Influence of Nonionic Surfactant Additive on the Properties of Ionic Surfactant Solutions

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ABSTRACT

The interaction of sodium dodecyl sulfate with a nonionic surfactant (a block copolymer of ethylene oxide and propylene oxide) has been investigated by the measurement of conductivity, surface tension and viscosity. The break point on the equivalent conductivity-square root of concentration (λ-$\sqrt{c}$) diagram which gives the critical micelle concentration (cmc) of sodium dodecyl sulfate became less definite by the addition of the nonionic surfactant, because of the decrease in conductivity below the cmc and increase above the cmc. The steep decrease in reduced viscosity took place in dilute concentration of sodium dodecyl sulfate solutions. In the surface tension vs. concentration diagram, the concentration at which the two linear portions of the curve intersect represents the cmc. The addition of nonionic surfactant decreases this crossed point of sodium dodecyl sulfate and finally obscures the crossed point. These reults are interpreted in terms of an interaction between sodium dodecyl sulfate and nonionic surfactant.

INTRODUCTION

Mixtures of surfactants such as ionic and nonionic surfactants are used widely in practice, but the study of these mixtures from the standpoint of physical chemistry is very limited (1-5). Previously the authors (1) reported on the influence of nonionic surfactants of the polyoxyethylene higher alcohol ether type on the micelle formation of anionic surfactants. In that report the authors showed that the break point in the λ-$\sqrt{c}$ diagram becomes unclear and finally disappears with the addition of nonionic surfactant.

Biswas and Mukherjee (2) showed that with sodium cetyl oleyl alcohol sulfate (Lissapol C), the typical break in the conductivity vs. concentration curve, which denotes cmc, gradually disappears with additions of nonionic detergents such as the fatty alcohol ethylene oxide condensation product (Lubrol L). All of the nonionic surfactants employed in the above experiments have the characteristic of forming micelles, and therefore the phenomena which occured between combinations of nonionic and ionic surfactants could be discussed as the interaction between micelles of both ionic and nonionic surfactants. The block copolymer of ethylene oxide and propylene oxide is an interesting surfactant in that it has the intermediate properties of a water soluble polymer and a surfactant which does not form the usual type micelle. We therefore have an interest in the interaction between this type of surfactant and ionic surfactants.

In this report the effects of nonionic surfactants, such as block copolymer types on micelle formation of sodium dodecyl sulfate will be reported by the measurement of conductivity, surface tension and viscosity.

EXPERIMENTAL PROCEDURES

Materials

The anionic surfactant used was sodium dodecyl sulfate (SDS) which was synthesized by the method of Dreger et al. (6). The surface tension vs. concentration curve showed no minimum.

The nonionic surfactant used was the block copolymer of ethylene oxide and propylene oxide named Epan 420, which was supplied by Daiichi Kogyo Seiyaku Co. Ltd. (Ep 420).

Preparation of Solutions

The water used in all the experiments was purified by passing through an ion-exchange column followed by distillation from alkaline permanganate solution. Specific conductance of this water is $K = 1.010 \times 10^{-6}$ ohm^{-1} cm^{-1}. Solutions of Ep 420 were prepared in this water. These aqueous solutions were purified by passing them through an ion-exchange column to eliminate some inorganic contamination such as catalyst. Specific conductance of various concentrations of Ep 420 are shown in Table I.

Conductivity

The conductivity measurements were made with an electroconductivity meter using a cell with a cell constant of 1.0000 (Toa Denpa Kōgyō Co. Ltd., Tokyo, Model CM–IDB). All measurements were made in a thermostat at 40 ± 0.2 C.

Surface Tension

The surface tension was measured by the drop weight method using a microsyringe. The measurements were made in a thermostat at 40 ± 0.2 C at intervals of a few minutes until the values agreed within 0.5 dyne/cm. Usually three measurements were required to obtain constant values.

Viscosity

The viscosity was measured at 40 ± 0.2 C with a suspended level Ubbelohde viscometer.

Krafft Points

It has been stated that ionic surfactants can be in solution as micelles only above the definite temperature known as the Krafft point; above this temperature the

TABLE I

Effect on Specific Conductivity of Ep 420
Solutions by Passing Them through an Ion-Exchange Column

Surfactant solutions, mmole/liter		Specific conductivity before purification (x 10^{-6} ohm^{-1} cm^{-1})	Specific conductivity after purification (x 10^{-6} ohm^{-1} cm^{-1})
Ep 420	0.1	6.010	1.940
	1.0	13.30	2.245
	5.0	16.80	1.110

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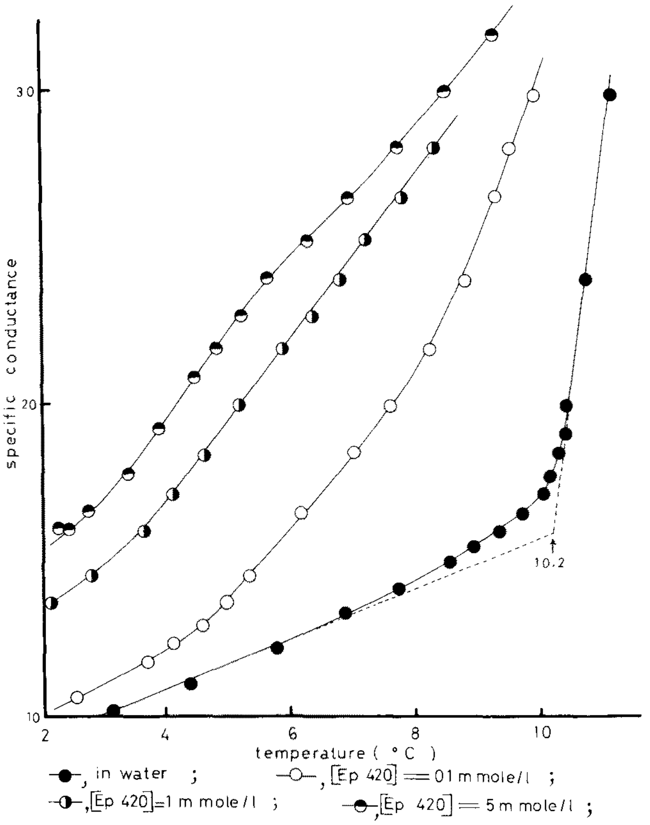

FIG. 1. Relationship between specific conductance and temperature of sodium dodecyl sulfate solution at various constant concentrations of Ep 420.

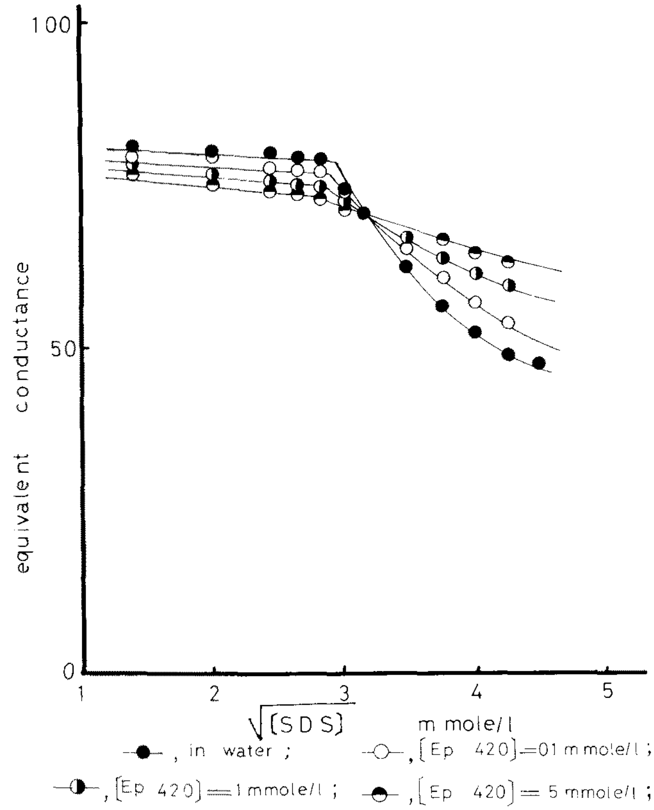

FIG. 2. Relationship between equivalent conductance and square root of concentration of sodium dodecyl sulfate at various constant concentrations of Ep 420.

solubility of surfactant increases rapidly. The Krafft point must be determined before the measurements of surface tension and electrical conductivity of the surfactant solution are taken for the micellar form.

The Krafft point of SDS was estimated from the temperature at which the abrupt change in conductivity occurred, there being an increase in solubility of the surfactant at this temperature. Excess SDS was present in a solid state (7).

The measurements of electrical conductivity for determination of the Krafft point were made in a cell containing 50 ml pure water and sufficient surfactant to give a separate phase.

A Yokokawa conductivity bridge was used to measure the conductivity of the solution. Before beginning the measurement, the cell constant at 40 ± 0.2 C was determined by the use of 0.01 mole KCl under gradual heating. Subsequently the conductivity of the solution containing excess SDS was measured under the same gradual heating. Figure 1 shows the temperature vs. conductivity curves.

RESULTS AND DISCUSSION

It is only at the temperature above the Krafft point that the ionic surfactant can exist as micelles in solution. Therefore it is necessary to estimate the Krafft point of a surfactant before studying the micelle formation of that surfactant. The estimation of the Krafft point of an ionic surfactant in the presence of a nonionic surfactant is important for the micelle study and also for solubility control of the ionic surfactant in practice.

The effect of addition of Ep 420 on the Krafft point of SDS is shown in Figure 1. The line of solid circles in Figure 1 shows the apparent solubility change of SDS as indicated by the change in conductivity with temperature. The temperature at the point of steep rise in the curve corresponds to the Krafft point. As shown in Figure 1, the addition of small amounts of Ep 420 makes the steep rise a more gradual rise and obscures the location of the Krafft point, which means an increase in solubility of ionic surfactant at low temperature. This phenomenon is very important in practical use of surfactants because of the possibility of improved detergency at low temperature by the addition of nonionic surfactant to ionic detergents such as SDS.

Figure 2 shows the equivalent conductivity of aqueous solutions of SDS-Ep 420 mixtures plotted against the square root of the SDS concentration with various concentrations of Ep 420. The pure SDS solution has a sharp break in λ-$\sqrt{c}$ curve, but this break became less definite with the addition of Ep 420, due to the decrease of the equivalent conductivity in the region below the cmc and the increase of the conductivity in the micellar region with increase of concentration of Ep 420. The effect of Ep 420 on the conductivity is the same as the effect of lower alcohols on conductivity, but very different in the amount to significantly change the conductivity. About 5×10^{-3} mole/liter of Ep 420 eliminates the break at the cmc; however, it requires ca. 30% methanol to eliminate the break. By detailed observation of the change of the break with the addition of Ep 420, it was found that the cmc of SDS shifted to lower concentration in the presence of small concentration of Ep 420. This behavior of Ep 420 is more apparent in the surface tension studies of solutions of SDS-Ep 420.

Figure 3 shows the surface tension plotted as a function of the concentrations of SDS solutions at various constant concentrations of Ep 420. The concentration at which the two linear portions of the curve intersect represents the cmc. The addition of Ep 420 initially decreases the value of the SDS concentration at the point of intersection, and eventually eliminates the intersection point on the surface tension curve. Ep 420 which does not form micelles has the same effect on the cmc as polyoxyethylene higher alcohol

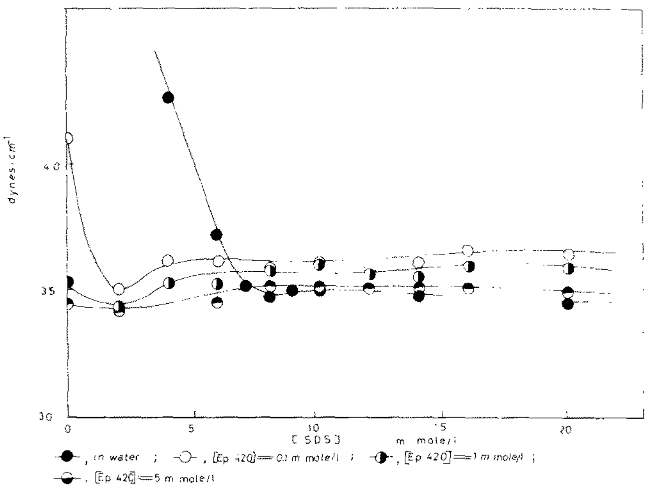

FIG. 3. Surface tension vs. concentration of sodium dodecyl sulfate at various constant concentrations of Ep 420.

ethers which do form micelles. This fact is important in understanding the mechanism of the action of nonionic surfactants on ionic surfactant micelles.

Isemura and Imanishi (8), Saito (9) and Botre et al. (10) found an interaction between water soluble polymers such as polyvinyl alcohol and polyvinyl pyrrolidone and surfactants. The properties of solutions containing both a polymer and a surfactant have been explained by assuming the formation of polymer-surfactant complexes resulting from the binding of the surfactant ions onto the polymer chain. Realizing that Ep 420 is one of the water soluble polymers, there is some possibility that a complex formation between SDS and Ep 420 exists. However it can not be decided, from the conductivity data discussed above, whether or not a complex is formed. Viscosity studies may give information as to the formation of a complex.

Sata and Tyuzyo (11) reported that the reduced viscosity vs. concentration curve of SDS has a break at the cmc. Figure 4 shows the reduced viscosity at 40 ± 0.2 C of a solution of Ep 420 at various constant concentrations as a function of the SDS concentration. The line of solid circles in Figure 4 shows the curve of SDS in aqueous solution, and the others give the curves of SDS in Ep 420 aqueous solutions. It is apparent that the addition of Ep 420 to the SDS aqueous solution eliminates the break at the cmc, and the curves of reduced viscosity vs. the concentration were similar to those obtained with polyelectrolyte solutions. The fact that the viscosity behavior is similar to the polyelectrolyte solution behavior suggests that the adsorption of SDS by the Ep 420 is similar to the adsorption of SDS by water soluble polymers. It may be concluded that the elimination of the cmc break with Ep 420 is caused by some complex formation between SDS and Ep 420. The reason for the lowering of the cmc by small additions of Ep 420 has not been explained. The effect of small amounts of lower alcohols in lowering the cmc is explained as the enhancement of the adsorption of counter ions on the micellar surface by the hydrophobicity of the alcohol. Ep 420 is a water soluble polymer having many times the molecular weight of the lower alcohols. It may be predicted that the power of Ep 420 to lower the cmc is greater than that of lower alcohols; that is, Ep 420 is more effective at much more dilute concentration. The conductivity decrease below the cmc region may be caused by the adsorption of SDS surfactant ions on the Ep 420, and the increase in conductivity above the cmc may be due to a decrease in adsorption of counter ions caused by the adsorption of SDS surfactant ions or molecules on Ep 420 molecules.

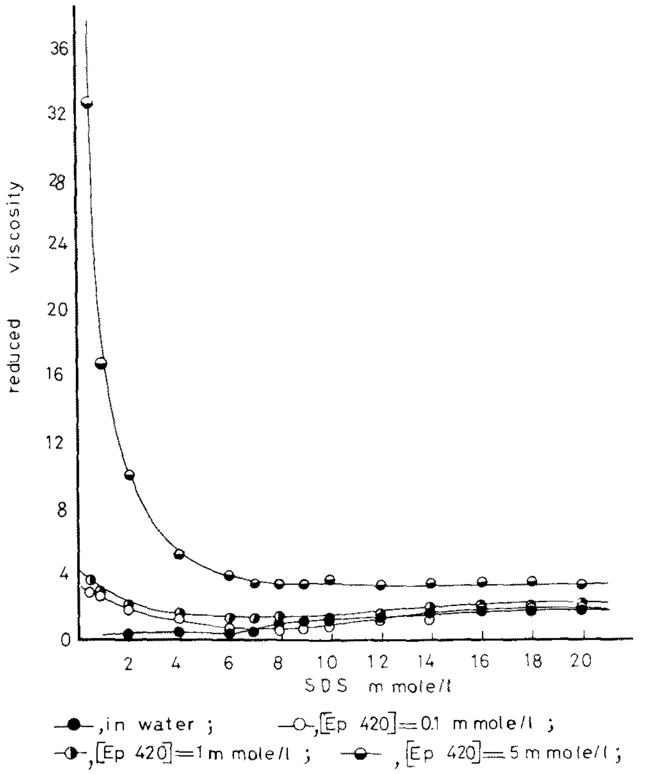

FIG. 4. Reduced viscosity vs. concentration of sodium dodecyl sulfate at various constant concentrations of Ep 420.

In conclusion, the addition of nonionic surfactants to ionic surfactant solutions results in polyelectrolyte type complexes between ionic and nonionic surfactant, and consequently the cmc phenomenon becomes less meaningful in this system.

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