Properties of Aqueous Solution of Sodium Cyclododecyl Sulfate

TAKESHI HIKOTA, MINORI NAKAMURA,[1] SATORU MACHIDA and KENJIRO MEGURO, Department of Chemistry, Science University of Tokyo, Kagurazaka, Shinjuku-ku, Tokyo, Japan

ABSTRACT

Sodium cyclododecyl sulfate was prepared from cyclododecyl alcohol and chlorosulfonic acid to investigate the physical and surface active properties of the surfactant. Its Krafft point, critical micelle concentration (CMC), surface tension, emulsifying power, wetting time and dispersing power were examined and compared with those of sodium dodecyl sulfate which has a linear structure and contains the same number of carbon atoms in the hydrophobic portion. The sodium cyclododecyl sulfate, in contrast to the sodium dodecyl sulfate, had a higher (about two times) Krafft point, much larger (about 10 times) CMC, showed the same excellent wetting property, but exhibited lower emulsifying power. Also the sodium cyclododecyl sulfate is more insoluble (as shown by the Krafft point) than the sodium dodecyl sulfate, while calcium ion stability of the cyclododecyl sulfate surfactant is greater than that of the linear anionic surfactant.

INTRODUCTION

The influence of a change in molecular structure on the surface active and colloidal properties of an anionic surfactant in aqueous solution has been studied by a number of workers. However a large number of these studies have described surfactants whose hydrophobic portion consists of long hydrocarbon chains. It is of interest to determine the effect of a large ring hydrocarbon in place of a long linear hydrocarbon chain in the hydrophobic portion of the surfactant. In practice an anionic surfactant possessing a large ring hydrocarbon can be anticipated to exhibit unusual surface active properties compared to surfactants possessing a long linear hydrocarbon chain such as sodium alkyl sulfates. However reports of this type of study have apparently not been published to date.

Cyclododecyl alcohol prepared from butadiene by trimerization has been known for some time, but its surfactant properties have not been studied. In this report sodium cyclododecyl sulfate was prepared from cyclododecyl alcohol and chlorosulfonic acid and was examined for Krafft point, critical micelle concentration, surface tension, dye spectra absorption, emulsifying power, wetting properties, calcium ion stability and dispersing power.

SYNTHESIS

The cyclododecyl alcohol manufactured by the Hüls Co. was further purified by recrystallization from acetone, and the dodecyl alcohol was purified by vacuum distillation from good commercial grade alcohol. The purity of each alcohol was confirmed by the elemental analysis (carbon and hydrogen analyses agreed with theoretical values within experimental error).

Sodium cyclododecyl sulfate (SCDS) was prepared by a modified method of Dreger et al. (1). A mixture of cyclododecyl alcohol and acetic acid was added dropwise into acetic acid solution containing chlorosulfonic acid while stirring at room temperature. The sulfate was neutralized with 2N aqueous solution of sodium carbonate and then extracted with butanol. The crude product thus obtained was recrystallized three times from ethanol. Then it was extracted for 100 hr with chloroform and for 40 hr with petroleum ether in order to remove all traces of the unchanged alcohol. The pure salt was a white powder.

Sodium dodecyl sulfate (SDS) was prepared as above but with the cyclododecyl alcohol replaced by dodecyl alcohol. The precipitate obtained was recrystallized five times from ethanol and extracted with petroleum ether for 100 hr to give a white flaky product.

The results of the elemental analyses of the carbon and hydrogen of these compounds gave the calculated values for their composition within ±0.3%.

PROPERTIES

The Krafft point, one of the most fundamental properties of the surfactant, was measured by the electro conductivity method. The rapid increase in solubility at the Krafft point accompanied the rapid increase in electro conductivity. Therefore the measurement of the change in the conductivity of the surfactant solution with the temperature in the presence of the surfactant to give a solid

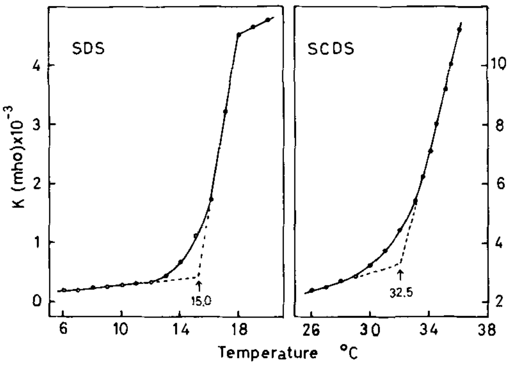

FIG. 1. Krafft point of the sodium dodecyl and sodium cyclododecyl sulfates. Specific conductivity of the surfactant solution vs. temperature.

TABLE I

Properties of SDS[a] and SCDS[b]

Property		SDS[a]	SCDS[b]
Krafft point (deg C)		15.0	32.5
CMC[c] (m mole/1)	Conductivity, 40 C	7.8	70
	Dye, 40 C	6.4	64
	Surface tension, 35 C	6.4	76
γ at CMC (dynes/cm)		38	40
Adsorption, mole/cm^2		3.31	1.79
Area/molecule, Å^2		50.2	93.2
Emulsion stability, sec		1486	689
Wetting time, sec		3.9	3.0
Calcium stability, ppm $CaCO_3$		170	〉 4500
Dispersion power, hr/min		〉 24:00	3:20

[a] SDS, sodium dodecyl sulfate.

[b] SCDS, sodium cyclododecyl sulfate

[c] CMC, critical micelle concentration.

---

[1] Present address: Dainihon Inki Chemical Co., Saitama.

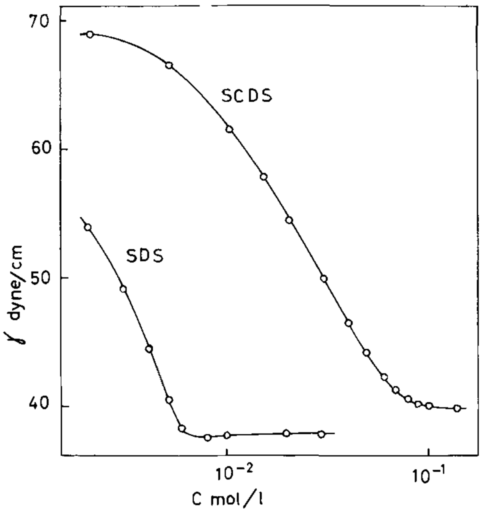

FIG. 2. Surface tension vs. concentration curves of sodium dodecyl and sodium cyclododecyl sulfates.

phase made it possible to estimate the Krafft point (2).

The Krafft point of SDS and SCDS was determined from the specific conductivity vs. temperature diagram. The result is shown in Figure 1 and Table I. As shown in Figure 1, the Krafft point of the SCDS is more than two times that of SDS. But little difference is observed in comparing the shape of specific conductance vs. temperature curves of the two surfactants.

Conductivities of aqueous solutions of the surfactants were measured with an apparatus made by Towa Denpa Co. at 40 C. The conductivity of the water used was about 1 x 10^{-6} reciprocal ohm. The curve of the equivalent conductivity against the square root of the concentration of the surfactant was inflected at the point which corresponds to the critical micelle concentration (CMC). The conductance against concentration curve of the SCDS has been found to be similar to the curve of a normal surfactant such as the SDS. But the CMC value of the SCDS is much higher than that of SDS. This means that probably the large ring hydrocarbon in the hydrophobic portion of the surfactant prevents micelle formation through steric hindrance. The CMC values obtained are shown in Table I.

The surface tension of the surfactant was measured by the Wilhelmy plate method at 35 C. The surface tensions for solutions of SCDS are plotted against the logarithm of concentration in Figure 2. For comparison there is included a similar curve of SDS. The CMC of each surfactant was obtained as the break point on the curve. The figure shows that the surface tension value of the SCDS at the break point is somewhat higher than that of the SDS.

The surface excess Γ at the air-water interface can be calculated by applying the Gibbs adsorption isotherm equation

$$\Gamma = -\frac{1}{2RT} \times \frac{\sigma\gamma}{\sigma \ln C}$$

where γ is the surface tension and C is the molar concentration of the surfactant. The area (A) occupied per surfactant molecule is calculated from $A = 1/N\Gamma$, where N is Avogadro's number. These values are recorded in Table I with the CMC and the surface tension values at the CMC. The area occupied per molecule of SCDS of 93.2A^2, by measurement, almost coincided with the theoretical value obtained from the model molecular structure. This value is larger than that of the SDS which shows 50.2A^2.

The change of the absorption spectra of pinacyanol chloride in aqueous solution of the surfactant (3) was measured by Hitachi recording spectrophotometer type EPS-3T using a 2 mm quartz cell at 40 C. The CMC was determined from the abrupt change of the absorption against concentration of the surfactant.

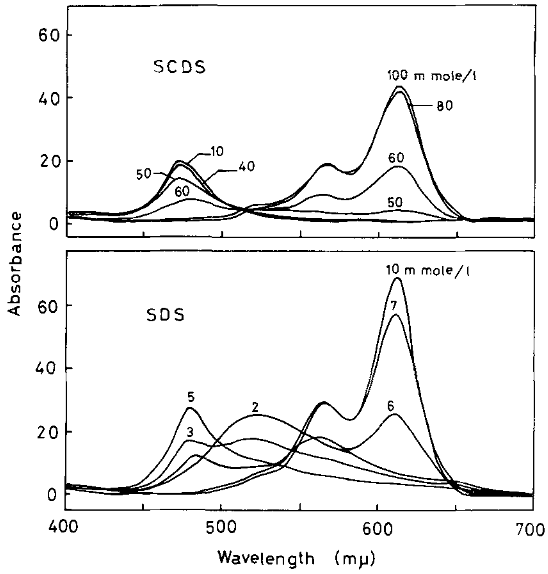

FIG. 3. Absorption spectra of pinacyanol chloride in aqueous solutions of sodium dodecyl and sodium cyclododecyl sulfates.

Figure 3 shows the absorption spectral curves of the pinacyanol chloride in various concentrations of SCDS and SDS at 40 C. It is found that the absorption spectrum of the dye changes with the concentration of the surfactant. However the change occurs rather suddenly at the CMC (Table I). Above the CMC the spectrum of the pinacyanol chloride in the SCDS was very similar to that of the SDS, the peaks being near 615 and 570 mμ. The intensity of these peak lengths increased with the concentration of the surfactant. However below the CMC there is some difference of behavior between the SCDS and SDS. It is observed that when the concentration of the SDS in the solution is very dilute, it possesses an absorption peak at 520 mμ. As the SDS concentration is increased it is observed that this peak at 520 mμ gradually decreases in intensity and disappears, while in the meantime a new peak arises at about 480 mμ. In the case of SCDS the peak of the dye below the CMC with the surfactant is not observed at 520 mμ, but is observed only at about 480 mμ.

As seen in Table I, the CMC values determined by the conductance, surface tension and dye spectral method for the SCDS and the SDS are observed to exhibit certain differences. Furthermore a comparison of the CMC value of the SCDS with that of the SDS shows that the figure for the SCDS is about 10 times higher than the value for the SDS.

The emulsion was prepared from 10 ml of a 100 m mole aqueous solution of the surfactant and 5 ml of toluene by using a well stoppered calibrated cylinder at 40 C. The stability of the emulsion was determined by a previously described method (4). As may be seen in Table I, the emulsion stability of the SDS was more than twice as stable as that of SCDS.

The wetting property of the surfactant was measured by the disk sinking method at 250, using a 20 mm diameter and 1 mm thick felt disk, and 75 ml of the 100 m mole surfactant. The time, in seconds, required for the disk to sink was recorded as the wetting time. The results obtained are shown in Table I. It is observed that the wetting properties of the SCDS are only slightly better than that of SDS.

The calcium ion stability of the surfactant was measured by a modified Hart method at 40 C (5) using the solution of 10 ml of the 10 m mole surfactant and 0.1N calcium chloride. A comparison of the calcium ion stability of SDS with that of the SCDS shows that the SCDS is more stable than the SDS. The results obtained are recorded in Table I.

Measurement of the dispersing power of SCDS has been carried out as follows: A solution of 20 ml of the 80 m mole surfactant and 60 mg alumina powder were placed in the sedimentation tube (1 cm in diameter and 30 cm height), and then the tube was shaken vigorously at 40 C. The dispersing power was defined as the time required for the alumina to precipitate completely from the solution, counting from the moment of the cessation of shaking. The result is shown in Table I, where a comparison is made with the SDS. The dispersing power of SDS is far better than that of SCDS.

REFERENCES

1. Dreger, E.E., G.I. Kelm, G.D. Miles, L. Shedlovsky and J. Ross, Ind. Eng. Chem. 36:610-617 (1944).
2. Hikota, T., and K. Meguro, JAOCS 47:158-161 (1970).
3. Corrin, M.L., and W.D. Harkins, J. Amer. Chem. Soc. 69:679-683 (1947).
4. Hikota, T., Bull. Chem. Soc. Jap. 43:2236-2240 (1970).
5. Wilkes, B.G., and J.N. Wickert, Ind. Eng. Chem. 29:1234-1239 (1937).

[Received March 10, 1971]