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TEACHING AID IN SURFACTANT SCIENCE & ENGINEERING

In English

SURFACTANTS in AQUEOUS SOLUTIONS

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SURFACTANTS IN AQUEOUS SOLUTION

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SURFACTANTS IN AQUEOUS SOLUTION

1. SURFACTANT SOLUTIONS

1.1. AMPHIPHILIC COMPOUNDS.

Surface active substances, so called surfactants, are amphiphilic compounds that can be represented by the symbol H-L. The hydrophobic or lipophilic part of the molecule (L) is generally an hydrocarbon chain such as dodecylbenzene or tridecane. On the other hand, the hydrophilic part of the molecule (H) contains heteroatoms such as O, N, S, P. Depending upon the kind of dissociation of their hydrophilic group in water, the surfactants are classified as:

- **Anionic** Surfactants (H = ester sulfate, carboxylic or phosphoric acid, sulfonate, etc.).
- **Cationic** Surfactants in which H is generally a quaternary ammonium.
- **Nonionic** Surfactants, the hydrophilic group of which is generally a polyether chain (poly ethylene oxide) condensate.
- **Amphoteric** or **zwitterionic** surfactants that bear both anionic and cationic polar groups, such as betaine or sulfobetaine.

Although there is a great variety of substances which bear the H-L type of molecular formula, it can be said that they behave quite similarly in spite of their differences.

Each L-H ionic or neutral molecule exhibits a dual polar/apolar affinity, and its overall behavior depends essentially on the balance of its hydrophilic and lipophilic features. In any case a surfactant solution always presents a very characteristic property, i.e., either H or L possess a strong affinity for the solvent, while the other undergoes a repulsion from it.

1.2. HYDROPHOBIC EFFECT IN AQUEOUS SOLUTION.

Amphiphilic molecules often display some association behavior in aqueous solution; the formation of dimers, trimer or higher polymers, reduces the contact area between the hydrocarbon chain (L) and the aqueous solvent, and this results in a decrease in free energy. When the hydrocarbon chain is long enough, say 10 or more methylene group, hydrophobic driving forces result in a large scale association structure so called micelle, which can gather tens or hundreds of surfactant molecules. In some case an actual phase separation can occur with the micelles rearranging into three dimensional structures such as microemulsions, liquid crystals or other mesophases.

When the surfactant molecules start to associate in micelles, the solution becomes a micellar solution; such micellar solutions are expected to exhibit characteristic properties, not unlike colloids, since the micelle size (50-100 Å) lays in the colloidal range.

1.3. SURFACE AND INTERFACE ACTIVITY.

At the air-water surface and at the oil-water interface, the medium undergoes a strong and sharp change in polarity, i.e., a situation which favors the orientation of the H-L molecules in a direction perpendicular to the surface or interface. In such perpendicular positioning, the hydrophilic head group is wetted by the aqueous solution, while the hydrophobic "tail" is out of the polar environment. As a matter of fact this is the only position which results in favorable interactions of both parts of the surfactant, and this is why a surfactant molecule is always seeking a superficial or interfacial location.

The variation of the superficial free energy, i.e., the superficial tension, with the surfactant concentration in the aqueous phase is to be discussed now, as a way to detect the onset of micellization. In the case of an oil-water interface, the situation would be more complex because the surfactant molecules can partition into both liquid phases. Since the interfacial tension change does not bring any more information than the superficial tension change, the latter is preferred for the sake of simplicity.

Figure 1 shows the change in surface tension versus the surfactant concentration in the aqueous phase at equilibrium with the surface. Starting at an initial value corresponding to pure water (72 dyne/cm or mN/m), the surface tension decreases as the surfactant concentration increases. In this first zone (I) most surfactant molecules which are introduced in the aqueous phase are driven to adsorb at interface. As a consequence the adsorption (concentration at interface in mole/area) increases rapidly, which triggers a strong decrease in surface tension, i.e., in surface free energy.

When the adsorbed molecules become densely packed, there is no more room at interface, and the adsorption becomes constant. The Gibbs isotherm formula allows us to know that the adsorption is proportional to the slope of the γ -logC curve. As a consequence a saturated surface will result in a straight line variation on the γ -logC plot, e.g., zone II on fig 1. When more and more surfactant molecules are introduced into the systems, the adsorption remains essentially constant and thus these additional molecules are to be solubilized in the aqueous solution, a not so favorable situation because it involves the contact between the surfactant hydrophobic tail and water.

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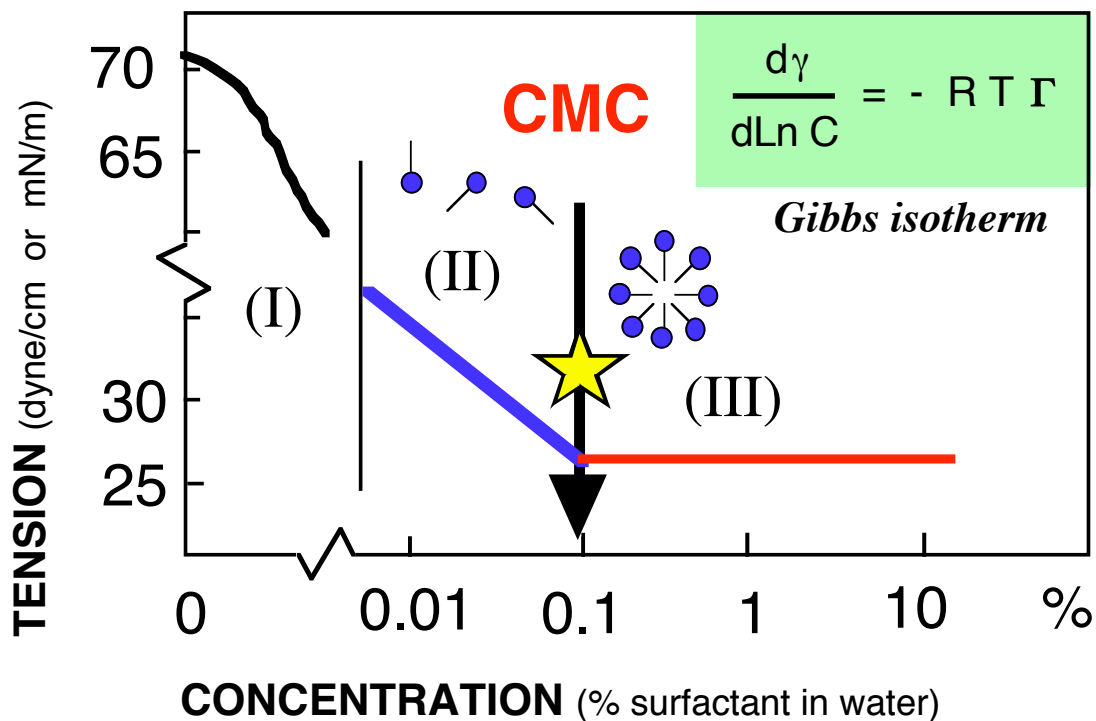


Fig. 1: Surface Tension vs. Surfactant Concentration. This Variation allows the determination of the Critical Micelle Concentration (CMC).

2. MICELLES AND CRITICAL MICELLE CONCENTRATION.

At some point the aqueous solution gets *saturated* by the surfactant molecules and the surfactant solution undergoes a transition and passes into zone III (see fig 1), in which the tension remains constant as more and more surfactant is added to the solution.

In most cases the surfactant solution does not exhibit a precipitation as it would occur to ordinary solutions when the saturation is reached. Instead the surfactant *solubilization* starts occurring under a new form, i.e., the micelle formation.

The words *saturation* and *solubilization* are italicized because they are not used according to their conventional meaning but rather as some layman colloquial language. Actually the correct wording would be to say that at some concentration, the hydrophobic interactions between surfactant molecules becomes important enough for an association to occur spontaneously.

In aqueous medium, micelles can gather several tens and even a few hundreds of molecules; the size and the geometry (spherical, cigar, rod-like) depends upon the surfactant molecular structure as well as upon the physicochemical environment (Mukerjee, 1977; Mukerjee et al., 1977).

Figure 2 displays the most simple spherical micelle model. In such an association structure the surfactant molecules can satisfy their dual affinity almost as well as at the surface, although the close neighboring of the polar head groups can be impaired by electrostatic repulsion if there are of the ionic type.

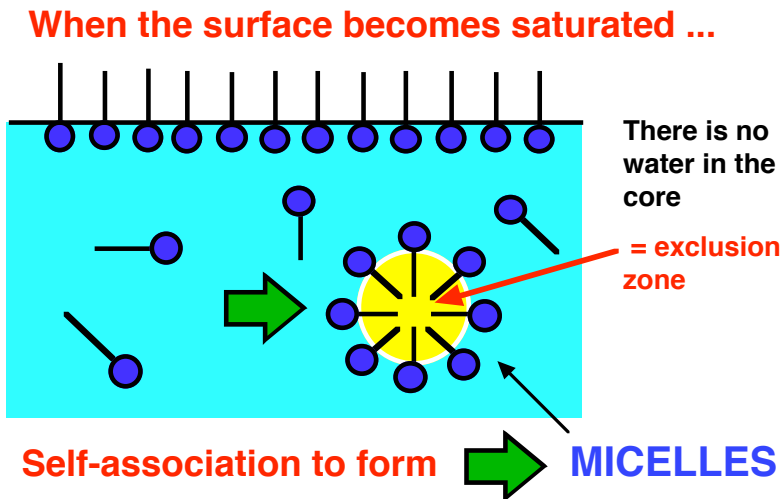


Fig. 2: Micelle: Aggregate of Surfactants Molecules

The critical micelle concentration (abbreviated CMC) is the transition between Fig. 1 zone II and III typical patterns. It does not actually correspond to an exact concentration but rather to some range of concentration, which can be widespread for systems containing mixtures of surfactants with quite different characteristics. The CMC is usually taken as the concentration at which the first micelles appear, an event that can be monitored through a change in the variation of several properties, not only surface tension, but also the cryoscopic lowering or the electrolytic conductivity as shown in Fig. 3 and 4. As a matter of fact it is worth noting that the mostly used method to determine the CMC are the measurement of surface tension (all types of surfactant) and the measurement of electrolytic conductivity (ionic surfactants). Osmotic pressure measurement, which are related with the cryoscopic lowering (and apparent MW) are also used.

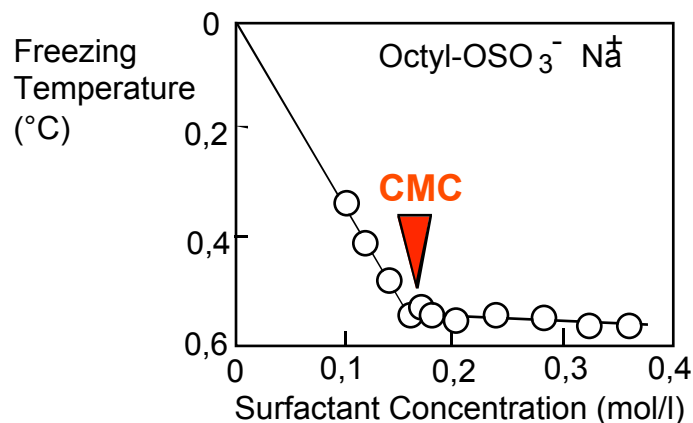


Fig. 3: Cryoscopic Lowering as a function of the Surfactant Concentration in Aqueous Solution .

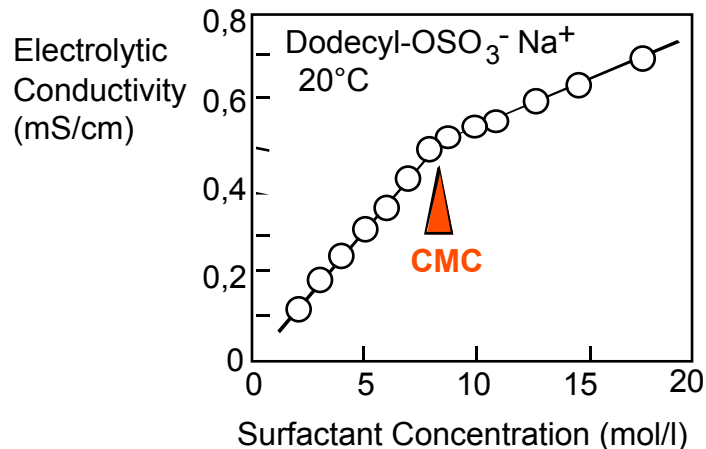


Fig. 4: Electrolytic Conductivity of the Solution as a function of the Surfactant Concentration.

A quick determination of the CMC can be carried out by measuring the micellar solubilization of oily substances, specially colored ones, or by detecting the onset of demixing of oil substances which can enter the micelle core.

As a general rule the measured change is spread over some range of concentration, sometimes with the presence of a minimum; the actual CMC is usually taken as the intersection of the extrapolated tendencies above and below the transition zone.

The adjective "critical" suggests that the micellization can be viewed as some phase transition, i.e., some "microprecipitation". Several models have been proposed and some of them deal with a phase separation feature. The review by O'Connell and Brugman (1977) provides a good insight of this topic.

As far as this introductory text is concerned, the properties to be remembered are the following ones:

- (1) Above the CMC, any additional surfactant molecule is incorporated into the micelles, and the concentration of the free molecules, i.e., the non-associated surfactant, remains constant. However it should be pointed out that there is a very fast dynamic equilibrium between the free surfactant molecules and the ones present in the micelles. Relaxation times as low as 10^{-6} sec are not uncommon; as a consequence a change in the physicochemical environment can trigger a micellar change in a glance.
- (2) The micellar size (10 - 100 Å) and the aggregation number, depend upon the type of surfactant, and upon the physicochemical environment (electrolyte, alcohol, temperature, etc.).
- (3) The superficial and interfacial tension of a system containing a pure surfactant is perfectly constant above the CMC. Thus, it can be stated that a change in the number of micelles does not affect the superficial or interfacial activity, which depends only

on the free surfactant concentration. However it should be pointed out that the magnitude of the micelle-related phenomena such as solubilization, depends on the amount of surfactant aggregated into the micelles (see following sections).

- (4) Below the CMC, the thermodynamic properties of the surfactant solutions (osmotic pressure, cryoscopic lowering) obey the usual ideal or regular solution laws, in a way similar to those conventional solutions which contains a solute with high molecular weight. On the contrary, the solution behavior is highly non ideal above the CMC, with an activity essentially independent from the surfactant concentration. In some particularly awkward cases, mesophases structures such as liquid crystals or gels can be produced with just a very few percents of surfactants in water, a hint of the occurrence of extremely strong interactions.

3. FACTORS WHICH AFFECT THE CMC.

3.1. COMPETITIVE INTERACTIONS.

The existence of the CMC as a well defined phenomenon implies that there exists several kinds of interactions, some of them favoring the formation of micelles, and others opposing it. It has been already said that the association of surfactant molecules into micelles is driven by the hydrophobic effect. The larger and/or more hydrophobic the surfactant tail, the stronger the hydrophobic effect is expected to be, and thus the easier the formation of micelles, i.e., the lower the CMC.

As far as the interactions which oppose micellization are concerned, they may be classified in two types. First, those which facilitate the molecular solubilization of the surfactant into water, mostly through the solvation of the polar head group. The more polar the head group is, the lesser is the tendency to form micelle, and the higher the CMC. Second, those which inhibit the formation of the micelle, particularly the ones coming from repulsive effects between neighboring head groups because of the presence of an electrical charge. If the Coulombian electrostatic repulsion is strong enough, the surfactant head groups cannot get close enough for the removal of the tail from the aqueous environment to take place, and the micelle formation is difficult or inexistent. This situation is responsible for the fact that nonionic surfactants form micelles easily (and at a much lower concentration) than their ionic counterparts. As a matter of fact it can be said that nonionic surfactants exhibit a CMC 1000-times lower than the ionic ones with similar hydrophile-lipophile balance (see table 1).

Because of the importance of the CMC as a yardstick to measure the surfactant characteristics, this property has been measured extensively, and many reports are available in the literature (Mukerjee 1971, Rosen 1978, Schick 1967). However the reader is warned to handle the data with care since there are many discrepancies, particularly in old publications. The reason for these inaccuracies will be easily understood later on, at the end of section 4, where the importance of trace impurities is displayed in a numerical example.

TABLE 1. The CMC of some Surfactants .

	CMC
NONIONIC SURFACTANT	10^{-6} mol/l
Octylphenol + 1 EO	45
Octylphenol + 2 EO	70
Octylphenol + 3 EO	105
Octylphenol + 4 EO	135
Octylphenol + 5 EO	180
Octylphenol + 7 EO	290
Octylphenol + 9 EO	325
n-Hexanol + 6 EO	74000
n-Octanol + 6 EO	11000
n-Decanol + 6 EO	860
n-Dodecanol + 6 EO	90
n-Tetradecanol + 6 EO	10
n-Hexadecanol + 6 EO	1.1
	CMC
IONIC SURFACTANT	10^{-3} mol/l
Octyl sulfate Na Salt	120
Decyl sulfate Na Salt	30
Dodecyl sulfate Na Salt	8
Tetradecyl sulfate Na Salt	2
Hexadecyl sulfate Na Salt	0.6
Octadecyl sulfate Na Salt	0.2
Dodecyl sulfonate Na Salt	9
Tetradecyl sulfonate Na Salt	2
Hexadecyl sulfonate Na Salt	0.5
Dodecyl sulfate Li Salt	9
Dodecyl sulfate K Salt	8
Dodecyl sulfate Ca Salt	3
Dodecyl sulfate tetra butyl ammonium Salt	1
Dodecyl trimethyl ammonium bromide	16
Tetradecyl trimethyl ammonium bromide	2
Hexadecyl trimethyl ammonium bromide	1
Hexadecyl pyridinium chloride	0.9
Octadecyl pyridinium chloride	0.2

Micromole

Millimole

3.2. EFFECT OF THE SURFACTANT STRUCTURE.

As seen in the previous section, the surfactant CMC depends upon both its hydrophilic head group (type, size, counterion) and its lipophilic tail group (length, branching).

3.2.1. HYDROPHOBE TAIL GROUP.

In aqueous medium, the CMC has been found to decrease as the number of carbon atoms in the hydrophobic group increases. Most experimental data can be fitted with a relationship of the type:

$$\log \text{CMC} = A - B N$$

Where N is the number of methylene groups - CH₂ - contained in the hydrophobic group when it is a linear hydrocarbon; A is a constant that depends upon the hydrophilic group and B is a proportionality factor (0.5 for nonionics, 0.3 for ionics). The benzene ring is found to be equivalent to 3 methylene groups. Rosen (1978) reviewed the values of A and B which were published in the literature for different surfactant families, as reproduced in table 2.

The branching of the hydrophobe is quite an important factor. It has been found that the CMC increases considerably with the branching, a tendency which matches the increase of aqueous solubility of the surfactant with their branching.

This remark explains that the relationship between log CMC and the number of methylene groups in the hydrophobe is no longer linear for chains longer than 15 methylene groups; in effect such long chain tend to fold, a conformation which decreases the interactions with the solvent.

3.2.2. HYDROPHILIC GROUP.

As far as the CMC is concerned, the most important characteristic of the hydrophilic group is its charge or lack of charge. It has been pointed out that the electrostatic repulsion between neighboring ionic polar heads in a micelle is an unfavorable effect that increases the CMC. Another reason for the polyether (polyethylene oxide) nonionics to have a lower CMC, is the presence of two methylene groups in each ethylene oxide link; this results in less face-to-face polar repulsion between oxygen atoms.

All these arguments corroborate that the CMC is a measurement of the overall hydrophile-lipophile balance of the surfactant.

On the other hand both the hydrophile type and the eventual counterion, have a strong effect on the CMC. It has been shown that the CMC of anionic surfactant salts of divalent cations, is much lower than the CMC of their monovalent cation counterparts, a result which can be readily related to the ionic dissociation level and thus to the actual polarity of the hydrophilic group.

The more dissociated, and the more ionized the ionic surfactant is, the stronger is the interaction with the water molecules, and the more hydrophilic is the polar group.

As a matter of fact this explains why a single sulfate group turns very hydrophilic a surfactant such as dodecyl sulfate, while at least 8 ethylene oxide groups are required to obtain a slight hydrophilicity in a nonionic surfactant.

The CMC of nonionic surfactants of the polyethylene oxide type has been reported to be related with the number of ethylene oxide groups per molecule (EON) according to a relationship of the following type (Becher, 1967a).

$$\log \text{CMC} = A' + B' \text{EON}$$

Where A' is a constant characteristic of the hydrophobe, and B' a multiplicative factor in the 0.02 - 0.03 range (see table 2).

These empirical relationships corroborate that the CMC is directly linked with the hydrophilic-lipophilic balance of the surfactant.

It has been found that the CMC is also related to the aggregation number, although it is rather a trend than a relationship: in general the aggregation number increases with the hydrophobic character of the surfactant, i.e., when the CMC decreases.

TABLE 2. CMC's VALUES (mol/l)

IONIC SURFACTANTS		$\log \text{CMC} = A + B N_{\text{CH}_2}$	
Surfactant Family	Temp (°C)	A	B
Na Carboxylates	20	1.85	0.30
K Carboxylates	25	1.09	0.29
N-alkyl-1-sulfates K or Na salts	25	1.50	0.30
N-alkyl-1-sulfonates K or Na salts	25	1.50	0.30
N-alkyl benzene sulfonates Na salts	55	1.60	0.29
N-alkyl benzene sulfonates Na salts	70	1.30	0.27
N-alkyl ammonium chloride	25	1.25	0.27
N-alkyl trimethyl ammonium chloride	25	1.70	0.30
N-alkyl pyridinium bromide	30	1.70	0.31
NONIONIC SURFACTANTS		$\log \text{CMC} = A' + B' \text{EON}$	
Surfactant Family	Temp (°C)	A'	B'
N-dodecyl alcohol-EON	23	- 4.4	0.046
N-dodecyl alcohol-EON	55	- 4.8	0.013
p.ter octyl phenol-EON	25	- 3.8	0.029
Nonyl phenol-EON	25	- 4.3	0.020
N-hexadecyl alcohol-EON	25	- 5.9	0.024

3.3. EFFECT OF THE PHYSICO-CHEMICAL ENVIRONMENT.

Since alcohols and electrolytes are known to modify the solubilizing power of aqueous solutions, they are also expected to exhibit some influence upon the formation of surfactant micelles, in particular on the CMC. As a matter of fact this kind of solute can modify the interactions that either facilitate or inhibit the formation of micelles.

3.3.1.- ELECTROLYTES.

When electrolytes are added to an aqueous solution, most substances result less soluble than in an electrolyte-free solution. In some case the reduction in solubility leads to the actual precipitation of a solid phase, a phenomenon which is often called "salting - out" in the surfactant literature. This effect is generally attributed to the reduction of the solvation of the polar group.

On the other hand the addition of an electrolyte results in an increase of the ionic strength in the neighboring of the micelle, where it produces some screen effect which decreases the electrostatic repulsion between the polar head groups.

Both effects tend to facilitate the gathering of the surfactant molecules into micelles, and as a consequence both tend to reduce the CMC. Figure 5 shows the variation of the surface tension versus the surfactant concentration, for different aqueous phase salinities.

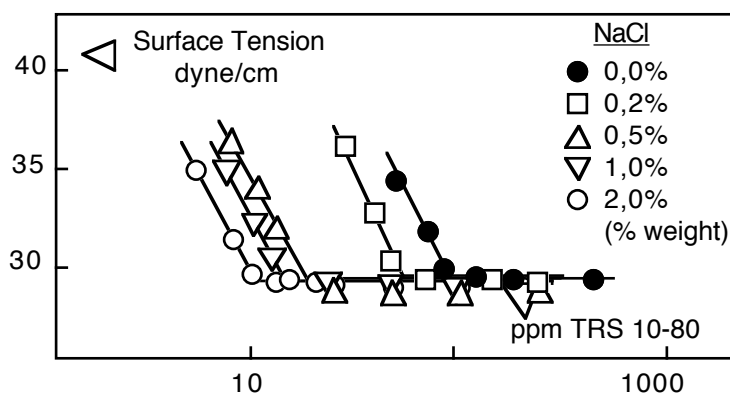


Fig. 5: Surface Tension vs. Surfactant Concentration (TRS 10-80 petroleum sulfonate) for different Salinity values. The CMC is affected by the Electrolyte Concentration.

For anionic surfactants, the following relationship has been found to account for the effect of monovalent electrolytes.

$$\log \text{CMC} = A'' - B'' \log S$$

Where S is the salinity; A'' and B'' are constants which depend upon the surfactant and the type of electrolyte.

The effect is even stronger with polyvalent cations (Ca^{++} , Mg^{++}), a consequence of their action on the electrical double layer which surrounds the micelle.

For nonionic and amphoteric surfactants the effect is qualitatively the same, but much lower in magnitude. It has been represented by a relationship with a linear salinity contribution.

$$\log \text{CMC} = A^* - B^* S$$

In this case the CMC decrease is attributed to the reduction of the solvation of the hydrophilic group, as well as an increase of interaction between some hydrophobe

(polypropylene oxide) and the aqueous phase. Furthermore, the presence of electrolyte can turn spherical micelles in cigar or rod-like ones.

3.3.2. ALCOHOLS

Very often surfactants are mixed with other amphiphiles, such as light alcohols. Alcohols are used either as co-surfactants, i.e., as modifiers of the surfactant hydrophile-lipophile balance, or as interfacial solvent. In this second role C3 - C4 alcohols adsorb at interface and pull apart surfactant molecules, whose interfacial concentration decreases. This results in less interactions per unit of interfacial area and thus less cohesion in any structure that can be formed; as a matter of fact ionic surfactants tend to form liquid crystals in absence of alcohol, and microemulsion, i.e., melted liquid crystal, when a proper alcohol is added.

All alcohols tend to decrease the CMC (as seen in Fig. 6); however the magnitude of the effect depends upon the alcohol type and concentration, as well as its molecular structure characteristics such as its branching. It can be said that the alcohol effect comes directly from its co-surfactant role in the so-called mixed micelles.

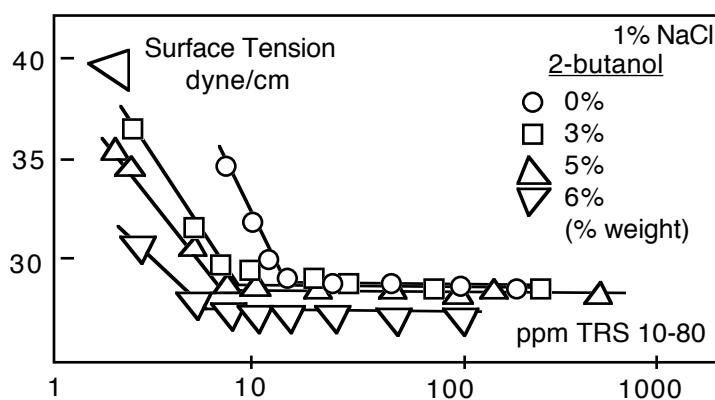


Fig. 6: Surface Tension vs. Surfactant Concentration (WITCO TRS 10-80) with different 2-butanol concentrations. Note the alcohol concentration influences the CMC.

Shinoda (1954) found that the effect of alcohol on the CMC can be rendered by the following relationship, which applies to the carboxylic acid sodium salts (a change of over one order of magnitude).

$$CMC = CMC_0 - K C(A)$$

Where CMC_0 stands for the corresponding CMC in absence of alcohol, $C(A)$ is the alcohol concentration and K is a proportionality constant which depends of both the alcohol type and surfactant nature.

Fig. 7 (lower) indicates that K varies exponentially with the number of carbon atoms in the alcohol hydrophobe. Thus, when more hydrophobic is an alcohol, more efficient it is in lowering the CMC of a given surfactant.

This effect is readily explained by the formation of mixed micelles in which the alcohol molecules are inserted in between surfactant molecules in the micelle palissade

layer. In the case of ionic surfactant, this reduces the face-to-face electrostatic repulsion of the polar head groups, an effect that facilitates the formation of the micelle, and thus decreases the CMC.

Almgren and Swarup (1983) as well as the Macromolecule Research Center Team in Strasbourg (Zana et al., 1981; Yiv et al., 1981) have reported in detail the influence of alcohols and other co-surfactants on ionic systems, by using sophisticated instrumental methods.

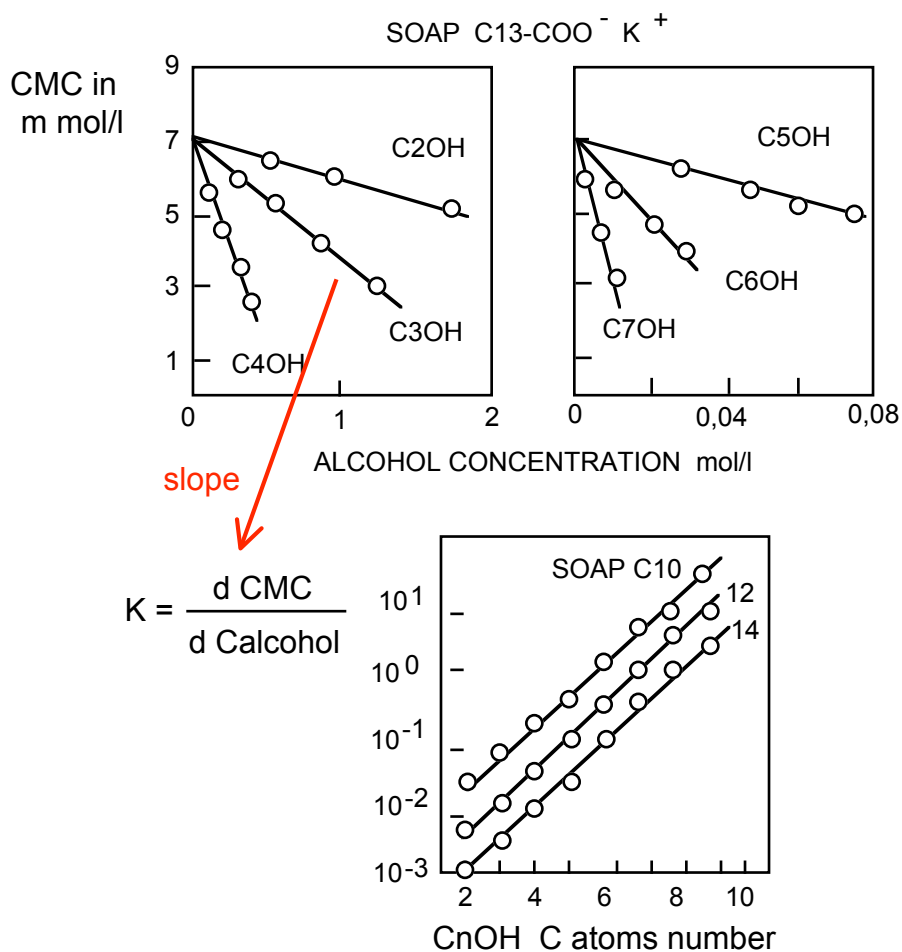


Fig. 7: Critical Micelle Concentration vs. Alcohol Concentration, and the proportionality constant K value after Shinoda (1954)

3.4. EFFECT OF TEMPERATURE.

The effect of temperature on the CMC of ionic surfactants is not straightforward. Singh et al. (1979) for instance, reported that when the temperature is increased, the CMC first decreases, then undergoes through a minimum, and finally increases.

Other authors (Crook, 1963) have observed a similar pattern with nonionic surfactant solutions. This up and down variations always occurs when two opposite effects are competing.

On one hand, an increase in temperature can bring a reduction in the hydration of the surfactant hydrophilic group; this is the well-known desolvation effect which is responsible for the cloud point phenomenon of nonionic surfactant solutions (discussed later on). This effect tends to drive the surfactant out of the aqueous solution and thus it favors the formation of micelles, i.e., it decreases the CMC.

On the other hand, an increase in temperature results in an increasing disorder in the structure of the water phase, in particular the molecules which are located next to the surfactant hydrophobe. The higher the disorder, the less defined the direction of the unfavorable polar/apolar contact, and as a consequence the weaker it becomes. Thus the hydrophobic effect which drives the surfactant molecule "tail" out of the water phase is also reduced when temperature is increased, i.e., the CMC is increased.

4. MODELS FOR MICELLAR SOLUTIONS

4.1. MONOMER-MICELLE EQUILIBRIUM

The dynamic equilibrium between the non-aggregated free surfactant molecules, which are referred to as monomer, and the micelle, which is some kind of association polymer, can be handled by two kinds of model: the phase separation model and the mass action model.

4.1.1. PHASE SEPARATION MODEL

In this phase separation model which was proposed by Shinoda and Hutchinson (1962), the micelle is considered as a pseudo-phase, i.e., the micellization is some kind of "microprecipitation". This model implicitly assumes that the surfactant activity remains constant above the CMC, and that the CMC is the monomer concentration at saturation.

The relationship between the surfactant concentration under the monomer form C_m , its concentration as micelles C_M , and its overall or total concentration C_T is:

$$C_m = C_T \text{ if } C_T < \text{CMC}$$

$$C_m = \text{CMC and } C_M = C_T - C_m \text{ if } C_T > \text{CMC}$$

If this model actually accounts for what happens, then properties which depend upon the surfactant monomer concentration, would remain constant above CMC.

4.1.2. MASS ACTION MODEL

The second model (Phillips, 1955; Vold, 1950) is a typical mass action treatment, in which there is a chemical equilibrium between "n" monomer molecules and a micelle containing "n" surfactant molecules.

A straightforward calculation leads to:

$$K = \frac{C_M a_M}{(C_m a_m)^n}$$

where K is the equilibrium constant, and "a" stands for the activity coefficient associated to the concentration.

Lets take an example to illustrate the phenomenology. Lets take $n = 50$ and let the activity coefficient be unitary for the sake of simplicity.

Lets call C_T^* the total surfactant concentration at which half of the surfactant molecules are found as free monomer while the other half forms micelles.

That is: $2 C_m^* = 2 C_M^* = C_T^*$

Replacing in the equilibrium expression leads to:

$$K = \left(\frac{C_T^*}{2} \right)^{-49} \quad \text{that is} \quad \frac{2 C_M^*}{C_T^*} = \left[\frac{2 C_m^*}{C_T^*} \right]^{+50}$$

Figure 8 shows the corresponding variation of the surfactant monomer concentration (C_m/C_T^*), and the mole percentage of surfactant occurring in micelle (C_M/C_T), as a function of the total surfactant concentration which is expressed as (C_T/C_T^*).

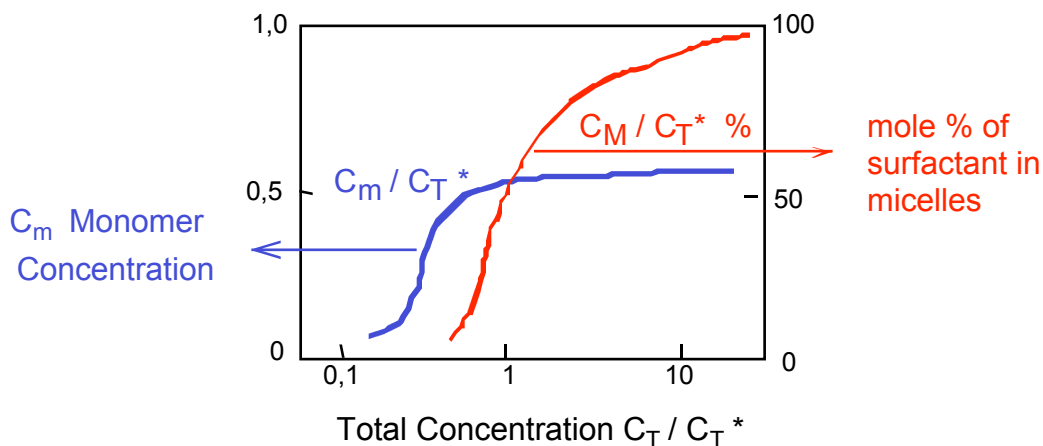


Fig. 8: Surfactant Monomer Concentration and Mole Percentage of Surfactant in Micelles, versus Total Concentration. C_T^* is the total concentration at which $C_m = C_M$.

The overall aspect of the curves indicates that the CMC is probably very close to C_T^* , may be slightly below, since there is essentially no micelle below C_T^* , and since the monomer concentration remains essentially constant above it.

Actually it can be calculated that the total surfactant concentration would have to exceed 10^{15} CMC for the C_m monomer concentration to attain 2 CMC.

This simple example is just illustrative. A real mass action model would have to take into account such complexities as non-unity activity coefficient, a distribution in aggregation number, the association-dissociation of ionic surfactant, and so forth (Mukerjee, 1977).

The mass action model can be handled in analogy with many homopolymerization processes, and can reach a high degree of sophistication. However, there is an unexpected drawback; the more complex the model is, the more numerous the adjustable parameters which are to be fitted or drawn from experience. The point is that since micelles are very elusive objects, there is no accurate data available on the aggregation number distribution or the value of the different equilibrium constants. As a consequence it is not certain that the mass action model can be considered as better than the phase separation model.

Some studies tend to support the mass action model (Elworthy & Mysels, 1966; Mc Bain & Brady, 1943; Huff et al., 1951), whereas others favor the separation model (Hutchinson et al., 1955; Shinoda & Hutchinson, 1962; Trogus, 1977).

At this point the most reasonable statement is to point out that the differences between the two models are often smaller than the actual inaccuracies in the experimental measurements, in particular with the pre-1980 literature in which trace impurities were not monitored; it can be concluded that the two models give very similar results, and the recommendation is then to use the model that best suits the needs of the handled problem.

4.2. CMC OF BINARY MIXTURES

The simplest mixture case deals with a binary mixture of surfactant species called (1) and (2), in which there is an equilibrium between both monomer species and a micelle which contains both surfactants and is called a mixed micelle.

The partitioning of the species of surfactant molecules is not the same in the aqueous phase, i.e., the monomer solution that surrounds the micelle, and inside the micelle (Trogus, 1977).

It has been shown both theoretically and experimentally that the less hydrophilic surfactant species, i.e., the one with the strongest hydrophobic driving force, tends to accumulate preferentially into the micelle.

Mysels and Otter (1961) have found that the molar fraction as monomer (x) and as surfactant in micelle (y) can be related by:

$$\frac{y_1}{y_2} = \left(\frac{\text{CMC}_2}{\text{CMC}_1} \right)^\theta \frac{x_1}{x_2}$$

where CMC_1 and CMC_2 are the CMCs of the pure species, and θ is a parameter which depends upon the influence of the counterions on the CMC.

If for instance a 50/50 binary mixture of dodecyl benzene sulfonate (1) and hexadecyl benzene sulfonate (2) is taken, the experimental data show that CMC_1 is 100 times higher than CMC_2 , and with $\theta = 2$:

$$\frac{y_1}{y_2} = 10^{-4} \frac{x_1}{x_2}$$

A straightforward calculation shows that when the total concentration reaches the mixture CMC, then the monomer phase (i.e., the solution outside the micelles) contains essentially 50 % of each surfactant species, whereas the first micelles to be formed contains 99.99 % of the most hydrophobic surfactant, i.e., hexadecyl benzene sulfonate. This correspond to situation B in figure 9.

On the other hand, when the concentration far exceeds the mixture CMC, say 1000 times or more, then most of the surfactant is contained into the micelles. As a consequence the micellar composition is essentially the same than the overall composition, i.e., 50 % of each surfactant species. In this case, which corresponds to situation A in fig 9, the monomer phase contains 99.99 % of the most hydrophilic surfactant, i.e., dodecyl benzene sulfonate.

Several authors (Lange & Beck, 1973; Mysels & Otter, 1961) have reported that the CMC of a binary mixture can be calculated by a relationship as the following one:

$$CMC_{\text{mixture}} = \frac{CMC_1 CMC_2}{[x_1 CMC_2^\theta + x_2 CMC_1^\theta]^{1/\theta}}$$

This and other similar relationships show that the binary mixture CMC is closer to the CMC of the more hydrophobic surfactant than expected intuitively from the binary mixture composition. This means that the mixture CMC versus Composition curve has its concavity as shown in figure 9.

If the previous binary is considered again (C12 and C16 benzene sulfonates), the CMC of a mixture containing only 0.5 % of hexadecyl benzene sulfonate is 20 times lower than the CMC of the pure dodecyl benzene sulfonate.

CMC_1	= 100	pure (1)
CMC_{mixture}	= 5	99.5 % (1) with 0.5 % (2)
CMC_2	= 1	pure (2)

These data show that a trace of impurity (0.5 %) can affect drastically the value of the CMC. This is the very reason why the published CMC data exhibit a lot of discrepancies, particularly in the cases where no special care has been taken to purify the studied surfactant.

In the case of binary mixtures of interacting surfactants, i.e., anionic and cationic, the mixture CMC can be several orders of magnitude lower than the CMC of any of the base surfactants. This so-called synergetic effect has been studied and modelized (Rosen, 1986; Graciaa, 1989; Abe & Ogino, 1993).

The micelles formed in aqueous solutions of nonionic surfactant mixtures can exhibit large variations in aggregation number and shape. Very elongated micelles can be produced when different surfactants are mixed. Hundreds of papers have been published on this topic in the past decade, particularly in journals such as Journal of Colloid and Interface Science, Journal of Physical Chemistry, and Langmuir. (see Abe and Ogino 1993)

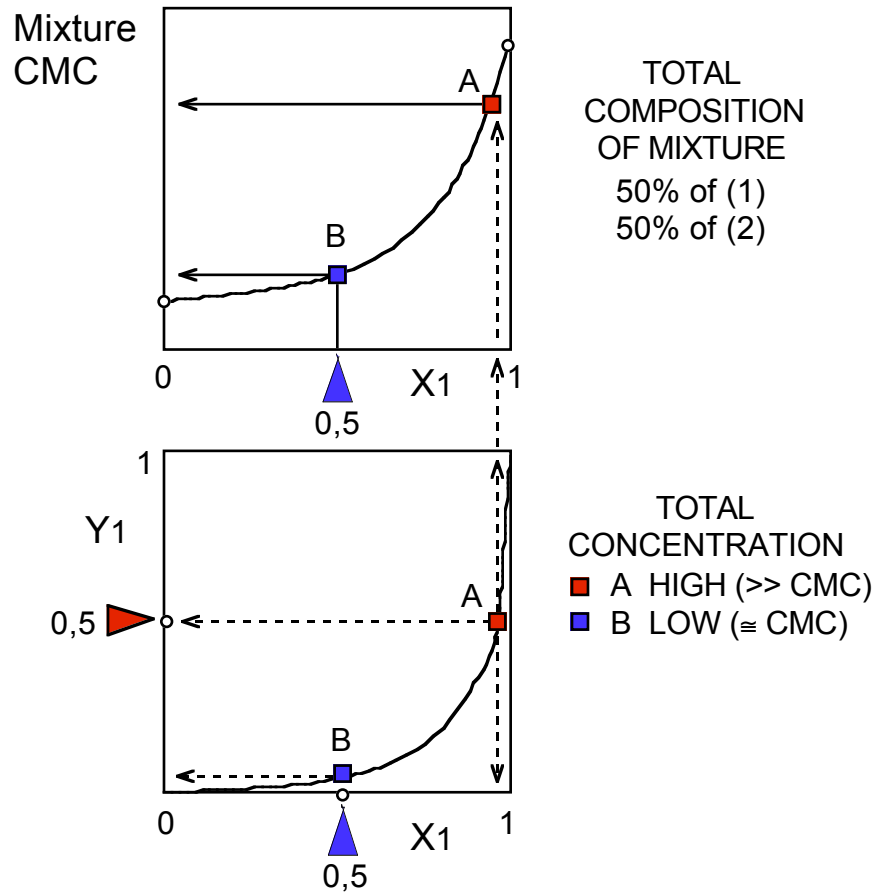


Fig. 9: Binary Mixture CMC, and micelles molar fraction (Y_1) as a function of the molar fraction as monomer (X_1) [Salager, 1977].

5. SOLUBILIZATION IN SURFACTANT SOLUTIONS

5.1. MICELLAR SOLUBILIZATION

When a third component is added to an aqueous surfactant solution, the observed effect depends on the eventual interactions between the added substance molecules and the surfactant micelles.

As a matter of fact the additive solubility in an aqueous surfactant solution below the CMC, is essentially the same as in pure water, unless the additive reacts in some chemical way with the surfactant. On the contrary, the additive solubility is generally enhanced by the presence of surfactant micelles, and in some cases it can attain extreme values.

Most investigators (Shinoda, 1967) make the difference between two principal types of solubilization, depending upon the nature of the added substance.

- a) If the additive is a nonpolar substance, such as an hydrocarbon or an oil phase in the broad sense, the solubilization occurs inside the hydrophobic core of the micelles (see fig. 10-a). If the micelles are able to incorporate a large amount of additive they get swollen until they turn up into microdroplets of oil covered with a surfactant layer. Such structures in the 100 Å range or above, have been called "microemulsion", a misleading terminology as will be discussed later on.
- b) The second type of solubilization deals with amphiphilic additives, such as alcohols. In this case the phenomenon is called co-micellization since it is actually the formation of mixed micelles containing two amphiphilic substances (fig 10-b). It can be said that the alcohol behaves as a co-surfactant, sometimes with some CMC lowering property which can be of great utility in some applications. In some cases the resulting mixed micelles can exhibit a very high solubilization capacity (with respect to a third component such as an oil phase - see case (a)), that often comes from some synergism. It is worth noting that such an occurrence is rather general and that it can happen with many amphiphilic binary, including very different surfactant mixtures (Antón, 1992), as found in many commercial products.

There are some less important types. For instance surfactants with a polyethylene oxide polar group tend to solubilize polar organic components, particularly the aromatic substances, in the folds of long polyether chains, i. e. their polar groups. The same happens when polyether polymers are added to a surfactant solution.

It can be easily verified that all the previously discussed cases correspond to a true micellar solubilization by diluting the aqueous solution. In effect, as the CMC is attained by dilution, the micelles are destroyed and the solubilized material release results in a turbidity or a phase separation.

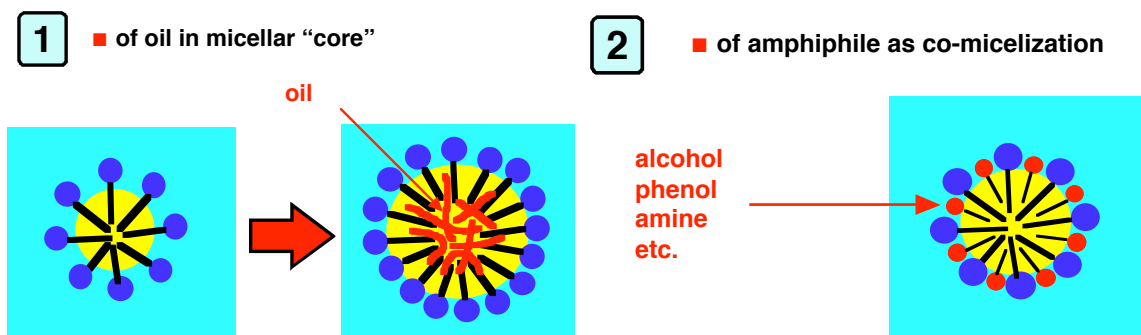


Fig. 10: Two Different Types of Micellar Solubilization.

The mechanism of micellar solubilization can be studied by scores of methods such as ultracentrifugation, X ray diffraction, neutron diffraction, change of properties of additives or probes, etc. (Baumuller et al., 1983; Bostock, 1980; Cazabat et al., 1978, 1980; Danielsson et al., 1982; Datyner, 1978; Dvolaitzky et al., 1978; Sauterey et al., 1978; Schulman et al., 1959; Sjoblom & Friberg, 1978; Taupin et al., 1978)

When the surfactant concentration is high, say several wt % or thousands times the CMC, the micelles get stuck into so-called mesophases, which are known under a

variety of names such as microemulsions, gels, liquid crystal, etc. Such cases are generally dealt with not in the micellar solution scope but rather as the phase behavior of surfactant-oil-water systems.

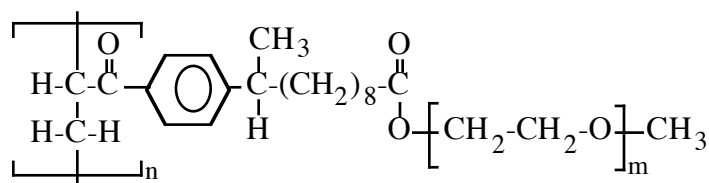
5.2. SURFACTANTS AND MACROMOLECULES

Other solubilization mechanisms have been proposed, which take place in particular and specific cases.

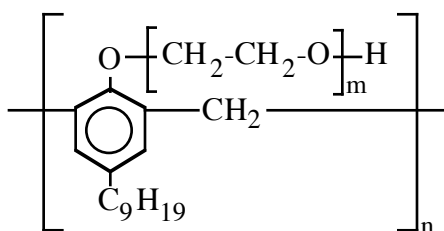
One of them is the case of the so-called poly-surfactants, which are synthesized by grafting hydrophilic groups, such as sulfate or polyether, on the hydrophilic backbone of a macromolecule. The grafting occurs on specific sites such as alcohol, phenol or carboxylic acid functions (see fig. 11).

Some of these substances come from recuperated by-products such as lignin compounds found in the liquid wastes from papermaking, so-called black liquors, or polypeptides from food processing, as well as 100 % man-made resin ethoxylates.

These polysurfactants can exhibit both a very high molecular weight and a good solubility in water, thanks to a proper amount of grafted hydrophilic groups. They are used in many industrial processes such as crude oil emulsion breaker, clay dispersant, protective colloid, emulsion polymerization stabilizer, and so forth.



Poly (methoxy-polyethoxy-p-(acrylphenyl)
undecanoate)



Poly ((m-nonyl)-polyethoxy-phenyl methane)

Fig. 11: Poly-Surfactant Examples.

It is believed that these polysurfactants are able to form intramolecular micelles, even at very low concentration. Such micelles may solubilize other organic molecules in a way similar to ordinary surfactant micelles. Moreover, they can form association complexes with molecules such as cholesterol and lead to interesting pharmaceutical applications.

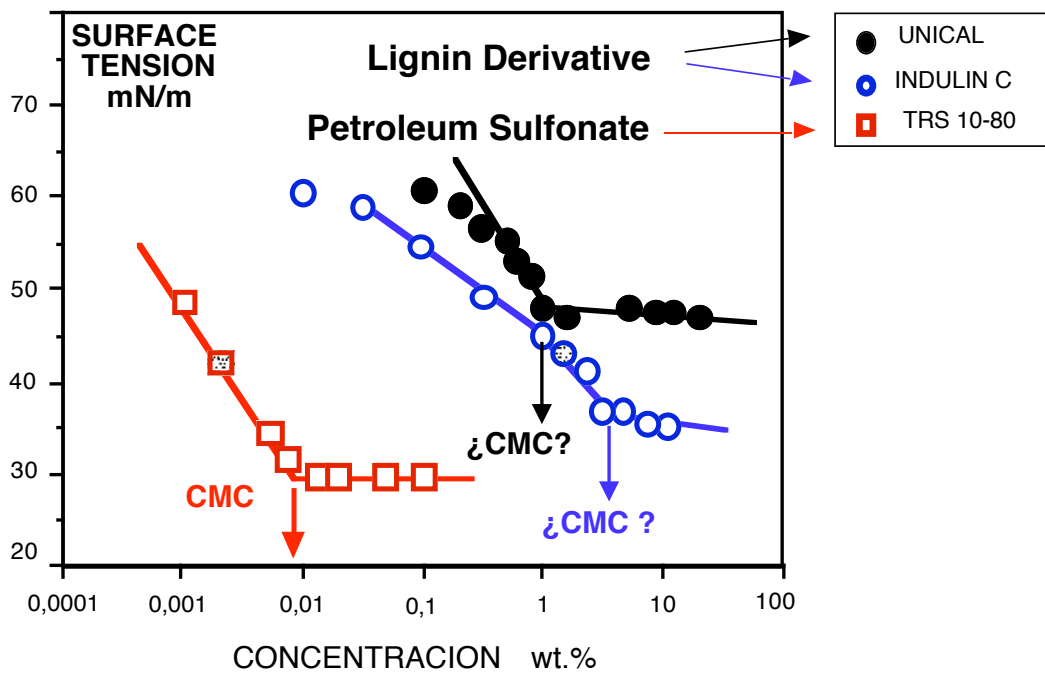


Fig. 12: Poly-Surfactants Tension-Concentration Curves with a pseudo CMC break for lignin derivative surfactants Unical and Indulin - TRS 10-80 is a petroleum sulfonate

It has been showed recently (Rojas, 1994) that some polysurfactants exhibit a tension-concentration curve with a pseudo CMC break (see fig. 12).

There is another mechanism of solubilization which applies to macromolecules with some partial solubility in water (proteins, polyvinyl alcohol polymers) through electrolyte groups. In this case some ionic surfactants molecules can adsorb (by the tail) on the macromolecule to provide extra hydrophilic groups for an enhancement of the solubility. Other arrangements implies the winding of the polymer on the micelle, with the hydrophobic segments going into the core. Figure 13 illustrates this mechanism of solubilization so-called necklace type.

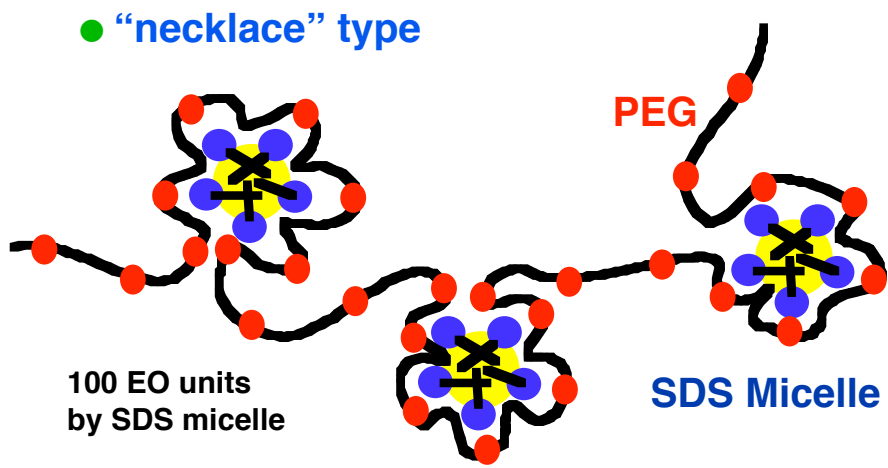


Fig. 13: Mechanism of co-micellization of a surfactant and a polyether.

5.3. MICROEMULSIONS AND HIGH SOLUBILIZATION STRUCTURES

When a micellar solution is taking up solubilized oil, the swollen micelles can reach a size in the 500 - 1000 Å range. In such a case the objects do not look anymore as micelles but rather as oil droplets whose interface is coated by a surfactant layer. This microdispersion was labeled as "W/O or O/W transparent dispersion" by some authors, as "oleopathic hydromicelle" by others, or simply and more practically "soluble oil" (Hoar & Schulman, 1943). Today most authors (Shah et al., 1977; Shinoda & Friberg, 1975; Friberg, 1971) use the word "microemulsion" for such systems.

However it is worth noting that microemulsions are basically different from micellar solution (Prince, 1975, 1977; Shah, 1974). In fact when a microdroplet gets bigger than 100 Å, i.e., much bigger than the surfactant molecule size, then the hydrophobic interactions between the surfactant tails, which were the main driving force to form the micelle, vanish almost completely. This group of authors applies the label microemulsion to liquid-liquid dispersed systems with droplets in the 0.01 - 0.02 µm diameter range.

This controversy is more semantic than scientific. However it was worth mentioning it, so that the reader can be kept aware that the definition may vary from a paper to another.

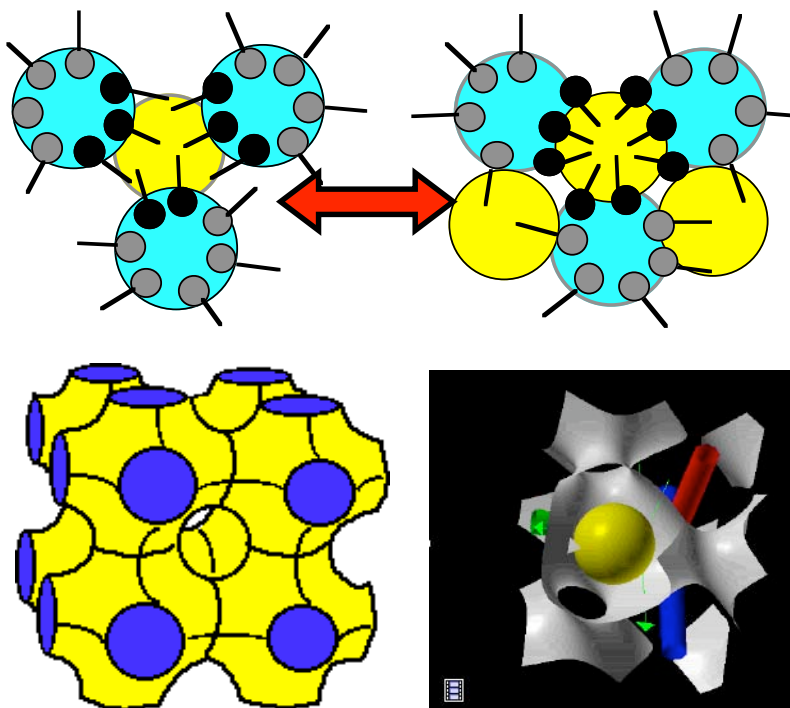


Fig. 14: Microemulsion structures models: Micelles and Inverted Micelles Mixtures, Bicontinuous System (Schwartz Surface).

It is true that a microemulsion is no ordinary micellar solution. The size of the droplets and other arguments provided by Prince (1975) are not the only differences. A microemulsion requires a high surfactant concentration, much higher than the CMC. Furthermore, a microemulsion contains large amounts of both oil and water phases, not only oil or water. Finally, it is now fairly well known that the occurrence of a microemulsion demands a proper hydrophilic-lipophilic balance between a surfactant and its physico-chemical environment (Shinoda & Friberg, 1975; Bourrel & Schechter, 1988). Specifically the interfacial curvature should be close or equal to zero, a condition that result in fancy geometrical surfaces, such as bicontinuous Schwartz's geometry shown in fig. 14. None of these characteristics generally applies to micellar solutions.

On the other hand the reader must be warned that the word microemulsion can be misleading, since a microemulsion is not a emulsion, i.e., a two-phase dispersed system, with very small droplets. Indeed a microemulsion is a monophasic system in which both oil and water are cosolubilized by the surfactant molecules; it is thermodynamically stable, and thus it forms spontaneously because it corresponds to a free energy minimum.

If it were a two-phase system, the spontaneous formation would imply a negative surface tension, a concept which is not generally accepted.

On the other hand the microemulsions behave as monophasic systems, and they can exhibit an interface with both their corresponding oil and water phase. Their "dilution" is a very awkward process, much more complex than in the case of an emulsion (Biais et al., 1981; Graciaa et al., 1976; Gerbacia, 1974; Rosano & Peiser, 1969).

Finally it can be shown that many systems can be found so that a microemulsion with oil microdroplets, can be transformed into a microemulsion with water droplets without macroscopic transition nor visible inversion (Salager, 1980). It is thus not proper to use the denomination O/W or W/O microemulsion, since it is extremely misleading. It is much more convenient to view the microemulsions as complex systems, bearing a very high interfacial area coated by surfactant molecules, which separate in its folds microstructures of both water and oil, as in the bicontinuous system suggested by Scriven (1976, 1977) and drawn in figure 14.

Of course a large interfacial area could be attained with extremely small droplets. However this can not happen here, since small droplets would imply a very high interfacial curvature and thus a very hydrophilic or hydrophobic surfactant, whereas microemulsions occur with well balanced surfactants.

This means that other large area zero curvature systems, are also candidates to the microemulsion label. Actually such lamellar systems in which alternate layers of oil and water are sandwiched in between layers of surfactant molecules are called liquid crystals, because of their rather solid consistency and their optical birefringence. Microemulsions can be viewed as molten liquid crystals, in which the disorder is due to the thermal molecular agitation or the presence of disorder agent such as alcohol or other amphiphile, whose size strongly departs from the surfactant one. Gerbacia and Rosano (1973) have shown the importance of the cosurfactant.

Ruckenstein and Chi (1975) have demonstrated by thermodynamic arguments that a microemulsion can spontaneously form when the mixing entropy offsets other mixing terms.

Recent works by Bourrel and Chambu (1982 a,b) and Graciaa et al. (1993), and Miñana (1994) dealing with the way to improve solubilization have shown that both the surfactant and physicochemical environment take an important part in the formation of

the microemulsion. It can be said that today solubilization can be lifted to values in the 20 g of oil/g of surfactant range, even with polar oils.

Since the knowledge on how to improve solubilization is very recent, the reader must be warned that many interpretations published before 1978 might be erroneous, obsolete or at best misleading.

6. INFLUENCE OF THE TEMPERATURE

6.1. KRAFFT TEMPERATURE (IONIC SURFACTANT)

When the temperature is increased, the solubility of ionic surfactants tends to increase, as it is usually the case for ionic substances, but in a few exceptions (see fig. 15). This trend generally corresponds to a slight increase with temperature (green line). In the case of ionic surfactants, there is a temperature, so called Kraft Temperature, at which the solubility increases drastically. A few degrees above the Kraft temperature the surfactant and water are often miscible in all proportions.

The experimental evidence indicates that the mechanism of solubilization changes at the Kraft temperature. From a monomolecular solubilization below the Kraft temperature, it becomes a micellar solubilization above it.

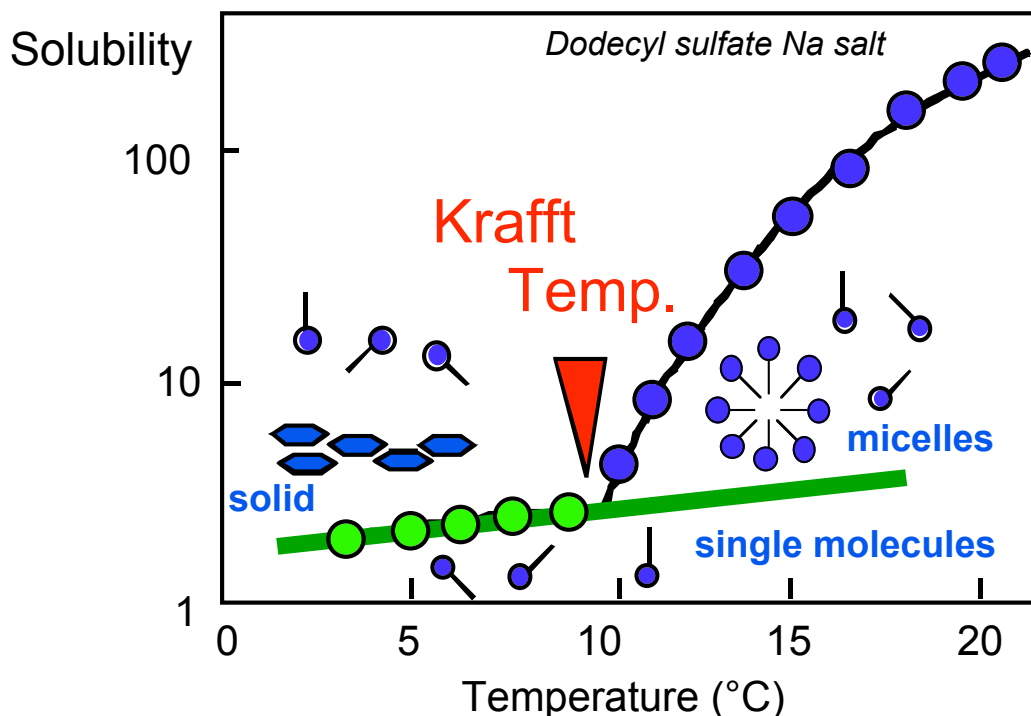


Fig. 15: Surfactant Solubility vs. Temperature; the dashed line indicates the tendency extrapolation in the case that there is no micelle formation.

Thus the Kraft temperature is the point at which the surfactant solubility (as single molecules) reaches the CMC. Below the Kraft temperature the surfactant is not soluble enough, and an excess of surfactant results in a precipitate.

Since the Kraft temperature corresponds to the point where the solubility curve crosses the CMC curve (both as a function of temperature), it depends upon any factor that can affect the CMC, as well as the solubility.

The effect of electrolytes is difficult to ascertain since both the CMC and solubility are reduced by adding this kind of substance. In some cases the main effect is a so-called salting-in, i.e., an increase of solubility which can reach the micellar solubilization, whereas in other cases the result is a so-called salting-out, i.e., a precipitation of a part of the surfactant.

6.2. CLOUD POINT OF NONIONIC SURFACTANT SOLUTIONS.

When a nonionic surfactant solution is slowly heated, it often undergoes through a transition, so-called Cloud Point. The experimental set up is very simple; a nonionic surfactant solution (1 % for instance) is poured into a test tube, which is slowly heated (1 to 2 °C/min) in a water bath. Meanwhile the transparency of the solution is monitored, preferably at 90° from the incident light. At some temperature, so-called Cloud Point, the solution becomes turbid. With some caution the Cloud Point can be determined within a 2° C accuracy. Actually the cloud point depends on the surfactant concentration as it is evident from the phase diagram (Figure 16). However the effect is weak and there is no significant difference in the 1-5 wt% range of surfactant concentration, which is generally used.

If the heating proceeds above the Cloud Point, the small droplets responsible for the turbidity grow up and a phase separation occurs, between an aqueous phase with a very small amount of solubilized surfactant, and a surfactant phase which contains some amounts of water.

The phenomenon can be explained in the following way. When the temperature increases the thermal agitation decreases the polar interaction between the water molecules and the ether links of the nonionic surfactant hydrophilic polyoxyethylene chain.

As a consequence the hydrophilic group is less and less hydrated as the temperature increases. As the solvation decreases, this favors the micelle formation, then the CMC decreases and the aggregation number increases. When the growing micelles attain some critical size (about 500 Å) they start interacting with the light and a Tyndall turbidity becomes apparent. As the temperature increases even further, the micelles reach the point where they are large enough to sedimentate (about 1 µm), and they become droplets that separate as a surfactant phase saturated with water.

Any factor that can facilitate or inhibit the formation of micelles or alterate the aggregation number, is liable to affect the Cloud Point (see table 3).

Added electrolytes tend to reduce the interaction between the surfactant hydrophilic group and the water molecules; as a consequence they produce a CMC decrease, and they make easier the phase separation, which then occurs at a lower temperature.

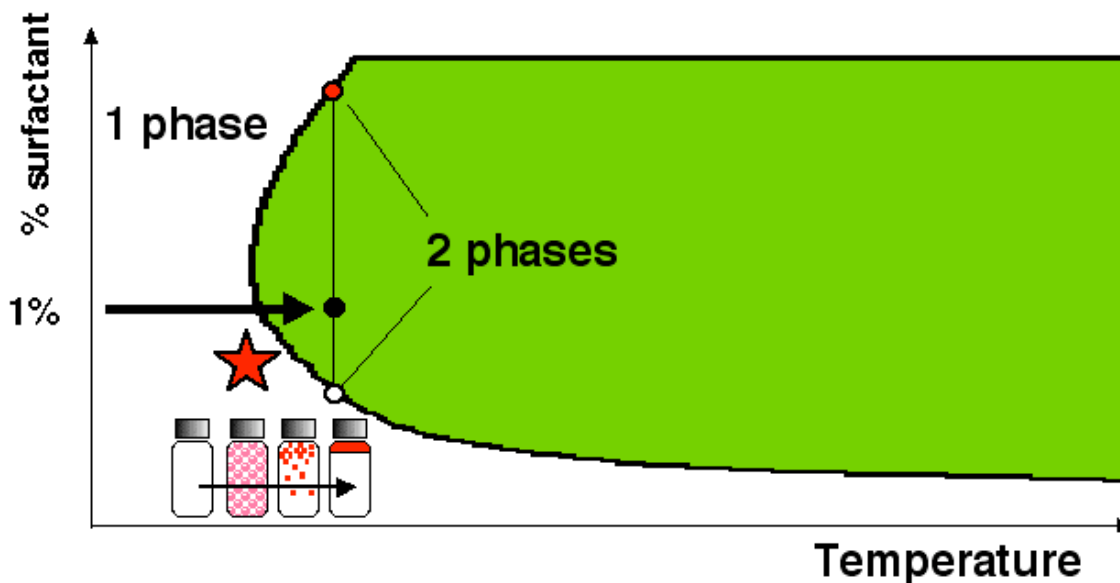


Fig. 16: Cloud Point Temperature on the surfactant-water-temperature phase diagram.

TABLE 3. Cloud Point of some Nonionic Surfactants.

Surfactant	Cloud Point (°C)
Nonyl Phenol 7.4 EO	22
Nonyl Phenol 9.6 EO	60
Nonyl Phenol 14 EO	92
Nonyl Phenol 18 EO	110
Dodecyl Phenol 9 EO	38
Dodecanol 10 EO	97
Nonyl Phenol 9.6 EO (1%, 4%, 6%, 10%)	60, 59.5, 60, 62

0.01. M nonyl phenol solution 15 EO with 1.5 M of electrolyte	
Electrolyte	Cloud Point (°C)
None	100
Na Br	88
NaCl, KCl	70
1/2 Mg Cl ₂	80
1/2 Ca Cl ₂	76

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