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212. Is Water Critical to the Formation of Micelles in Apolar Media?

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Summary

Photon correlation studies in H_2O/sodium di-2-ethylhexylsulfosuccinate (AOT)/i-C_8H_{18}-systems, pertinent IR. investigations, and vapor pressure osmometric measurements with alkylated quaternary ammonium di-2-ethylhexylsulfosuccinates strongly suggest water to be pre-requisite for the micellization in apolar media.

In spite of more than twenty years of research in the chemistry of non-polar surfactant solutions, the question as to the stabilizing factors responsible for the micelle formation is still not definitely settled. Although, the existence of concentration-independent aggregates over considerable concentration regions has been frequently reported by different research groups, *e.g.* [1-5], it appears that still more hypotheses rather than experimental evidence were offered in order to explain micellar stability in apolar media.

Recent results (confirming an apparently neglected explanation by *Kitahara* [6]) obtained from photon correlation spectroscopy [7] and positron annihilation technique [8] together with information from IR. investigations [9] are believed to permit a reinterpretation of earlier findings and to obtain an unexpected insight into the general aggregation phenomenon. Precise photon correlation spectroscopic determinations of the micellar size of Aerosol OT (Sodium-di-2-ethylhexylsulfosuccinate) molecules in isooctane yielded a concentration and temperature independent *Stokes* radius of 15 ± 0.5 Å [7] compared to about 12 Å which corresponds to the linear length of an AOT molecule. In addition, determinations of the water content in apolar solvents (dried by standard procedures) clearly

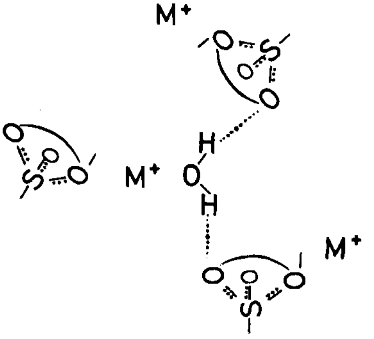

Fig. 1. *Formation of sodium sulfonate trimers at low degree of hydration according to* Zundel [9]

indicated that the aggregational phenomenon in non-polar surfactant solutions had to be reconsidered.

Moreover, there exist a number of pertinent IR. investigations by *Zundel et al.* [9] on 5 μ thick membranes of polystyrene sulfonates under conditions of controlled humidity and temperature. From the experiments with sodium polystyrene sulfonate membranes at low degree of hydration it was concluded that one water molecule is attached to the counterion (=sodium) which connects, simultaneously, *via* two hydrogen bridges two other sulfonate molecules, thus forming a trimer *(Fig. 1)*. Such trimers were frequently detected with different techniques [10] and considered (in the frame of the pseudophase model) as nuclei with respect to the micellization process [11].

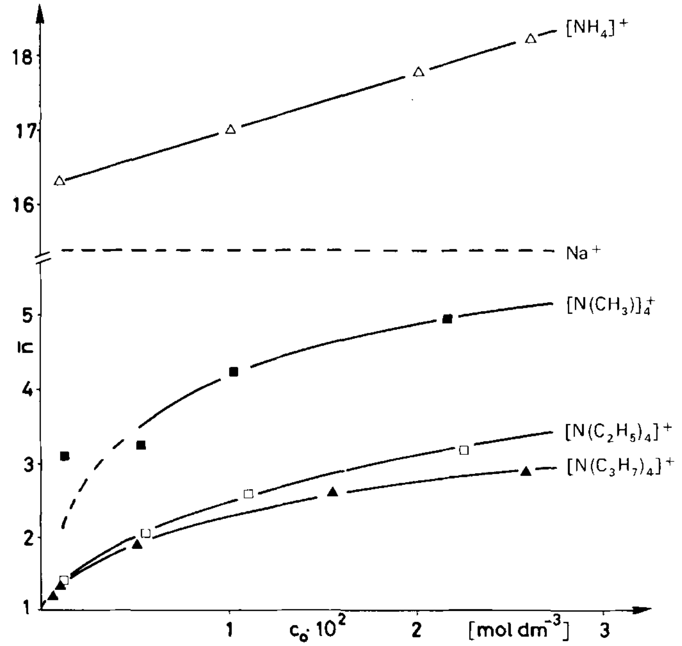

Fig. 2. *Average aggregation number* (n̄) *of di-2-ethylhexylsulfosuccinate with different tetraalkylammonium counterions* versus *surfactant concentration in* C_6H_6 (25°)

In order to check this concept the most obvious approach would have been to reduce the water content of the components, *i.e.* solvent and surfactant. This, however, is limited by experimental reasons, particularly, with regard to drying of the solvent and the following measurement under controlled humidity. Also the surfactant could not be completely desiccated without partly decomposing the compound. Therefore, another procedure was suggested, *i.e.* replacing the alkaline counterions by tetraalkyl derivatives of the quaternary ammonium ion, thus taking $[N(CH_3)_4]^+$, $[N(C_2H_5)_4]^+$, or $[N(C_3H_7)_4]^+$. According to the above concept, these quaternary ammonium counterions were expected to show a pronounced effect on the aggregation behaviour of the surfactant. With regard to sterical considerations it appears worth mentioning in this connection that the distance of closest approach by another ion is identical both for the sodium and tetramethyl ammonium ions [12]. From *Figure 2* it is seen that the effect of replacing Na^+ by $[N(CH_3)_4]^+$ or by other alkylated ammonium ions is indeed striking.

These results are understandable along the line of *Zundel*'s findings [9] concerning the OH-stretching vibrations of the hydrogen bridges originating from water

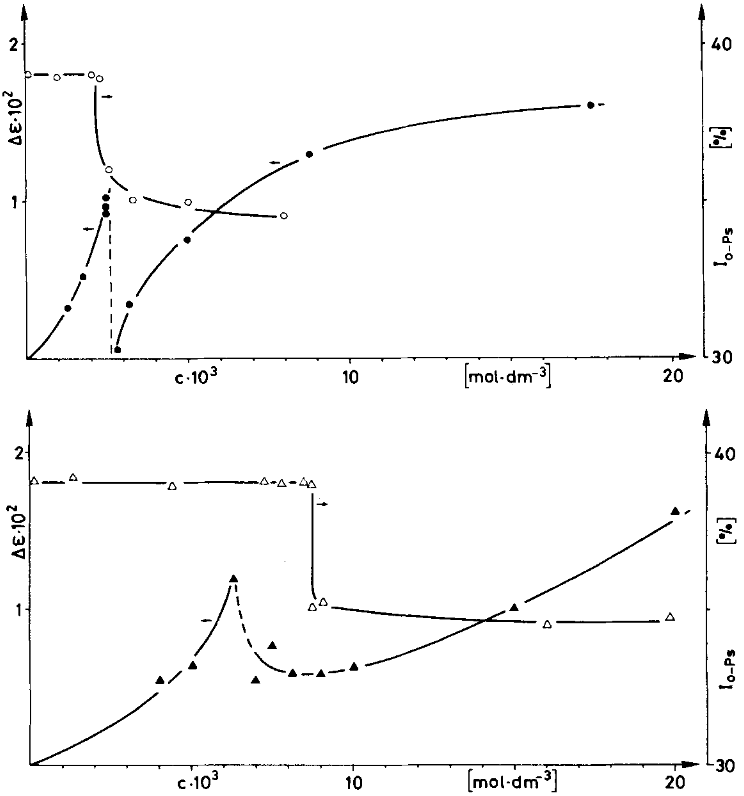

Fig. 3. *Comparison between intensity of* o-*Positronium* ($I_{o\text{-}Ps}$) *in Positron annihilation experiments* (see [8]) *and dielectric increment* ($\Delta\varepsilon$) versus *surfactant concentration* (top: AOT/C_6H_6, bottom: DAP/C_6H_6, 25°)

molecules which interact only weakly with cations like $[N(CH_3)_4]^+$, $[N(C_2H_5)_4]^+$ *etc.* These vibrations are shifted closely towards the wave numbers corresponding to those found in pure bulk water. Thus it appears increasingly improbable that an ordered hydrogen bond network can be formed in the sense as sketched in *Figure 1.* For comparison, the association pattern of AOT has also been plotted in *Figure 2* which displays the well known concentration independent mean aggregation number over the investigated concentration region while the aggregation number of the ammonium di-2-ethylhexylsulfosuccinate exhibits a linear concentration dependence. The same behaviour has already been reported by *Kaufman et al.* [13] with respect to the analogous dinonylnaphthalene sulfonate surfactant. These observations are indicative of a decreased hydration interaction between water and the ammonium ion compared to the sodium ion.

Also, very preliminary results obtained from experiments with D_2O in AOT/isooctane solutions may be mentioned in relation to the foregoing. It appears that the smallest aggregates (micelles) in the presence of D_2O which can be observed with the photon correlation technique are smaller, which would be in agreement with the fact [14] that the heats of ionic hydration are smaller and the hydrogen bonds (OD...X) to a foreign acceptor (X) are weaker in D_2O compared to H_2O. This confirms the considerable decreased stability of AOT aggregates in isooctane if more D_2O is solubilized [15] as compared to the solubilization capacity with respect to water at 25°. From the above mentioned observation it is now concluded that small amounts of water are pre-requisite to the formation of closed,

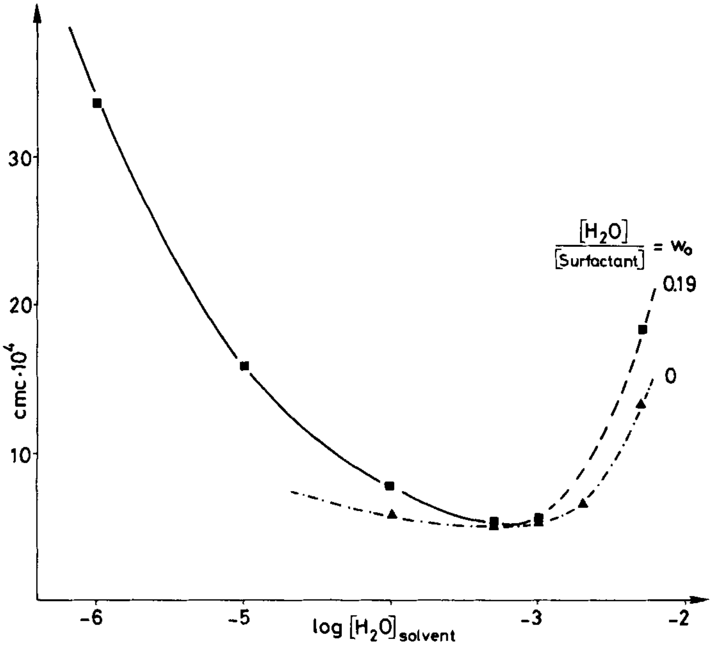

Fig. 4. *'CMC'* versus *water content of apolar solvent.* Parameter: $[H_2O]/[surfactant]$ = water initially attached to the surfactant.

concentration independent surfactant aggregates. However, these hydrogen bridges are not very stable. According to *Zundel* [9], the hydrogen bridges connecting the counterions and the oxygen atoms of the sulfonates (see *Fig. 1*) are weaker than hydrogen bridges in pure bulk water. This might be one reason that the solubilized water in AOT/isooctane solutions already boils at 70° [7]. On the other hand, the surprising stability of the AOT micelles in isooctane between $-85°$ and $+95°$ [7] can probably be understood on the basis of a cooperative process. This, then, displays the cooperative process of the hydrogen bond formation *(Fig. 3)*. Surfactants containing alkylated quaternary ammonium counterions should show a less pronounced tendency to form concentration independent aggregates according to *Zundel*'s results [9] as is generally observed. This does not exclude, however, an initially cooperative (or quasi-cooperative) process (see *Fig. 3* bottom) followed by a continuous concentration dependent aggregation. If the above proposed concept regarding the effect (of small amounts) of water on the surfactant aggregation in apolar solvents proves to be correct some interesting consequences have to be considered. According to the thermodynamical meaning of the CMC (see eq. 3) it appears evident that in a ternary system, *i.e.* surfactant in oil (+ small amounts of water) this quantity must depend on the water concentration of the system. Under these circumstances this operational defined concept looses any significance with respect to a surfactant property since it is changing with the water content. Thus, to be more precise one could start with the two relevant equations

$$S + zW \overset{K_1}{\rightleftharpoons} SW_z \quad \text{and} \quad (n-1)S + SW_z \overset{K_2}{\rightleftharpoons} S_nW_z \tag{1}$$

where SW_z may be interpreted as 'nucleus' in this connection which contains z water (W) molecules. The latter combines with $n-1$ surfactant molecules to form the inverted micelles S_nW_z. Considering the mass conservation for the respective components, W and S, *i.e.* $W_0 = [W] + z[SW_z] + z[S_nW_z]$ and $S_0 = [S] + [SW_z] + n[S_nW_z]$, the aggregate concentration is equal to

$$[S_nW_z] = K_1K_2(S_0 - n[S_nW_z])^n (W_0 - z[S_nW_z])^z \tag{2}$$

where the 'nuclei' have been neglected. At the onset of the aggregational process $[S_nW_z] \ll S_0, W_0$, *i.e.*

$$\frac{[S_nW_z]}{S_0} = \left(\frac{S_0}{\text{'CMC'}}\right)^{n-1} \qquad \text{where 'CMC'} = \left(\frac{1}{K_1K_2 \cdot W_0^z}\right)^{\frac{1}{n-1}}. \tag{3}$$

Hence it follows, as was to be expected, that the apparent 'CMC' depends on the amount of water present in the system. A more detailed analysis of the general case distinguishes the influence of the water content of the apolar solvent and that which is originally attached to the surfactant (= 'water of hydration'). This distinction corresponds to the experimental procedure, *i.e.* following the aggregational process by increasing the surfactant concentration. The complete equations (1) together with the boundary conditions (mass conservation) have been solved by an iterative procedure. The respective results were used to construct *Figure 4.* The detailed analysis yields two essential results: (1) with extremely dried surfactant the 'CMC' appears to be almost independent on the water content of the apolar solvent; (2) for large initial values of [H_2O]/[surfactant] the 'CMC' becomes strongly dependent on the water concentration as is exhibited by the second part of eq. (3).

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