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Effect of Choline Derivatives on the Critical Micelle Concentrations of Anionic and Cationic Surfactants

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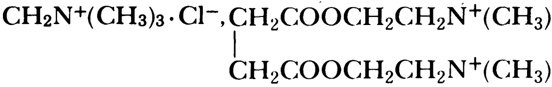
Synopsis. The decrease of the critical micelle concentration (cmc) of sodium dodecyl sulfate (SDS) was larger, while the decrease of that of dodecyltrimethylammonium chloride (DTAC) was smaller in the presence of choline derivatives than in the presence of NaCl at the same molar concentration.

A large number of studies have been reported on the effect of various electrolytes[1—10] and alcohols[8—15] on the micellization of ionic surfactants. The association of ionic surfactant in aqueous solution is governed by two opposing forces. The hydrophobic force between the hydrophobic tails attracts the surfactant molecules or ions to the micelle core from the aqueous bulk solution. The ionic head groups, on the other hand, favour the aqueous bulk phase, because the electrostatic repulsive force between the head groups prevents the surfactant molecule to associate. In this connection, the decrease of the critical micelle concentration (cmc) by addition of inorganic salts and alcohols may be discussed. The effect of the inorganic electrolytes is explained in terms of the shielding of the electrostatic repulsion by the counterions, while the effect of alcohol is explained from the reduction of the free energy of mixing and the reduction of the surface charge density by the alcohols entering in the palisade layer of the micelle.

Moreover, it has been found that the mixed micelle composed of anionic and cationic surfactants is not formed.[16] Therefore, the effect on the micellization of the salts which have a short hydrophobic part and a polar part of the opposite sign may be interesting.

From these points of view, we studied the critical micelle concentration of anionic and cationic surfactants in aqueous solutions of choline chloride and its esters ($HOCH_2CH_2N^+(CH_3)_3 \cdot Cl^-$, $CH_3COOCH_2CH_2N^+(CH_3)_3 \cdot Cl^-$,  $\begin{array}{l} CH_2COOCH_2CH_2N^+(CH_3)_3 \cdot Cl^- \\ | \\ CH_2COOCH_2CH_2N^+(CH_3)_3 \cdot Cl^- \end{array}$), by the measurements of the surface tension.

Experimental

Materials. Sodium dodecyl sulfate (SDS) supplied from Nihon Emulsion Co., Ltd., Japan was extracted with petroleum benzine in a Soxlet apparatus for at least 20 h, recrystallized twice from ethanol, and dried under vacuum for a day and night. Dodecyltrimethylammonium chloride (DTAC) purchased from Nakarai Chemicals, Ltd. was extracted with petroleum ether in a Soxlet apparatus for at least 20 h, recrystallized twice from aceton, and dried under vacuum for a day and night. Choline chloride (Ch), acetylcholine chloride (Ach) and succinylcholine chloride (Sch) purchased from Nakarai Chemicals, Ltd. were of a guaranteed reagent grade and were used without further purification. All solutes were dissolved in deionized and redistilled water.

Surface Tension Measurements. The surface tension was measured by Du Nouy tensiometer. The platinum ring with diameter 23 mm was heated by oxidizing flame before use. All glass apparatus were preserved in chromate-sulfuric acid mixture and linsed well with distilled water before use. Temperature of the thermostat was maintained at 25±0.2 °C. For the calculation of the surface tension of aqueous solutions, the value of 71.96 m N·m^{-1} was used as the surface tension of pure water at 25 °C. The experimental determination of the surface tension was precise to ±0.1 m N·m^{-1}. cmc was obtained from the break point in the curve of surface tension, γ, as a function of logarithm of the concentration of SDS or DTAC, at various values of the concentration of choline derivatives.

Results and Discussion

cmc of SDS in the presence of choline chloride and its derivatives, *i.e.* Ch, Ach and Sch is shown in Fig. 1 together with the data of inorganic salts and normal alkanols quoted from the references.[13,17] cmc of DTAC in the presence of choline derivatives is shown in Fig. 2 together with the data of NaCl quoted from the reference.[17] The measured values of cmc of SDS and DTAC in the absence of additives (8.1 m mol·dm^{-3},

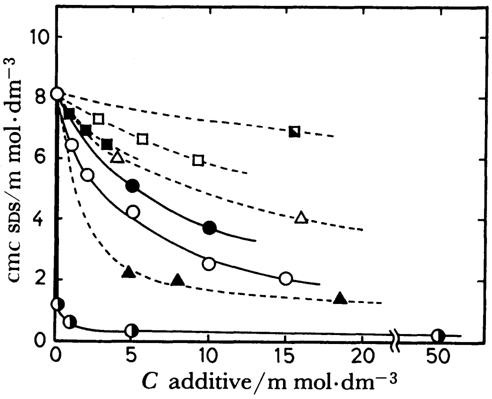


Fig. 1. Effect of Additives on the cmc of SDS at 25 °C.
●: Ch, ○: Ach, ◑: Sch, △: NaCl, ▲: $MgCl_2$,[17] ▨: 1-pentanol, □: 1-hexanol, ■: 1-heptanol,[13] ——: measured results by us, -----: reference results.

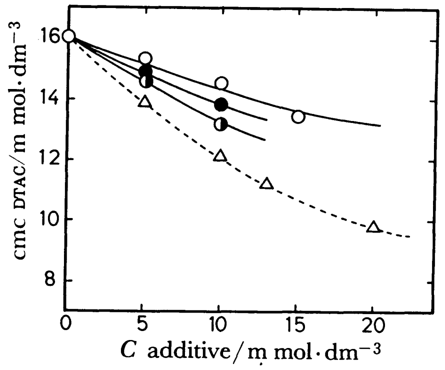


Fig. 2. Effect of Additives on the cmc of DTAC at 25 °C.
The symbols are same as Fig. 1.

16.0 m mol·dm^{-3}) and the values in the presence of NaCl of 5 m mol·dm^{-3} (6 m mol·dm^{-3}, 14 m mol·dm^{-3}) are consistent well with the values from the reference,$^{17)}$ so the values obtained by us are considered to be adequate.

cmc of SDS and DTAC decreased with increase of the concentration of choline derivatives. The effectiveness of choline derivatives is larger than that of NaCl on the cmc of SDS, while the effectiveness of choline derivatives is smaller than that of NaCl on the cmc of DTAC. Furthermore, in the case of SDS, the order of effectiveness to decrease the cmc is Sch>Ach>Ch>NaCl, while in the case of DTAC, the order is NaCl>Sch>Ch>Ach. These results are considered to be due to the followings: (1) In the case of SDS, the electric charge of micelle has opposite sign to that of choline derivatives: The choline derivatives, as organic ions, may have specific interaction rather than the simple electrostatic effect of shielding by the counterions. In addition, choline derivatives lead to the reduction of the free energy of mixing by entering in the micelle. The difference of effectiveness is explained from the distribution of choline derivatives to micelle from bulk phase and the deepness of penetration, due to the hydrophobic property (Sch is more hydrophobic because Sch has the structure that two molecules of Ach have condensed). Regarding the distribution of choline derivatives between micellar and bulk phases, we have measured the distribution of Ach by means of ultrafiltration and it has been found that Ach enter indeed in the micelle. According to the result, the distribution ratio of Ach of 5 m mol·dm^{-3} in the micellar phase is 30—40% in the presence of SDS or DTAC of 30 m mol·dm^{-3}. The results of ultrafiltration will be reported in detail in a later paper. (2) In the case of DTAC, the electric charge of micelle has same sign to that of choline derivatives: The choline derivatives decrease the cmc by the shielding effect of the electrostatic repulsion by chloride ions as the effect of NaCl, while the choline derivatives entered in the micelle prevent the surfactant molecule to associate by the electrostatic repulsive force between the head groups. Therefore, the effectiveness of the choline derivatives is smaller than that of NaCl. The reason that Sch is more effective than Ch or Ach is considered mainly to be due to the counterion effect because that Sch has the structure composed of two Ach. It can, therefore, be concluded that the facts that the order of the effectiveness to decrease the cmc is Sch>Ach>Ch>NaCl for SDS, and NaCl>Sch>Ch> Ach for DTAC, are explained by the electrostatic effect and the distribution of choline derivatives between micellar and bulk phases.

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