44. The Effect of Choleates on the Solubilization of Water in Water/AOT/Cyclohexane (W/O)-Microemulsions

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Dedicated to Professor *Bun-Ichi Tamamushi* on the occasion of his 80th birthday

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Summary

Experimental investigations on the cosurfactant effect of alkali and tetraalkylammonium choleates in water/AOT/cyclohexane (W/O)-microemulsions were carried out. The results prompted considerations on a thermodynamic and molecular level. The molecular view emphasizes the significance of hydration interactions between cosurfactant and solubilized water.

In relation to recent theoretical considerations on the cosurfactant concept [1], and due to new insights into the possible role of water in the aggregational process of surfactants in nonpolar media [2], the effect of cosurfactants on (W/O)-microemulsions is reconsidered. An appropriate approach to the proposed problem appears to be the variation of the counterions according to the hydration interaction, choosing choleates as well-known ionic cosurfactants [3]. The procedure essentially corresponds to a change of the so-called hydrophile-lipophile property of the particular compound. As in previous investigations a ternary (W/O)-microemulsion, *i.e.* H_2O/AOT/oil (*e.g.* C_6H_{12}), was selected as a reference state with regard to the cosurfactants. Experimentally, the stabilizing properties of the various choleates with respect to the microemulsion were chosen to be investigated. Together with suitable data from other sources, the paper aims at a better understanding of the molecular and thermodynamical background of the cosurfactant function.

Experimental. - Highest grade *cholic acid* and analytical grade *sodium choleate (Fluka SA)* were used.

The lithium, potassium, rubidium, cesium, ammonium and tetraalkylammonium salts of cholic acid were prepared by potentiometric titration using the corresponding hydroxides: 1.5 g cholic acid were dissolved in 30 ml methanol (0.122 mol dm^{-3}) and titrated with a 0.25 molar methanolic solution of the hydroxide. The end point was determined within ± 0.1 pH-units. The solution was evaporated and dried under vacuum (0.5 Torr).

Sodium-di-(2-ethylhexyl)sulfosuccinate (AOT) from *Fluka SA* was purified according to the procedure employed in this laboratory [4]. Isooctane or cyclohexane of high grade purity *(Fluka SA* or *Merck AG)* were used without further purification. Drying appeared unnecessary for this investigation.

The equilibrium concentration of water in the solvent was determined with an automatic *Karl-Fischer* titrator (error about $\pm 1.10^{-4}$ mol dm^{-3}). The water to be solubilized was deionized and distilled twice.

The maximal solubilization capacity ($w_{0,max} = [H_2O]_{max}/[AOT]$) with respect to water of a 4.10^{-2}M AOT solution containing different amounts of the corresponding cosurfactants was determined using a 20 ml thermostated test-tube closed by a ground teflon stopper. The temperature was kept constant at 20.0°C. Water was added in portions of 10 µl to the continuously stirred solution using a *Hamilton* syringe. This minimum amount of added water corresponds to $w_0 = 0.28$. The error in $w_{0,max}$ was, accordingly, ± 0.14. Stirring the solution was as efficient as ultrasonic treatment.

The temperature dependence of the microemulsion region in the presence of cosurfactants was determined by increasing the temperature above the transparent region and then cooling until the onset of turbidity. The upper boundary of the microemulsion region was determined by this procedure. The lower boundary was found by cooling the solution below the coexistence curve and then warming it up again with continuous stirring. The turbidity was observed by placing the thermostated test-tube in daylight against a white background.

Results and Discussion.– The mutual dependence of the different variables was investigated in order to facilitate the interpretation of the results. Thus, in *Figure 1* the temperature shift of the microemulsion region of the water/AOT/cyclohexane-system was followed as a function of added amounts of sodium choleate. Increasing amounts of cosurfactant caused change in extension, shape, and position of the microemulsion region. In particular, the lower boundary of the region, *i.e.* the coexistence curve, separates the pseudo-one phase (W/O-microemulsion) from a pseudo-two phase region where microemulsion aggregates coexist with free water [1], (compare also [5]). Since the upper boundary has been shown to have a different, less well defined meaning [1] [6], the discussion will be confined to the coexistence curve. The temperature dependence of the latter with respect to small amounts of additives (cosurfactants) can be interpreted on thermodynamical grounds. The temperature variation due to small amounts of cosurfactants is quite remarkable; the addition of $5.57 \cdot 10^{-3}$ mol dm^{-3} sodium choleate causes a negative shift in the coexistence curve of 79 °C compared to the reference state (H_2O/AOT/

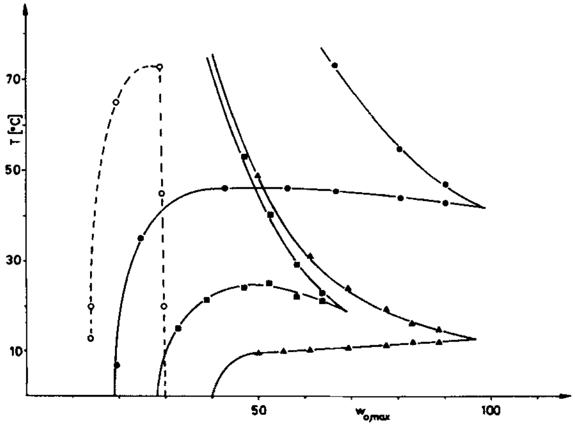

Fig. 1. *Effect of cosurfactant* (sodium choleate) *concentration on (W/O)-microemulsion* (H_2O/AOT/C_6H_{12}) *domain* (≙ *mixing temperature*). *Mixing temperature* (T) versus *solubilization capacity* ($w_{0,max}$). Parameter: [Na-choleate] · 10^3 mol dm^{-3}: ● 2.83, ▲ 5.57, ■ 8.96, ○ 16.40.

C_6H_{12}). Larger amounts of additive increase the mixing temperature again since competition between surfactant and cosurfactant increases. However, this concentration range of the additive cannot be described quantitatively, due to the assumptions on which the theoretical approach is based. Only low additive concentrations may be considered [1] [7]. Analogous diagrams, *Figures 2a* and *2b* can be plotted, in which the composition of a cosurfactant is varied by exchanging the counterions in the order of increasing radii. In addition, the ammonium ion, which has many properties in common with the alkali ions, and some of its increasingly lipophilic tetraalkyl derivatives were added. A comparison of *Figure 1* with *Figures 2a* and *2b* clearly shows that different concentrations of a particular cosurfactant produce the same results as varying the counterions of the amphiphilic compounds. These mutual relations, as well as the cosurfactant effect on the mixing temperature, can be explained by visualizing the mutual dependence of the relevant variables,

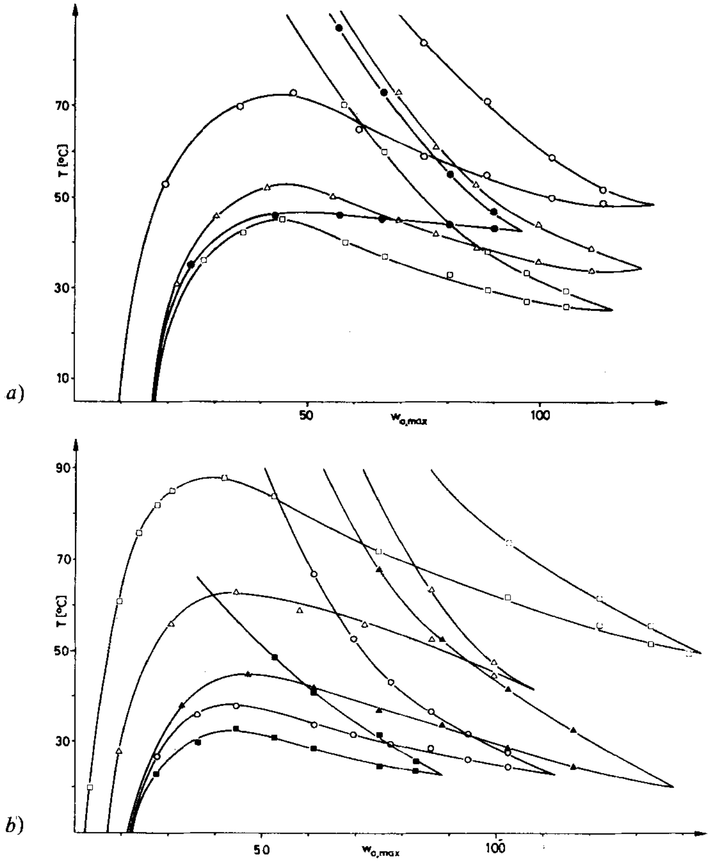

Fig. 2. *Dependence of mixing temperature on choleate counterions at constant cosurfactant concentration of 2.79 · 10^{-3} mol dm^{-3}* (H_2O/AOT/C_6H_{12}) (W/O)-microemulsion. *Mixing temperature* (T) versus *solubilization capacity* ($w_{0,max}$). a) Parameter: choleate counterions: ○ cholic acid; ● Na^+; △ K^+, Rb^+, Cs^+; □ Li^+. b) Parameter: choleate counterions: □ no surfactant, △ NH_4^+, ○ $N(CH_3)_4^+$, ■ $N(C_2H_5)_4^+$, ▲ $N(C_3H_7)_4^+$.

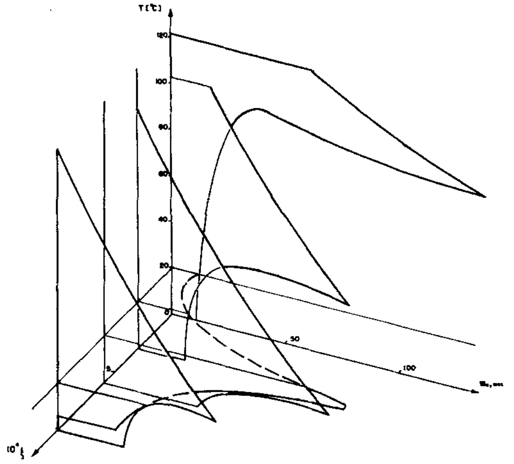

Fig. 3. *Mutual relations between the dependences of mixing temperature* (T) *and solubilization capacity* ($w_{0,max}$) *on the mole fraction* (ξ) *of cosurfactant*

i.e. temperature, solubilization capacity and cosurfactant concentration (mole fraction ξ), shown in *Figure 3*. The plot of mixing temperature *versus* solubilization capacity at constant cosurfactant concentrations exhibits several microemulsion regions. These diagrams are known from *Figures 2a* and *2b*. At constant temperature (e.g. 20 °C) different representations result. These plots describe the $w_{0,max}$-

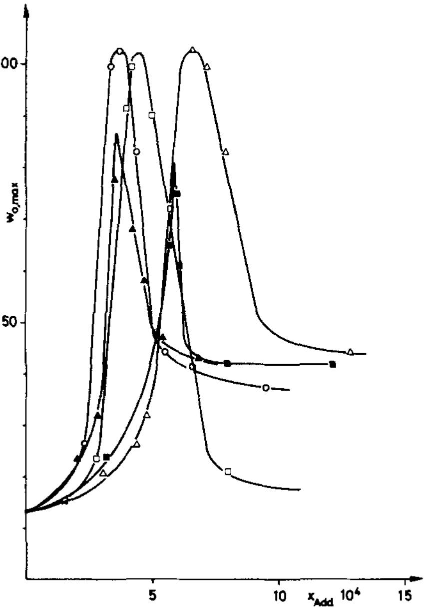

Fig. 4. *The efficiency of choleates as cosurfactants on the solubilization capacity in a* (W/O)*-microemulsion* ($H_2O/AOT/C_6H_{12}$) at 20°. *Solubilization capacity* ($w_{0,max}$) versus *mole fraction of cosurfactant* (x_{Add} 10^4). Parameter: counterions of choleates: ■ Na^+, △ NH_4^+, ▲ $N(C_2H_5)_4^+$, ○ $N(CH_3)_4^+$, □ $N(C_3H_7)_4^+$.

dependence on the additive concentration ξ. The isothermal plane represents the geometric locus of all points of intersection of the 20 °C-isotherms and the boundary curves of the W/O-microemulsion regions (as determined by the onset of the turbidity). Experimental verifications of such diagrams with respect to different salts of the cholic acid in C_6H_{12} are given in *Figure 4.* Moreover, *Figure 3* exhibits the maximum solubilization at the temperature defined by the intersection of the isothermal plane and the upper boundaries of the microemulsion regions. In this case the solubilization maximum (again indicated by the onset of a permanent turbidity) is determined by the size of the droplets at which multiple scattering starts. As mentioned above, this maximum solubilization region is not predicted by thermodynamical reasoning [6].

Based upon some recent investigations [1], and information from other sources [7] [8] [9], the above observations are amenable to some thermodynamical and molecular interpretation. It was shown [1] that the effect of an arbitrary additive, *i.e.* a cosurfactant, on the solubilization capacity is given by

$$\frac{dw_{0,\max}}{(w_{0,\max})_{\xi=0}} = \frac{2V^{a}_{H_2O}}{s^a \cdot r} \cdot C \cdot \left\{ \left(\frac{\partial s}{\partial x} \right)_{x^a} - \frac{s^p - s^a}{x^p - x^a} \right\} x^a d\xi \qquad (1)$$

This equation describes the relative change of the solubilization capacity ($w_{0,\max}$) by small amounts of cosurfactant (ξ).

The expression is essentially derived from a consideration of the interfacial free energy change ($d\gamma$) under the influence of an additive which in turn determines the transfer of water from a two-phase into the W/O-microemulsion region, *i.e.* $dw_{0,\max}$.

The expression

$$C = \frac{x^a}{1-x^a} \Gamma_1 - \Gamma_2 - \frac{x^p - x^a}{1-x^a} \cdot \frac{\Delta^{\sigma}_{a} V}{\Delta^{p}_{a} V}$$

arises from the equilibrium condition between the polar and apolar phases in the presence of a surfactant [10]. $V^{a}_{H_2O}$ is the molar volume of water in the continuous oil phase, r the radius of the water droplets in the (W/O)-microemulsion, s^a, s^p the solubilities of the additive (= cosurfactant) in the apolar and polar phase of the system in the presence of surfactant; x^a, x^p denote the composition of the respective phases, Γ_1, Γ_2 are the amounts of the first component (H_2O) plus the polar head of the surfactant in a unit area of the interface (σ) and the amount of the second component (oil) plus the apolar tail of the surfactant per unit area of the interface. Finally, $\Delta^{\sigma}_{a}V$ is the volume increase forming a unit area of interfacial layer (σ) at constant T and P by taking both components (together with the respective parts of the surfactant) from the apolar phase; $\Delta^{p}_{a}V$ is the volume increase upon forming the polar phase at constant T and P, similarly taking both components from the apolar phase (see [10]).

In the context of this investigation C is of minor importance and considered to be constant. The essential features of the experimental results can be elucidated by the bracketed term in (1). According to the definition of a cosurfactant given elsewhere [1], it is assumed that $dw_{0,\max}/d\xi > 0$. Eq. (1) satisfactorily describes the dependence of the solubilization capacity on the thermodynamical properties of the particular cosurfactant. The term in brackets multiplied by $d\xi$ (= differential amount of cosurfactant) predicts, within the limits given by the approximations on which (1) is based, the effectiveness of the cosurfactant with respect to the water solubilization. Thus, for example, the solubility of sodium choleate in water is about 1 mol dm^{-3} [11], in cyclohexane about $7 \cdot 10^{-5}$ mol dm^{-3} at 20 °C, therefore

$s^p \gg s^a$. If x is the molar fraction of water in C_6H_{12} and if the oil-rich side of the mixing gap is considered, then $x^a \ll 1$ and $x^p \simeq 1$ at small amounts of added water and surfactant. These conditions yield a simplification of (1), hence

$$\frac{dw_{0,\max}}{(w_{0,\max})_{\xi=0}} = \mathrm{const}\left\{\frac{1}{s^a}\left(\frac{\partial s}{\partial x}\right)_{x^a} - \frac{s^p}{s^a}\right\} d\xi \tag{2}$$

where $(\partial s/\partial x)_{x^a}$ has to be taken at the composition $x = x^a$. With increasing $x(=H_2O)$ the solubility of sodium choleate should grow considerably, in order to conform to the experimental findings.

Generalizing, it is seen that increasing the solubilities of the choleates in the dispersed aqueous phase promotes the solubilization capacity. The initial slopes $dw_{0,\max}/d\xi$ at $(w_{0,\max})_{\xi=0}$ display this dependence as shown in *Figure 4*. A detailed discussion concerning the possible modes produced by the cosurfactant solubilities in the two phases has been given elsewhere [7].

Within the same approximations the temperature dependence of $w_{0,\max}$ can be derived. Thus, from [1] [7] [12] where C has the same meaning as before,

$$\frac{d\,w_{0,\max}}{(w_{0,\max})_{\xi=0}} = -\frac{C}{RT^2}\left\{\left(\frac{\partial \bar{H}^E}{\partial x}\right)_{x^a} - \frac{\bar{H}^E_{x^p} - \bar{H}^E_{x^a}}{x^p - x^a}\right\} x^a\, dT \tag{3}$$

$\bar{H}^E_{x^p}$, $\bar{H}^E_{x^a}$ are the molar excess heats of mixing with respect to the polar (H_2O) and apolar (oil) phase in the presence of surfactant. In the case of a relatively large mixing gap the second term in the bracket in (3) is small compared with $(\partial \bar{H}^E/\partial x)_{x^a}$ which itself is positive for $x^a \ll 1$ (see [7]). If such a condition holds, as is apparently the case with cosurfactants, an increase in the mixing temperature is accompanied by a decrease of the solubilization capacity. This can be visualized from *Figure 1* for a particular cosurfactant concentration.

A closer consideration of the dependence of the cosurfactant efficiency on the counterions, taking the special case of the cholic acid salts, shows a remarkable difference between the alkali ions and the ammonium ions, *i.e.* NH_4^+, $N(CH_3)_4^+$, $N(C_2H_5)_4^+$, and $N(C_3H_7)_4^+$. The apparent decrease of the cosurfactant efficiency from lithium to cesium *(Figure 2a)* corresponds with the fact that the binding between the cations and water molecules becomes progressively weaker in the same order and the number of hydrogen bonds between the water molecules simultaneously increases [8]. The same conclusions can be derived from NMR. relaxation time measurements [9]. This finding is supported by a decrease in the solubility of the salts and a lowering of the solubilization capacities as predicted by (2). However, replacing the proton of the cholic acid by NH_4^+ causes a shift in the mixing temperature close to the value observed in the presence of cholic acid. This result contrasts with the effect of the tetraalkyl derivatives on the mixing temperature which exceeds even that of sodium choleate and follows from a comparison between *Figures 2a* and *2b*. The poor effect of ammonium choleate as a cosurfactant is not fully understood. It might be noted in this context that replacing the sodium in AOT by the ammonium ion suppresses its well-known micellization property in apolar media [2] [13]. According to recent views regarding the formation of hydrogen bonds as a pre-requisite for a micellization in apolar solvents [2], the interaction between water and cation appears to be reduced while the electrostatic interaction between cation and anion is probably increased. This effect becomes more intense as the cations become larger and more hydrophobic as is the case with alkylated ammonium ions. The conclusions are based on IR. investigations [8] and activity measurements with tetraalkylammonium halides [14]. In connection with the present measurements, the phenomenon of 'water structure-enforced ion pairing' which occurs especially with large hydrophobic cations and anions, was discussed [14]. This process is expected to minimize their interaction with the water and to decrease the electrostatic free energy of the system. This situation could prevail in the present case since cholic acid (from which the anion derives) is poorly soluble in water and the cations become increasingly hydrophobic with size. It is, therefore, not unreasonable to expect (see [14]) that the tetraalkyl derivatives of the ammonium ion form micelles in water. This would easily explain their qualitatively observed remarkable solubilities.

The particularly large solubilities of the tetraalkylammonium choleates in the dispersed water phase, probably with participation of the hydrophile-lipophile interface, is assumed to be due to a suitable solvation of cation and anion in this amphiphilic environment. An orientation of the ions is easily visualized in which the polar portions of the respective ions are exposed to the water core, thus facilitating hydrogen bond interaction with the solubilized water [15]. This process would then be responsible for the considerable increase of the solubilization capacity in the presence of ionic cosurfactants.

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