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Effect of choline derivatives on the cloud point of mixed ionic–non-ionic surfactants

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One of the characteristic features of the non-ionic surfactants is their cloud point which is defined as the temperature at which the sudden turbidity appears in the solution on raising temperature. Information on the effect of additives on the cloud point of non-ionic surfactants often has practical use. Dosage forms stabilized with non-ionics frequently break down when heated above the cloud point, e.g., during thermal sterilization (Schott and Royce, 1984).

The incorporation of an ionic surfactant into the non-ionic micelles introduces electrostatic repulsion between the micelles, thus hindering the coacervate phase formation and raising the cloud point (Scamehorn, 1986). At very small concentrations of ionic surfactants (e.g., sodium dodecyl sulfate; SDS), a linear rise in the clouding temperature of non-ionic surfactant (e.g., Triton X-100) was interpreted in terms of the increase in the surface charge of the micelle (Valaulikar and Manohar, 1985).

In a recent article we demonstrated with inorganic electrolytes as an example and using cloud point measurements, that the original charge distribution of such mixed micelles was swamped and the corresponding repulsions are screened, depending on the electrolyte concentration and that the effect was greatly affected by the SDS Triton X-100 ratio (Marszall, 1987). The change in the original charge distribution of mixed micelles at a fixed ionic–non-ionic surfactant ratio depends mostly on the valency number of counterions and to a lesser extent on the kind of the co-ion and is independent of the kind of monovalent inorganic counterion.

Dependent on the amphiphilic character of the organic counterion, the counterion can either be located mainly at the micelle surface or penetrate more deeply and bind more tightly to micelles. Therefore, the effect on the cloud point of the substances which have a short hydrophobic part and a polar hydrophilic part in relation to mixed micelles may be interesting. From these points of view, we investigated the changes in cloud point of mixed surfactants in aqueous solutions of tetraalkylammonium derivatives of biological importance such as choline chloride (ChCl), acetylcholine chloride (AchCl) and succinylcholine chloride ($SChCl_2$).

Triton X-100 (ethoxylated *p-tert*-octylphenol with an average of 9–10 ethylene oxide units) of scintillation grade (Riedel–de Haën, Seelze, F.R.G.) and sodium dodecyl sulfate (SDS-99%) (Henkel, Düsseldorf, F.R.G.) were used as a non-ionic and ionic surfactants, respectively. ChCl,

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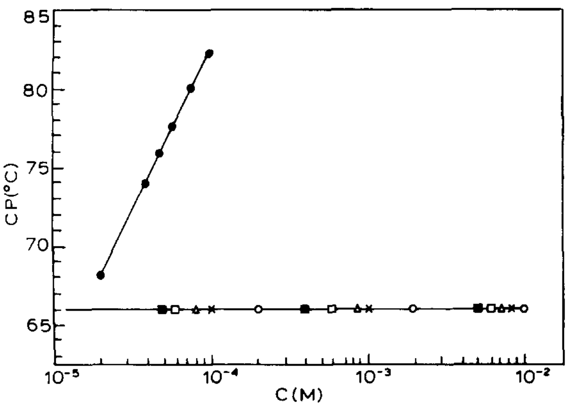

Fig. 1. Cloud point of a 1% solution of Triton X-100 as a function of the molar concentrations of added: SDS (●), ChCl (×), AChCl (△), $\frac{1}{2}$ $SChCl_2$ (□), NaCl (○) and $\frac{1}{2}$ $CaCl_2$ (■).

AChCl and $SChCl_2$ were products of International Enzymes Ltd., Windsor, and BDH, Poole.

Cloud points were determined visually by noting the temperature at which a solution heated above the clouding temperature lost its turbidity on cooling. The cloud point of a 1% Triton X-100 solution in the absence of SDS was 66 °C.

Fig. 1 shows the cloud point measurements on 1% Triton X-100 solutions as a function of the SDS and the choline chloride and its derivatives concentrations together with the data of inorganic electrolytes (NaCl and $CaCl_2$). For concentration below 0.01 M investigated additives have no effect on the cloud point of Triton X-100 solution as opposed to results noted for higher electrolyte concentrations (Maclay, 1956; Kuriyama, 1962). On the other hand, the cloud point of non-ionic increases linearly upon addition of very small concentrations (about 10^{-5} M) of SDS. The ionic–non-ionic micelles composed mainly of non-ionic surfactant are charged. This leads to electrostatic repulsion between the micelles, thus increasing the cloud point. If we take into account that the counterion binding on mixed ionic-non-ionic micelles varies little with temperature and fractional counterion binding is nearly zero (Rathman and Scamehorn, 1984) (for low SDS concentrations comparable with those used in our experiments) then the important role of the uncompensated charge on the micellar surface in maintaining the repulsion between the micelles becomes evident.

However, when choline chloride and its derivatives are added to the Triton X-100 solution in the presence of SDS (one molecule of SDS per micelle of Triton X-100 *) the cloud point curve changes significantly even below the 0.01 M concentration of the additives (Fig. 2).

In the case of non-ionic surfactant alone, investigated choline derivatives molecules, at such low concentrations, exist almost entirely in the free form and the cloud point is unchanged (Fig. 1). With increase of mole fraction of SDS in the system of mixed micelles, investigated additive molecules are bound at the surface of the micelles by the electrostatic attractive force between the negative charge of SDS and the positive charge of ChCl, AChCl and $SChCl_2$. Similarly, from the distribution study of AChCl between the micellar and bulk phases using an ultrafiltration technique, it was found that for non-ionic micelles, the concentration of bounded AChCl was very small, but for mixed micelles, the amount increased with mole fraction of ionic surfactants (Nakagaki and Yokoyama, 1985). AChCl molecules were bound to one locus within the surfactant micelles. Furthermore, in the system of negatively charged mixed micelles and AChCl, the concentration of bound AChCl was found to depend on the surface potential of the micelles and the dependence was explained well by the Gouy–Chapman theory.

Thus, in the presence of choline derivatives the original charge distribution of mixed micelles is swamped and the corresponding repulsions are screened in a similar manner as in the case of inorganic electrolytes. The effect of ChCl and AChCl on the cloud point curve is the same as in the case of NaCl, and $SChCl_2$ as in the case of $CaCl_2$. The organic ions of higher charge (SCh^{2+}) suppressed the cloud point of mixed ionic-non-ionic surfactant at much lower concentrations than did the monovalent ones (Ch^+, ACh^+). The similarity between the effect of choline chloride derivatives and inorganic electrolytes suggests that the factors responsible for variations in the cloud-

* For calculation of the ratio we used the same approach as did Valaulikar and Manohar (1985).

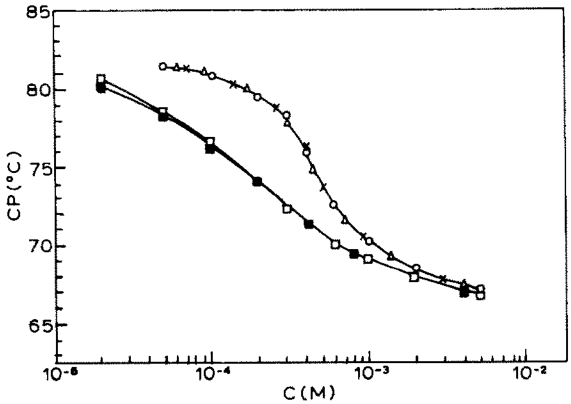

Fig. 2. Cloud point of a 1% solution of Triton X-100 in the presence of SDS (1 molecule of SDS per micelle of Triton X-100) as a function of the molar concentrations of added: ChCl (×), AChCl (△), $\frac{1}{2}$ $SChCl_2$ (□), NaCl (○) and $\frac{1}{2}$ $CaCl_2$ (■).

ing phenomenon of mixed surfactants at such low concentration of additives and SDS are primarily electrostatic in nature, whereas the hydrophobicity of the counterions in such conditions play only a minor role as results from comparison of behavior, e.g., ChCl and AChCl.

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