

**Amphiphilic Mixtures versus Surfactant Structures with Smooth Polarity Transition  
across Interface to Improve Solubilization Performance**

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**INTRODUCTION and BACKGROUND**

Microemulsions are single phase systems in which a considerable amount of oil and water may be cosolubilized by a limited quantity of amphiphilic substances, i.e. surfactant and cosurfactant, which are structurally organized around or in between the usually incompatible polar and apolar components [1-4]. Compared to diphasic emulsions, microemulsions exhibit unique characteristics which could be from worth to irreplaceable for some applications. [5]

First of all, microemulsions eliminate capillary effects and consequently the trapping forces responsible for keeping 70% of the original oil in place in a petroleum reservoir after secondary recovery [6]. Because of the current market price, microemulsion-based enhanced oil recovery methods are likely to come back strongly in the very near future [7]. For the same reasons microemulsions are used in cleaning and remediation techniques in porous media, particularly to clean polluted soils or to unplug the neighborhood of petroleum and gas wells and increase the return permeability, and thus improve the output sometimes in an impressive extent. They have been recently as the basis of a new technology for cleaning “pill” systems in well treatment.

Secondly. Microemulsions are able to replace organic solvents, particularly in fat and oil extraction methods and in (no-stirring) detergency [8-11], with an extra bonus when both polar and nonpolar substances must be dissolved at the same time, like in leather cleaning [7] or for (the still unused but potentially attractive) medical procedures such as in-situ solubilization of bladder stone, or oily drug injection directly in the blood stream.

Finally, microemulsions are handy precursors for the preparation of monodispersed nanoemulsions by low-energy techniques for score of applications [12-14].

The main issue in the use of microemulsions is the required proportion of surfactant and cosurfactant to reach the single phase behavior, which has been typically high, e. g. 20%, too high in view of cost and toxicity issues in most instances. Hence, the attainment of microemulsion with less surfactant is paramount for the spread-out use of microemulsions. This paper analyses the physicochemical approaches which have resulted in a steady improvement in solubilization up to the current encouraging situation, which is mature enough to forecast a rapid development.

**(1) MAXIMUM SOLUBILIZATION AT OPTIMUM FORMULATION**

Half a century ago Winsor presented a theoretical analysis [15] that qualitatively related the phase behavior of surfactant-oil-water systems with the physicochemical formulation. It introduced the ratio R of the molecular interactions of the adsorbed surfactant at interface with the oil ( $A_{co}$ ) and water ( $A_{cw}$ ) molecules, per unit interface area.

$$R = A_{co}/A_{cw}$$

Winsor extensive work showed that at  $R = 1$ , i.e. when the adsorbed surfactant molecule exhibits exactly the same interaction with neighboring oil and water molecules, then a three-phase behavior (so-called Winsor III type) is exhibited at low to moderate surfactant concentration. It consists in a bicontinuous microemulsion with equal amounts of excess oil and water phases. When enough surfactant is present in the system, the microemulsion solubilizes all the oil and water and a monophasic so-called Winsor IV type system is attained.

This three-phase (or corresponding single-phase) behavior occurrence corresponds to the so-called optimum formulation, whose name comes from the fact that it was the situation in which the interfacial tension is extremely low, so that the crude oil could be displaced from the porous medium in an enhanced oil recovery process. The inverse relationship between interfacial tension and solubilization was demonstrated on a simple model [16] and corroborated experimentally. Hence, a higher solubilization is equivalent to a lower tension as far as applications are concerned.

Optimum formulation was linked with a zero natural curvature, which could be matched either by a lamellar liquid crystal or a bicontinuous microemulsion with averaged zero curvature as in Schwartz surface [17-18]. In most cases such a microemulsion may be considered as a lamellar liquid crystal in which enough disorder has been incorporated, either by a thermal or geometric effect, e. g. by mixing differently sized surfactants, or surfactants and cosurfactants such as alcohols. Winsor showed that when a formulation scan is carried out, the solubilization passes at a maximum at optimum formulation. Hence, optimum formulation, i.e., a physicochemical situation in which  $R = 1$  or equivalent criteria in terms of PIT [19], SAD or HLD [20-22], is the *first* condition to optimize solubilization (see figure 1-a). More detailed information on phase behavior and optimum formulation is available in the literature. [1, 3-4, 20-22].

In what follows, the solubilization is expressed as the value of the solubilization parameter at optimum formulation ( $SP^*$ ) which is the amount of oil or water (which are equal) in the microemulsion per unit mass of surfactant in the microemulsion. Solubilization parameters are usually expressed in relative amounts, i.e., ml/ml, ml/g or g/g units. A  $SP^* = 9.5$  g/g means that 1 gram of surfactant is able to cosolubilize 9.5 grams of oil and 9.5 grams of water; in such a case, the microemulsion is attained with 5 wt.% of surfactant in a system with equal amounts of oil and water, which is by the way considered as a good solubilization. In other terms, it means that the polyphasic region in a Winsor III type diagram exhibits a height of only 5 % at optimum formulation.

## (2) WINSOR PREMISE AND CONSEQUENCES

The optimum formulation condition  $R = 1$  (i.e., when numerator  $N =$  denominator  $D$ ) may be attained in many different ways, for instance as  $R = 2/2$  or  $R = 5/5$ , and one may wonder what are the differences as far as the solubilization is concerned. Winsor stated that solubilization should be improved when both  $N$  and  $D$  are increased, i.e., when interactions by unit interface area are increased on both sides of interfaces (and kept equal). This premise was systematically confirmed 20 years later [1, 23-24] by studying double changes in formulation which started at a  $R = 1$  case and ended at another  $R = 1$  case, but with other numerator and denominator values.

For instance it was shown that with system containing ethoxylated alkylphenols an increase in both the alkyl tail length and the number of ethyleneoxide groups (EON), i. e., a concomitant increase in both numerator and denominator of  $R$  (so that it remained unity), was resulting in an improved solubilization [25]. The same thing was reported with two surfactants  $C_{12}OSO_3Na$  and  $C_{18}CH(COONa)NHCONH_3$ , the second one being “bigger or bulkier” on both sides of interface, but with the same balanced interactions.

The **second** stipulation to improve solubilization is thus to increase the size of the head and tail groups of the surfactant molecule so that it reaches further in both the oil and water sides of the interface (see arrows in figure 1-b). This is essentially equivalent to increase the thickness of the interfacial zone through which the polarity changes from polar (water) to apolar (oil). The increase in both the polar and apolar group is however restricted by solubility problems, particularly with linear alkyl group which are limited to C16-C18, beyond which precipitation is likely to happen.

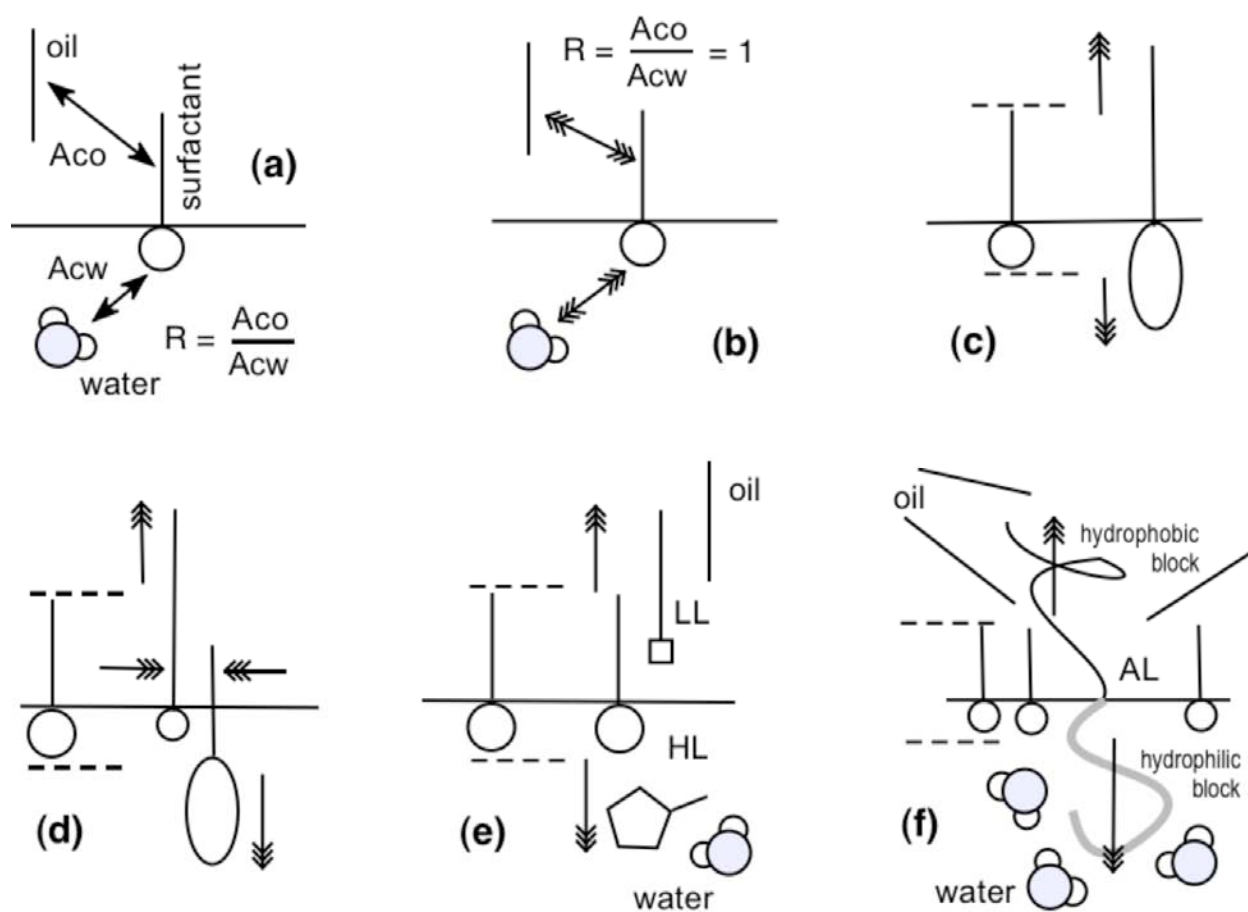


Figure 1. (a) Interactions between the adsorbed surfactant and the neighboring oil and water molecules. (b) maximum solubilization in a formulation scan is attained at optimum formulation when  $R = 1$ . (c) Increasing the interactions on both sides increases solubilization. (d) Mixing hydrophilic and lipophilic species increases the surfactant reach in both phases, produces a denser packing and increases solubilization. (e) Lipophilic and hydrophilic linkers (LL and HL respectively) increase the solubilization. (f) Amphiphilic linkers are short block polymers that increase interactions with both oil and water.

### (3) MIXING DIFFERENT AMPHIPHILES CAN INCREASE THE INTERFACIAL ZONE THICKNESS AND PACKING

The precipitation problem may be circumvented by using not a single amphiphilic molecule but several molecules which are on the first hand individually solubles, and on the other hand able to produce an extended reach on both sides of the interface. This may be attained by mixing a hydrophilic surfactant with a lipophilic one, the first one increasing the reach on the water side of the interface and the other doing the same on the oil side. (Figure 1-c)

This arrangement also allows a better packing at the interface because it reduces direct electrostatic repulsion between charged head groups or steric repulsion between nonionic groups, and thus result in a better interaction per unit surface area because each surfactant molecule occupies less area at interface [26-27].

Characteristics which tend to decrease the packing such as double bond or branching in the tail group of the surfactant, tend to decrease solubilization [28]. Alcohol cosurfactants are often used to prevent the formation of liquid crystalline mesophase, but they tend to pull apart the surfactant molecules adsorbed at interface; as a result, they reduce the interactions of the amphiphile mixture with both phases, and consequently the solubilization. The alcohol cosurfactant with the worse solubilization effect is the sec-butanol, which is the more likely to adsorb at oil-water interface, and whose branching increase its interfacial occupancy, thus reducing even more the surfactant packing [25]. figure 1-d. alcohol reduces the packing

The *third* thing to do to enhance solubilization is thus to make the packing denser with mixtures of surfactants with different affinities for the oil and water, so that they place themselves in some kind of stacked position with resulting closer packing and increased transition zone thickness. On the contrary the use of equal surfactant molecules, the insertion of short alcohol molecules, the presence of double bond or branching in the surfactant tail tend to reduce the packing, and to shrink the transition zone, thus resulting in poorer solubilization.

Mixing different surfactants is often what happens spontaneously when a commercial polyethoxylated nonionic surfactant or a mixture of two of them is used. Because of the mechanism of the polycondensation of ethylene oxide, these nonionics contains widely different oligomers, whose mixtures exhibit enough disorder to avoid the formation of liquid crystals at optimum formulation, and display the extended reach and increased packing features favorable to enhanced solubilization. However, there is again a limit to the mixing of different surfactants, which has to do with the so-called fractionation effect which has been studied in details for polyethoxylated nonionics [29-30]. When a too lipophilic surfactant are present in a mixture, e.g., a nonylphenol with 2 EO groups, it exhibits a very strong tendency to migrate into the oil phase where its critical micelle concentration is quite high. As a consequence, a large portion of this surfactant is no longer available to adsorb at interface, and a higher amount of this surfactant is required to make up the proper interfacial mixture. The same preferential migration takes place with sulfonated anionics, but this time with a strong fractionation of the very hydrophilic disulfonates into the water phase. Consequently, mixing very different surfactants may lead to an improved solubilization as far as the surfactant necessary to produce the microemulsion is concerned, but it also tend to drive a large portion of the surfactant into one of the phase, where it is lost as far as the solubilization effect is concerned. The improvement might then turned out to be associated with an hidden extra cost.

#### (4) LINKER EFFECT.

When a very lipophilic amphiphile, e.g., dodecanol, is added to a system, it does not adsorb at interface in the sense that it participates to the interfacial mixture with a surfactant. Instead, it is found to stay in the oil phase, but with a strong tendency to accumulate close to the interface because of Van der Waals long range forces. This means that this slightly “polar” oil tends to be segregated close to the interface [31]. This phenomenon is easily demonstrated by measuring the interfacial tension of a mixture of polar oil and non-polar oil against water (with no surfactant) as a function of the oil mixture content. It is found that when the oil composition is 50 % of each, the interfacial tension is essentially equal to the tension against the most polar oil, thus indicating the accumulation of this later close to the interface.

This kind of very lipophilic amphiphile that segregates in the oil phase close to interface was called lipophilic linker [26, 32], and it was shown to increase solubilization by extending the reach of the surfactant hydrophobic tail in the oil phase as indicated in figure 1-e. It is worth noting that this effects takes place in the oil phase, thus, that the lipophilic linker does not play a role in the attainment of the  $R = 1$  condition at interface. Moreover, it does not alter the packing at interface.

The segregation of the lipophilic linker in a oil layer close to interface [31] is actually a *forth* way to increase the transition zone thickness by making the oil layer close to interface slightly polar. This lipophilic linker effect was found to take place in quite a general way with many slightly polar oil phases and its optimized length was analyzed [33].

A few years later the hydrophilic linker effect was proposed to take place in the water phase, close to interface [34] although with less effect on solubilization. Then, the concomitant use of both lipophilic and hydrophilic linkers was found to result in improved solubilization [35]. Figure 2-e illustrates clearly that the lipophilic and hydrophilic linker layers on both sides of interface, both contribute to build up the thickness of the transition zone. It actually means that in such a case, the fractionation of the amphiphilic (linker) species in oil or water could be favorable to improve solubilization; this happens when the fractionated product is so unbalanced that it does not adsorb at interface at all, but is different enough from the rest of the phase where it migrates, to segregate close to the interface. However, it is worth noting that fractionation is inherently unfavorable because some amphiphilic material is definitely no longer at interface.

A few years after the introduction of the lipophilic linker approach, the addition of short block polymers [36-37], sometimes referred to as amphiphilic linkers [cosima book], was found to increase the solubilization according to the effect indicated in figure 1-f, which is like a soldered lipophilic/hydrophilic linker, which boosts the reach of the interfacial amphiphilic mixture into both oil and water phases.

However, this kind of approach is limited by the potential polymer precipitation. Actually, it should be short enough, i. e. at most 3-4 times the surfactant size, and secondly its concentration should be low enough, so that its proportion at interface is low compared with surfactants.

In any case, it may be said that all kinds of linker molecules tend to extend the thickness of the interfacial zone over which the transition from polar to apolar phase takes place.

The drawback of this approach is that there is sometimes a need to an large excess of some substance to have enough of it at the right place. This is called fractionation effect and it is a consequence of the fact that very different molecules are likely to move where they find the better physicochemical environment.

## (5) EXTENDED SURFACTANT

The next step after realizing why the linker effects were effective in enhancing solubilization, was to design the so-called extended surfactant structure, whose principles were to cummulate the advantages of the previously discussed features without the drawbacks.

First, the new structure ought to be a single molecule that is compelled to go and stay at interface (like the amphiphilic linker) so that fractionation cannot take place and no surfactant is lost into the oil or water. Second, the molecule must be longer than a conventional surfactant to exhibit an increased reach on both sides of the interface, but not too large to avoid precipitation as when the apolar group is too long. It seems better to make it more extended on the apolar side to mimic the improved solubilization efficiency attained with the lipophilic linker effect. Consequently, a somehow polar lipophilic spacer (polypropyleneoxide —PPO— chain) is placed between the conventional hydrophilic and lipophilic groups (see figure 3) [38-40].

Because this spacer is polar to a certain extent and has some branching, it is less likely to induce precipitation like comparably sized n-alkyl groups. This spacer is nevertheless globally lipophilic, hence, it drives the lipophilic (hydrocarbon) group further away from interface. The lipophilic groups are generally n-alkyl chains, but they could be also branched alkyl chains which are both more lipophilic (to interact with oil) and more water soluble (to reduce the precipitation inconvenience). The typical extended surfactant type is the alkyl polypropyleneoxide sulfate shown in figure 2-a which is representative of the first and only generation available on a semi-commercial way. Some have one or two ethyleneoxide groups between the polypropylene chain and the sulfate group to facilitate the sulfatation reaction and eventually contribute as a hydrophilic linker feature (fig.2-b), and other have a linear alkyl chain attached close to the center to produce some branching without a slow biodegradability penalty (fig 2-c)

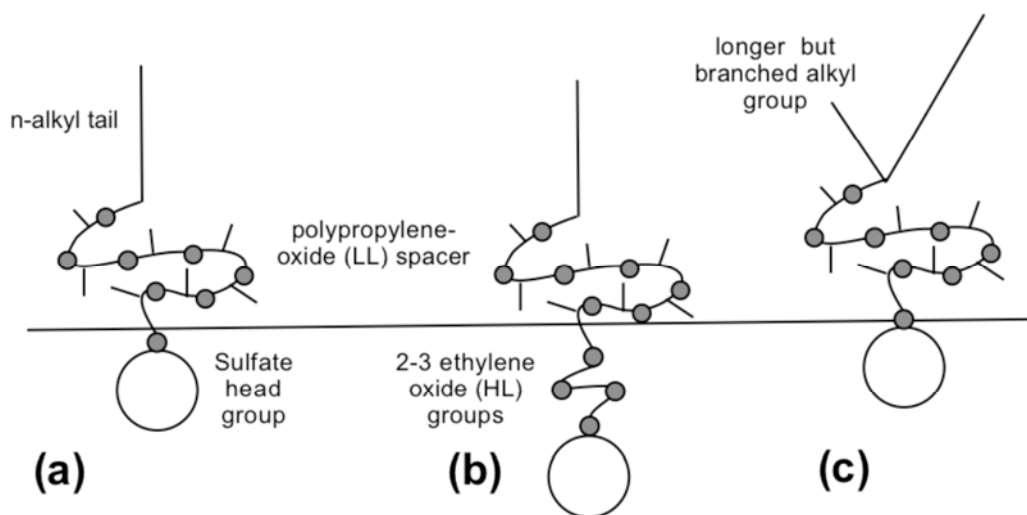


Fig. 2 Extended surfactants

As a matter of fact, extended surfactants may be viewed as intramolecular mixtures with some of the favorable features attributed to mixing, without the inconvenience of fractionation inherently associated with the presence of different molecules.

The principle of extended surfactant is a *fifth* manner (and probably the best one), to increase the thickness of the transition zone, which could become quite extensive when 15 propylene-oxide groups are placed in the spacer arm. Recent research has shown that extended surfactant structure works with differently head groups such as galactose, xylitol, carboxylate, polyethylene-oxide and combinations [40-44], with linear and branched tail groups and with longer or shorter spacer groups.

Some general trends have been found, although not always published in the open literature, which may be summed up as follows.

Exploratory studies indicate that Winsor's premise concerning the relationship between the concomitant increased of head and tail groups to produce increased solubilization seems to apply to extended surfactants with the corresponding advantages over the conventional ones (no precipitation, no fractionation, mixture effect). For instance an increase in alkyl tail from C12 to C18 properly compensated on the head group (for instance by a change in salinity) almost duplicate the solubilization of soya oil by an alkyl-PPO-sulfate (see figure 3).

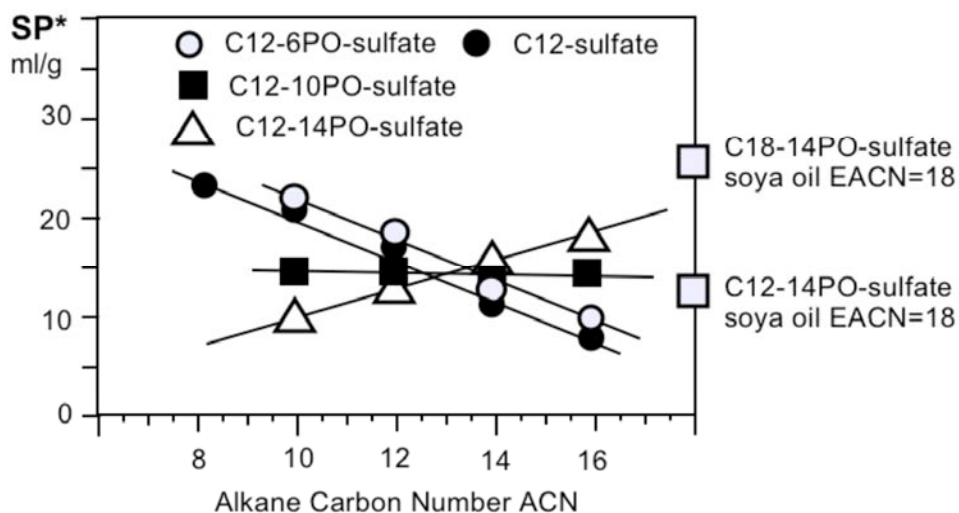


Fig. 3. Solubilization parameter at optimum formulation  $SP^*$  for different extended surfactants with n-alkane, unless otherwise indicated.

The lipophilic linker mimic obtained with polypropylene-oxide spacer arm is definitely a contribution to the lipophilic part of the molecule, with decreasing optimum formulation and decreasing critical micelle concentration as the number of propyleneoxide units (PON) increases.

Alkyl-polypropylene-oxide-sulfates have both anionic and nonionic characteristics. The effect of the salinity on formulation decreases as the length of the polypropyleneoxide chain increases. This indicates that the polypropylene-oxide spacer has some effect on the polar side of interface, in spite of being part of the lipophilic tail.

Solubilization changes with the type of oil as with conventional surfactants [45], but quite differently as indicated by figure 3. For short spacers the solubilization decreases as the n-alkane size (referred to as the alkane carbon number ACN) increases, but for long spacers (14PO indicated with triangle symbols) it increases with ACN, a trend opposite to the general rule [45], and a very fortunate occurrence for some applications. Extended surfactants have been found to produce microemulsions with polar oils like ethyl-oleate, di and triglycerides [38-39]. The reported values (see table 1) indicate a high performance in the solubilization of these oils, when

compared to the results attained by conventional surfactants. As a consequence of the inverse relationship [16] between solubilization and tension, extended surfactants are producing ultralow interfacial tensions with polar oils [46].

Extended surfactants mix with other (conventional) surfactants according to the usual linear mixing rules [47-48] as far as formulation is concerned, and with additive solubilization performance in a first approximation, in particular when the conventional surfactant does not exhibit a significant solubilization if used alone.

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