Properties of Aqueous Solutions of Disodium Di-3-Sulfopropyl α,ω-Alkane Dicarboxylate

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ABSTRACT

A series of disodium di-3-sulfopropyl α,ω-alkane dicarboxylates $NaO_3S(CH_2)_3OOC(CH_2)_nCOO(CH_2)_3SO_3Na$ (n = 10, 12, 14,and 16) were prepared by the reaction of propane sultone with decane, dodecane, tetradecane or hexadecane dicarboxylic acids, and were estimated as to Krafft point and critical micelle concentration (cmc). The Krafft points of these α,ω-type surfactants were determined from the temperature at which the abrupt changes in the conductivities of the aqueous solutions in the presence of the solid surfactant were below 0 C for n = 10, 23.5 C for n = 12, 31.0 C for n = 14 and 38.5 C for n = 16. The α,ω-type surfactant solution showed two break points in each plot of electroconductivity as a function of surfactant concentration. These results were considered to be due to the existence of the second cmc characteristic of these surfactants. A plot of the values obtained from the 1st cmc and the 2nd cmc of the α,ω-type surfactants decreases logarithmically according to the increasing total number of methylene groups (N). Their relationship is given as follows: log cmc = -0.142N + 3.77 (1st cmc); log cmc = -0.143N + 4.20 (2nd cmc).

INTRODUCTION

Numerous studies have been reported by a number of workers in the field of effects of surfactant molecular structure, i.e., the size and shape of the hydrocarbon chain, and the nature and position of the polar group on surface and colloidal properties, especially the critical micelle concentration, of the surfactant. However in most of these studies, only surfactants possessing one hydrophilic group on the long hydrocarbon chain were treated. Surfactants which have a polar group at each end of a long hydrocarbon chain are interesting, as they exhibit unusual surface active properties compared to normal surfactants. However few studies have been performed concerning the surface and colloidal properties of surfactants which contain α,ω-dihydrophilic groups in their molecular structure (1-4).

In the last few years authors have studied the relationship between molecular structure and properties of surfactants containing an ester group. The present report concerns the preparation of α,ω-type surfactants in which ester groups are attached to the alkyl chain, and the investigation of the cmc and Krafft points of these surfactants. The surfactants used in this experiment were a series of disodium di-3-sulfopropyl α,ω-alkane dicarboxylates with 16, 18, 20 or 22 total methylene groups. The cmc values of these surfactants were determined by using electroconductance and dye absorption spectra methods.

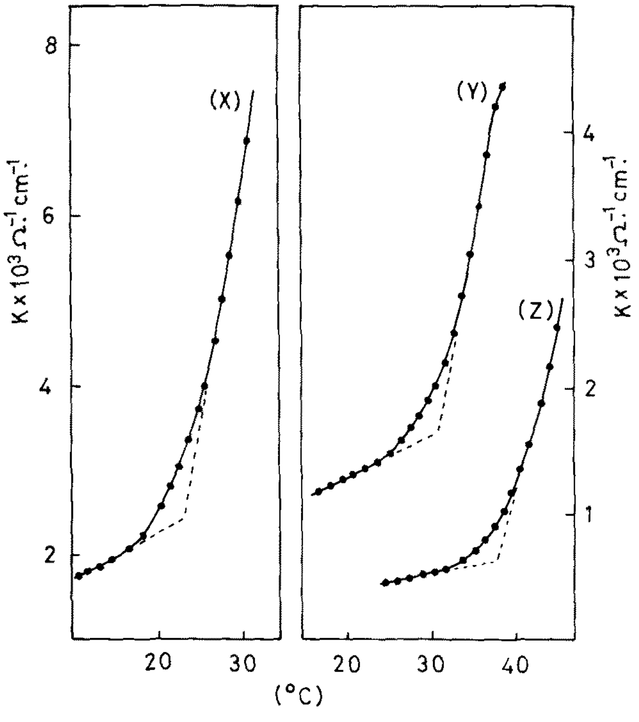

FIG. 1. Krafft points of disodium di-3-sulfopropyl α,ω-alkane dicarboxylates. Specific conductivity of surfactant solution vs. temperature curves; α,ω-12 (X), α,ω-14 (Y) and α,ω-16 (Z).

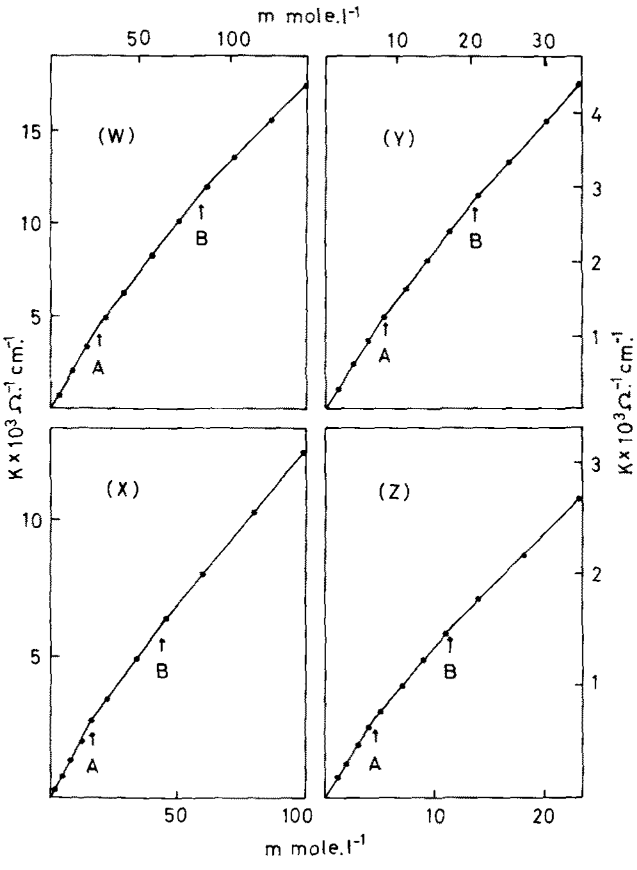

FIG. 2. Specific conductivities of disodium di-3-sulfopropyl α,ω-alkane dicarboxylates; α,ω-10 (W), α,ω-12 (X), α,ω-14 (Y) and α,ω-16 (Z).

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TABLE I

Elementary Analysis of Disodium Di-3-Sulfopropyl α,ω-Alkane Dicarboxylate

		C		H	
Disodium di-3-sulfopropyl	Abbreviation	Found	Calculated	Found	Calculated
1,10-decane dicarboxylate	α,ω-10	41.45	41.69	6.17	6.22
1,12-dodecane dicarboxylate	α,ω-12	43.48	43.95	6.58	6.64
1,14-tetradecane dicarboxylate	α,ω-14	45.69	45.98	7.31	7.02
1,16-hexadecane dicarboxylate	α,ω-16	47.73	47.83	7.54	7.36

EXPERIMENTAL PROCEDURE

Materials

A series of disodium di-e-sulfopropyl α,ω-alkane dicarboxylates was prepared according to the following procedure.

$$HOOC(CH_2)_nCOOH \xrightarrow{\text{methanol esterification}}$$
$$H_3COOC(CH_2)_nCOOCH_3 \xrightarrow{\text{hydrolysis}}$$
$$HOOC(CH_2)_nCOOCH_3 \xrightarrow{\text{Kolbe's electrolysis}}$$
$$H_3COOC(CH_2)_{2n}COOCH_3 \xrightarrow{\boxed{O(CH_2)_3SO_2}\ \text{NaOH}}$$
$$NaO_3S(CH_2)_3OOC(CH_2)_{2n}COO(CH_2)_3SO_3Na$$

Dimethyl dodecane 1,12-dicarboxylate, tetradecane 1,14-dicarboxylate and hexadecane 1,16-dicarboxylate were prepared from the monomethyl esters of suberic, azelaic and sebacic acids, purified by distillation from good commercial grade dicarboxylic acids, according to the

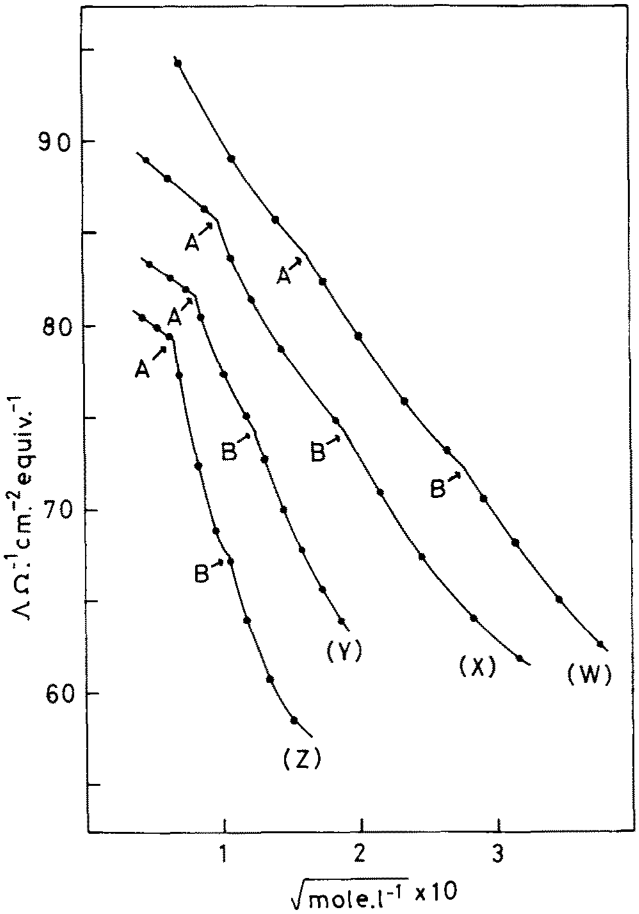

FIG. 3. Equivalent conductivities of disodium di-3-sulfopropyl α,ω-alkane dicarboxylates; α,ω-10 (W), α,ω-12 (X), α,ω-14 (Y) and α,ω-16 (Z).

TABLE II

Krafft Point and Critical Micelle Concentration (cmc) of Disodium Di-3-Sulfopropyl α,ω-Alkane Dicarboxylate

		cmc, (mmole/liter)		
		Conductivity		
Abbreviation	Krafft point	1st cmc	2nd cmc	Dye spectra
α,ω-10	Below zero	30.5	84.0	30.0
α,ω-12	23.5	16.5	44.0	15.8
α,ω-14	31.0	8.5	22.5	8.2
α,ω-16	38.5	4	11	3.8

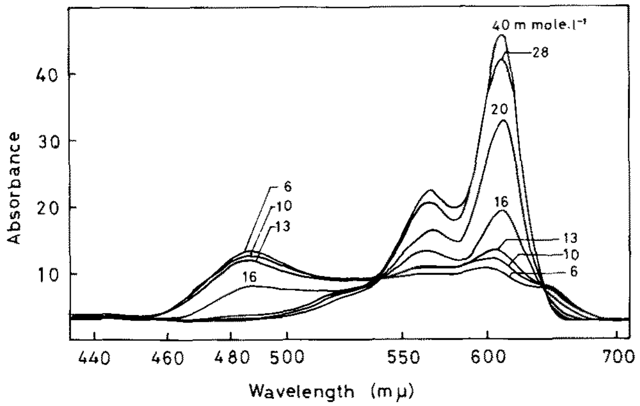

FIG. 4. Absorption spectra of pinacyanol chloride in aqueous solution of disodium di-3-sulfopropyl α,ω-dodecane dicarboxylates.

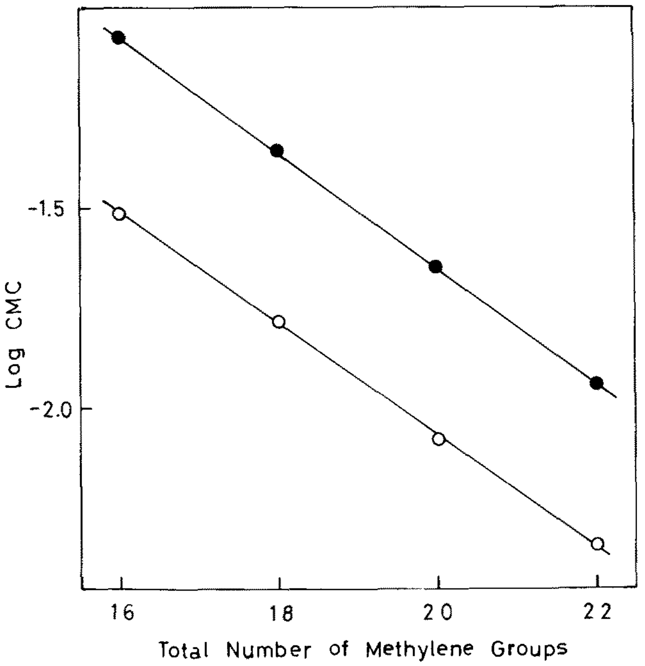

FIG. 5. Relationship between log critical micelle concentration (cmc) and total number of methylene groups in the alkyl chain of disodium di-3-sulfopropyl α,ω-alkane dicarboxylates. First cmc (○) and second cmc (●).

method of Kolbe's electrolytic synthesis (4). The methyl ester of 1,10-decane dioic acid, provided by the Hüls Co., was further purified by distillation.

Disodium di-3-sulfopropyl α,ω-alkane dicarboxylate was prepared from the corresponding dimethyl alkyl α,ω-dicarboxylate, sodium hydroxide and propane sultone purified by vacuum distillation, by using a method given in a previous paper (5). The crude material was recrystallized three times from methanol, and then was extracted for 100 hr with petroleum ether in order to remove all traces of unreacted materials. The purity of the surfactant prepared was confirmed by elemental analysis. The results of the chemical analyses of these compounds for carbon and hydrogen are summarized in Table I.

Measurements

Krafft point: The Krafft point was taken as the temperature at which there was a rapid increase of the solubility of the surfactant in water when gradually heated. The rapid increase of solubility at the Krafft point was in proportion to the rapid increase in electrical conductivity. Therefore the measurement of the rapid increase in the conductivity of the surfactant solution with the temperature in a surfactant sufficient to give a solid phase made it possible to estimate the Krafft point. A test tube was used as the vessel for measuring conductivity. The surfactant solution (50 ml of 50 mmole) and the cell (electrodes) were placed in the test tube. Then the vessel was immersed in a heating bath. The solution was stirred with a mechanical stirrer, and the temperature was increased at a rate of about 0.1 C/min.

Conductivity: The conductivity of the solution was measured by using a CG201PL conductivity cell and a No. C68174G conductivity resistivity indicator (Towa Denpa Co.) at 40±0.1 C. The cell constant was determined by using 0.001 mole potassium chloride solution. The water used in all the experiments was prepared by passing it through an ion exchange resin column and then distilling it from alkaline potassium permanganate in a Pyrex glass vessel.

Absorption spectra: The change of the absorption spectra of pinacyanol chloride in the surfactant solution was measured by using the Hitachi recording spectrophotometer type EPS-2, adding 2 mm quartz cell at 40 C. Distilled water was used in the reference cell.

RESULTS

It has been well-established that soaps and ionic surfactants possess Krafft points, above the temperature of which their solubilities increase enormously. Therefore the Krafft point must be determined before measurement of electroconductivity and other surface active and colloidal properties of the surfactant solution. The specific conductances of the aqueous solution of these surfactants, except disodium di-3-sulfopropyl 1,10-decane dicarboxylate, are plotted in Figure 1 against temperature. The Krafft point of disodium di-3-sulfopropyl 1,10-decane dicarboxylate is below 0 C. The curves obtained here almost coincide with those of ordinary surfactants such as sodium alkyl sulfates. The Krafft point of each surfactant, which was evaluated from the intersection of two extrapolated straight line portions, are listed in Table II.

The plots of specific conductance against concentration for the disodium di-3-sulfopropyl α,ω-alkane dicarboxylate series are shown in Figure 2. Furthermore, in Figure 3, the equivalent conductivity is plotted against the square root of concentration curves for the same surfactants as shown in Figure 2. As is evident from the two figures, two break points are observed in every curve. The first break point (A) has a fairly sharp change in slope of the type usually associated with micelle formation, while the second break point (B) has a slight change in slope. These break points are shown in Table II.

As an example, the absorption spectra of pinacyanol chloride in various concentrations of disodium di-3-sulfopropyl 1,12-dodecane dicarboxylate are shown in Figure 4. The absorption spectra for disodium di-3-sulfopropyl 1,10-decane dicarboxylate, 1,14-tetradecane dicarboxylate and 1,16-hexadecane dicarboxylate were examined, but are omitted here because their behavior is substantially the same as that of disodium di-3-sulfopropyl 1,12-dodecane dicarboxylate. As seen in Figure 4, the spectral curve of the dye varies with the concentration of surfactant. In the low concentration region of the surfactant solution, the spectrum of pinacyanol chloride has a band of absorption near 490 mμ and its intensity is low. With an increase in surfactant concentration, the absorption spectra changes to 565 and 610 mμ, and the intensities become greater, in direct proportion to the increase in concentration of the surfactant. The values of the changing points of the absorption spectra for each α,ω-type surfactant are shown in Table II.

DISCUSSION

In general it is known that the critical micelle concentration of an ionic surfactant solution is in the region in which binding of the counterion to the micelle surface occurs. Hence a break point corresponding to the cmc is observed on the plot of electroconductivity against concentration. However in this experiment two break points are observed on the electroconductivity vs. concentration curves, as shown in Figures 2 and 3. These data seem to represent for each concentration a limit where some discontinuity occurs in the properties of the solution. This phenomenon is not observed in sodium 3-sulfopropyl alkanoates and other single hydrophilic group type surfactants.

On the other hand it is well known that the spectral change of a dye has been used in the determination of cmc. Corrin and Harkins (6) found that the absorption spectrum of pinacyanol chloride in aqueous solutions of anionic surfactants changed abruptly at the cmc, and they reported that the bands above the cmc appeared at 610 and 565 mμ, while below the cmc absorption occurred at 490 mμ. Tori and Nakagawa (7) studied the spectral change of a dye by the addition of surfactant, and reported that, above the cmc, absorption bands of pinacyanol chloride in solutions of sodium dodecyl sulfate are near 570 and 610 mμ. From these data it can be concluded that the values of the changing points of the absorption spectra in Figure 4 are the critical micelle concentrations, and these surfactants seem to form micelles in solution at concentrations higher than the cmc.

The results given in Table II show that the first break points obtained by the electroconductivity method are in satisfactory agreement with the critical micelle concentrations determined by the absorption spectrum method. This indicates that there are micelles at the concentration of the first break point (first cmc). However the micelle of α,ω-type surfactant is considered more complicated than that of normal surfactant. For instance disodium di-3-sulfopropyl 1,12-dodecane dicarboxylate has a first cmc of 16 mmole/liter, in comparison with that of 0.4 mmole/liter for sodium 3-sulfopropyl hexadecylate (8) with the same number of methylene groups. The higher values of the first critical micelle concentrations of the α,ω-type surfactants show that their tendency to undergo association is much weaker than that of ordinary surfactants. The reason for this is that obviously the presence of the two polar groups in the molecule opposes the association. Accordingly the first micelles of α,ω-type surfactant solutions seem to be loosely packed micelles.

On the other hand the concentration limit of the second break point is due either to a change in the shape of the micelle caused by an increase in the number of molecules aggregated, or to a change in the electrical properties of the micelle by hard-fixing of the counter-ion, since the second micelle seems to be so closely packed.

The values of the cmc of normal paraffin chain salts are known to depend on the length of the chain so that the logarithm of the cmc is a linear function of the number of methylene groups in the salt. The cmc values of α,ω-type surfactants, as estimated by the conductivity method, were plotted as a function of the number of methylene groups in Figure 5. It shows the linearity of this relationship, as in usual surfactants. The values for first cmc lie closely to the straight line given by: $\log \text{cmc} = -0.142N + 3.77$; and likewise for the second cmc: $\log \text{cmc} = 0.143N + 4.20$, where N is the total number of methylene groups.

The value of the slopes of the two lines prepared is -0.142 and -0.143, which is equivalent to the half of the value of -0.29 obtained for normal surfactants (5). From the above description it is recognized that the value, in the cmc, of a methylene unit situated between two hydrophyilic groups is equivalent to half that of one in a normal surfactant (9).

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