density and graft flexibility on surface tension.

EXPERIMENTAL

Materials

SDS, 99%, was obtained from Sigma Chemical Company (St. Louis, MO). Polyquaternium 10, UCARE Polymer JR-400, was obtained from Amerchol Corporation (Edison, NJ). 2-Trimethylammoniummethyl carbamoyl cellulose chloride (MQNNED) was prepared from the corresponding *N,N*-dimethylaminoethyl carbamoyl cellulose by quaternization with methyl iodide followed by ion exchange with 1.0M sodium chloride in a cellulose acetate dialysis tube with a 6–8,000 D cut-off. Treatment of *N,N*-dimethylaminoethyl carbamoyl cellulose with *N,N,N*-trimethylammonium-3-chloro-2-propanol (Quat 188) yielded the diquaternary derivative, 3-trimethylammonium-2-hydroxypropyl-*N,N*-dimethylammoniummethyl carbamoylmethyl cellulose chloride (DQNNED).^{16,17} Water was purified by reverse osmosis, deionization, and filtration (Osmonics, Inc.).

Methods

Solutions were prepared by addition of a concentrated polymer solution (1–3%) to a solution of SDS. The solutions were stirred and allowed to equilibrate overnight. Surface tension measurements were obtained using a Kruss K14 tensiometer using the Wilhelmy plate method at $20 \pm 0.5^\circ\text{C}$. The tensiometer was calibrated with distilled deionized water. All surface-tension measurements were made in triplicate and error bars are based upon these measurements.

RESULTS AND DISCUSSION

A plot of surface tension versus concentration of the surfactant alone exhibits a significant decrease with initially increasing concentration, followed by a plateau where the surface tension remains essentially constant. The plateau is due to the formation of surfactant clusters (micelles)

and the break point is called the critical micelle concentration (CMC). Above this concentration, almost all of the added surfactant monomers are consumed in micelle formation and the monomer concentration in solution does not increase appreciably. Therefore the surface tension remains essentially constant above the CMC and can be related directly to the activity of the monomers in solution. Any solute which has a positive adsorption at the interface will decrease the surface tension. Similarly, a component which has a negative surface excess can actually lead to an increase in surface tension of the solvent. Since the changes in surface tension can be related to the activity of the monomeric surfactant species in solution, interactions of surfactant with other species which result in changes of monomer activity can be monitored.

Using the Wilhelmy plate method, surface tension was studied as a function of surfactant concentration at fixed concentrations of polymer. The results for the interaction of Polyquaternium 10 and SDS (Fig. 2) indicate that the polymer by itself is only slightly surface-active at the air-water interface. The reduction in surface tension by a 0.1% Polyquaternium 10 solution is approximately 8 mN/m greater than that of a $3.5 \times 10^{-5} M$ (0.001%) solution of SDS. This result agrees with a result previously published by Goddard and Hannan.⁴

The complex formed by association of the negatively charged SDS monomers with this cationic polymer is highly surface-active (Fig. 2), as shown by the reduction of surface tension. This effect is especially pronounced at low concentrations of surfactant and high levels of polymer. A solution comprised of 0.1% Polyquaternium 10 and $3.5 \times 10^{-5} M$ SDS reduced surface tension of water to the same extent as a $1.7 \times 10^{-3} M$ SDS solution. This reduction in surface tension continues despite precipitation of the polymer surfactant complex and eventually coincides with the curve for SDS as the complex is resolubilized at higher SDS concentrations where micelle formation occurs. This lowering of the surface tension has been attributed to modification of the polymer by adsorption of SDS anions at the cationic sites.⁴ However, any synergistic effect is difficult to describe because the slope of the surface tension plots in the presence of polymer is governed by the free SDS monomer concentration, the activity of the polymer-surfactant complex, and the amount of precipitate formed.

Surfactant "efficiency," the concentration of

surfactant necessary to reduce the surface tension by 20 mN/m,²¹ is $1.7 \times 10^{-3} M$ for solutions of SDS in water. In contrast, for the 0.1% Polyquaternium 10-SDS complex, the requisite reduction occurred at a surfactant concentration of $3.5 \times 10^{-5} M$ or even below this value. Therefore, the complex is at least 50 times more efficient in reducing surface tension than the surfactant alone. Surfactant "effectiveness" is defined as the maximum reduction in surface tension that can be obtained regardless of the bulk-phase concentration of surfactant.²¹ "Effectiveness" is measured²¹ by the amount of reduction in surface tension obtained at the CMC of the surfactant because further reduction of surface tension beyond the CMC is relatively insignificant. Effectiveness for the polymer-surfactant complex is defined as the maximum reduction in surface tension that can be obtained regardless of the bulk-phase concentration of the polymer and surfactant. Polymer-surfactant complex effectiveness is measured by the amount of reduction obtained by the complex at the CMC of the surfactant. The complex of 0.1% Polyquaternium 10 and SDS is more effective at reducing surface tension than SDS alone, whereas solutions containing 0.001 and 0.01% Polyquaternium 10 and SDS are slightly less effective at reducing surface tension than SDS alone.

In a similar manner (Fig. 3), complexation of SDS with a slightly surface-active monoquaternary polymer (MQNED) derived from carboxymethyl cellulose was studied. Large decreases in surface tension at low concentration of SDS were observed. This effect also remained in the presence of precipitated complex, and the curve eventually coincided with the surface-tension curve for SDS as resolubilization of the complex occurred. Increasing the polymer concentration also produced greater decreases in surface tension. The solution that produced the most efficient decrease in surface tension was 0.1% MQNED- $3.5 \times 10^{-5} M$ SDS. In general, solutions of 0.1% MQNED-SDS were more effective at reducing surface tension than SDS alone. Solutions of 0.001 and 0.01% MQNED and SDS were slightly less effective at reducing surface tension than SDS alone around its CMC.

Finally, the effect of complexation of SDS with the slightly surface-active diquaternary polymer (DQNNED) on surface tension was studied. Initially, at low concentrations of surfactant and 0.1% polymer, surface tension decreased markedly relative to the surface tension of SDS solutions (Fig. 4). Again, the most efficient polymer-

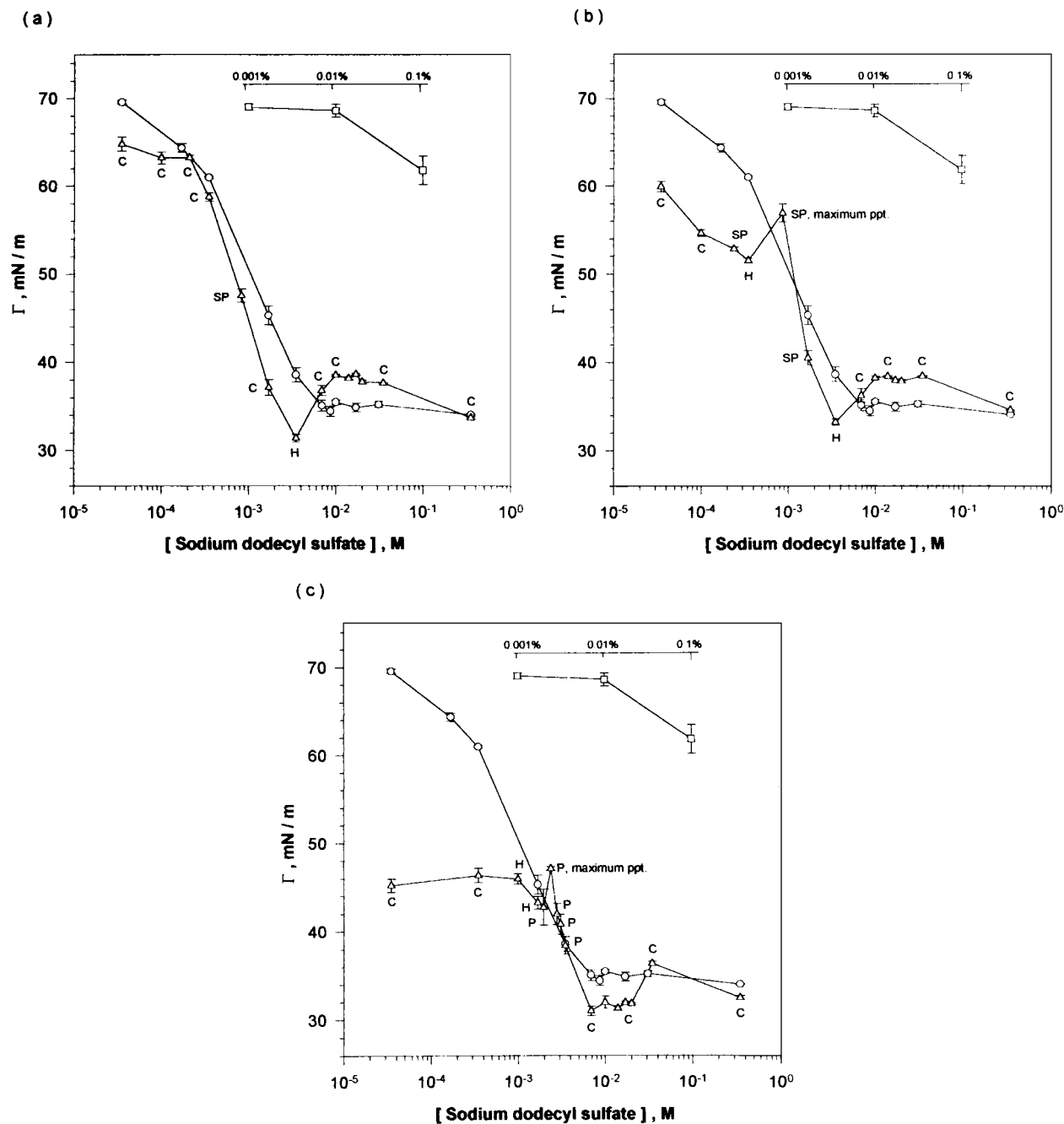


Figure 2 Surface tension of Polyquaternium 10–SDS complexes. (○) SDS; (□) Polyquaternium 10. (a) (△) 0.001% Polyquaternium 10 and SDS; (b) (△) 0.01% Polyquaternium 10 and SDS; (c) (△) 0.1% Polyquaternium 10 and SDS. C, clear solution; H, hazy solution; SP, slight precipitate; P, precipitate.

surfactant system observed contained 0.1% DQNNED and 3.5×10^{-5} M SDS.

Regardless of polymer architecture, the solutions that contained 0.1% polymer and SDS were more effective in reducing surface tension than

SDS alone. We propose (Fig. 5) that addition of increasing amounts of surfactant results in further decreases in surface tension as the air–liquid interface becomes saturated until the SDS : polymer ratio approaches a stoichiometric balance.

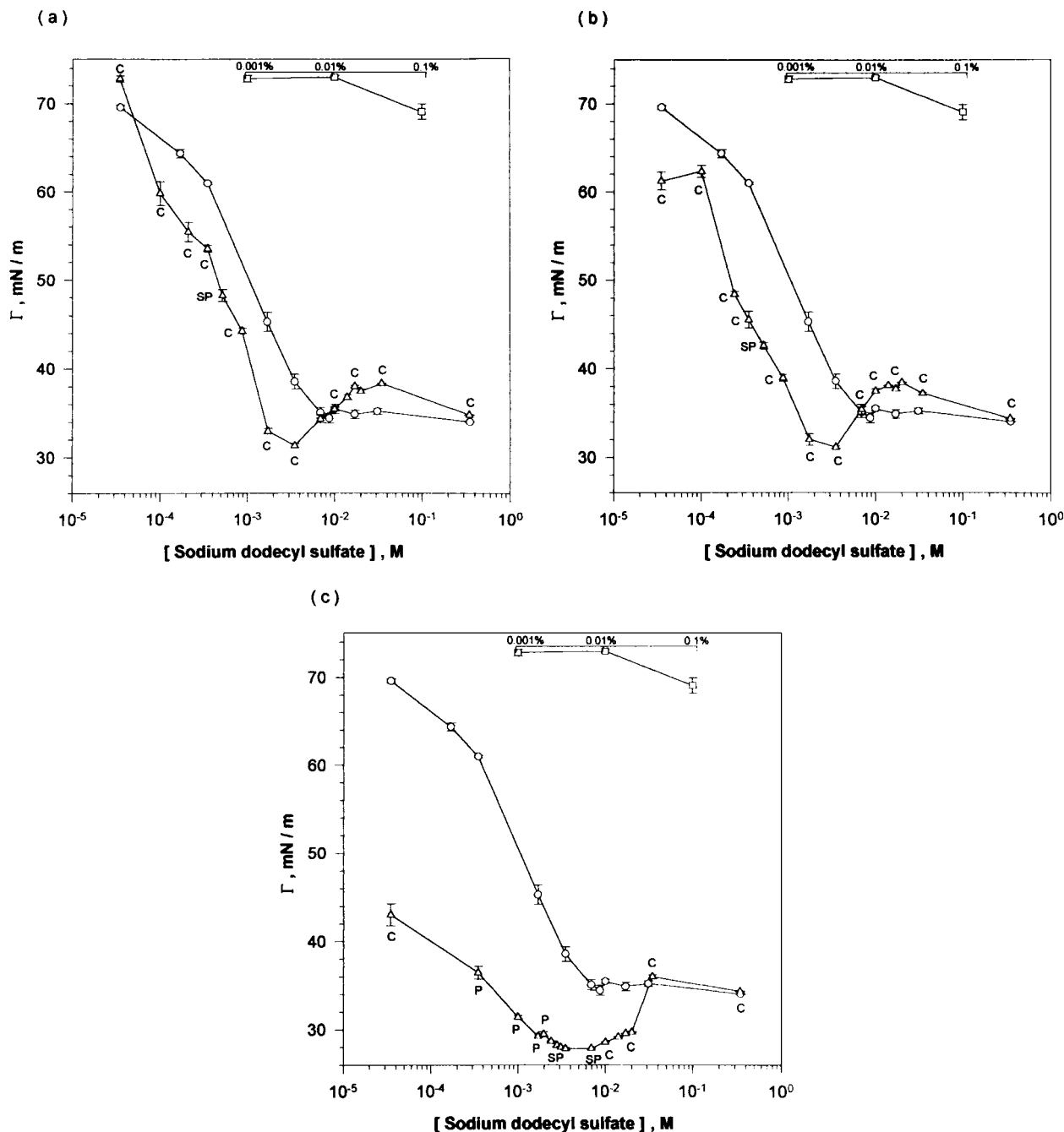


Figure 3 Surface tension of MQNED-SDS complexes. (○) SDS; (□) MQNED. (a) (△) 0.001% MQNED and SDS; (b) (△) 0.01% MQNED and SDS; (c) (△) 0.1% MQNED and SDS. C, clear solution; H, hazy solution; SP, slight precipitate; P, precipitate.

Upon neutralization by SDS, the polymer-surfactant complex appears to precipitate maximally and surface tension increases slightly. Beyond this point of apparent maximum precipitation, surface tension again begins to decrease as the

partitioning of the surfactant between the polymer-surfactant complex and free micelles in solution controls the surface tension of the liquid. Surface tensions of the polymer-surfactant solutions eventually coincide with the surface tension of

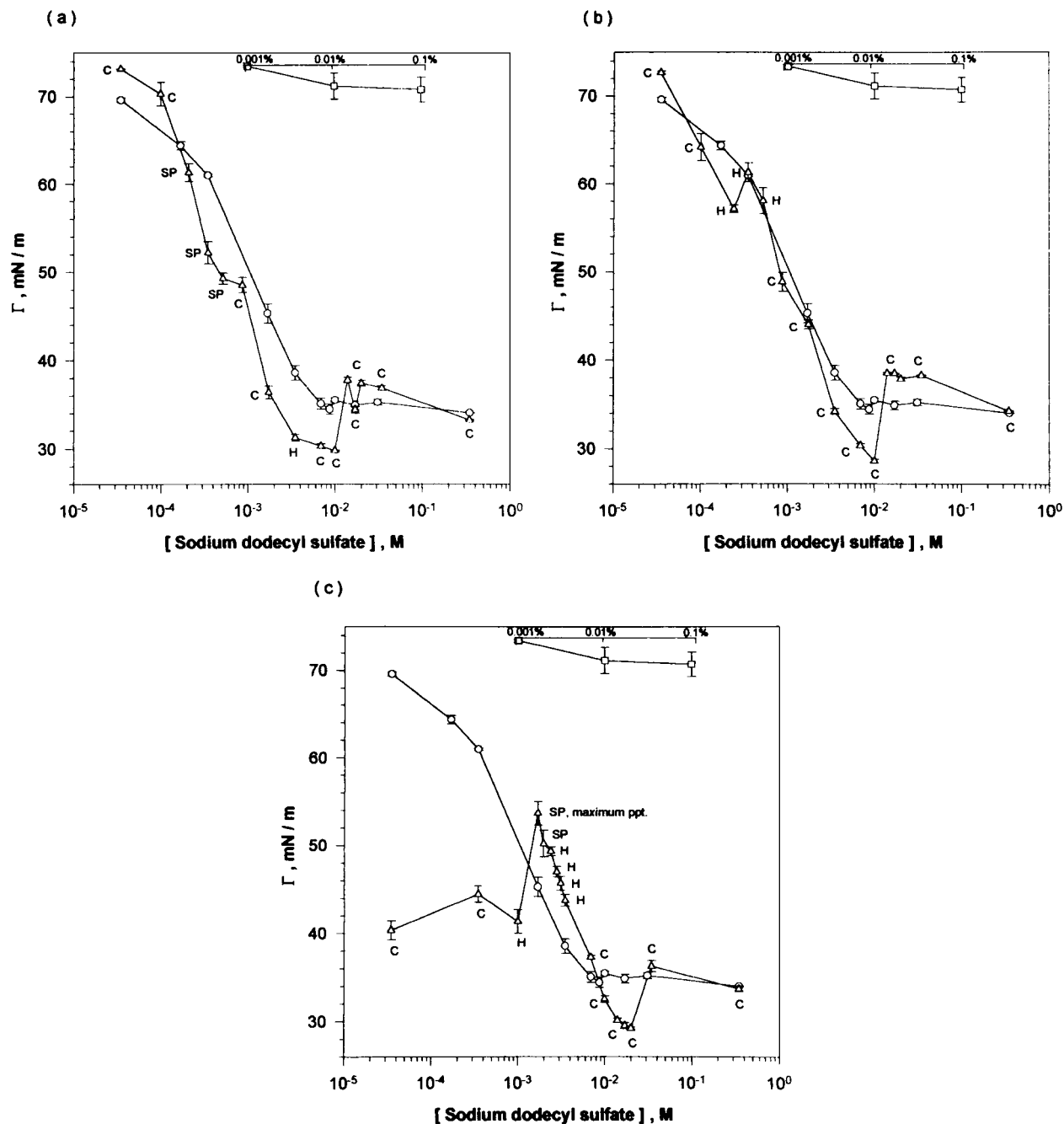


Figure 4 Surface tension of DQNNED-SDS complexes. (○) SDS; (□) DQNNED. (a) (△) 0.001% DQNNED and SDS; (b) (△) 0.01% DQNNED and SDS; (c) (△) 0.1% DQNNED and SDS. C, clear solution; H, hazy solution; SP, slight precipitate; P, precipitate.

SDS as the precipitated complex is resolubilized by formation of polymer-bound micelles and free micelles. The dip in the surface-tension curves at the CMC of SDS may indicate that a more surface-active component is being solubilized in the surfactant micelles.

CONCLUSIONS

When a slightly surface-active polymer is added to a surfactant solution, reduction of surface tension occurs due to formation of a highly surface-active complex. The evidence of this complexation is the

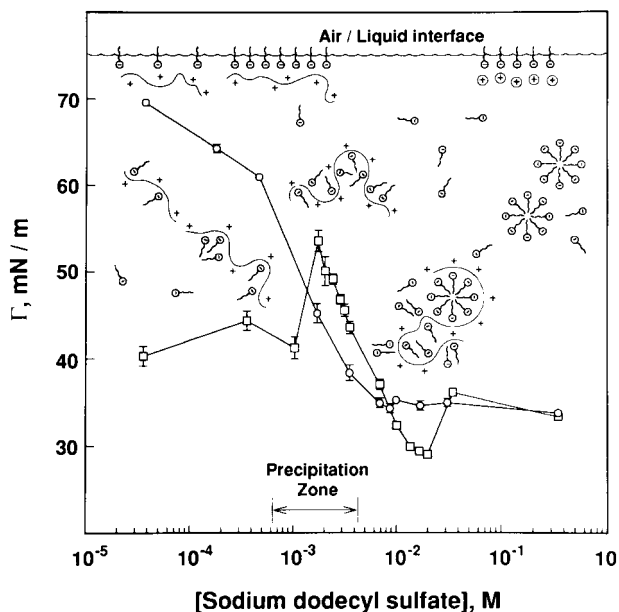


Figure 5 Conditions at the air-liquid interface and in the bulk solution of a solution containing a fixed concentration of a cationic polymer and an anionic surfactant. (○) SDS; (□) 0.1% DQNNED and SDS.

formation of an insoluble precipitate which is more efficient at reducing surface tension than the surfactant alone. The surface-tension plots show evidence of three interaction zones corresponding to formation of the surface active complex, precipitation of the complex due to adsorption of surfactant, and, finally, resolubilization of the complex. The interaction zones are present regardless of polymer structure or charge density. The ability of the polymer-surfactant complex to reduce surface tension appears to be independent of polymer architecture and dependent only upon adsorption of the surfactant species at the cationic polymer sites.

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