



Solubilization of polar oils with extended surfactants[☆]

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Abstract

Starting with previous results showing that the solubilization of oil and water in a microemulsion can be improved by the introduction of an additive, i.e. a so-called lipophilic linker, a new surfactant type that mimics the additive effect is tested. The so-called extended surfactant has a poly-propylene oxide chain inserted in between the conventional alkyl and ether sulfate groups. These surfactants exhibit a critical micelle concentration and a cloud point that changes with the number of propylene oxide groups per molecule (ranging from 6 to 14). They show three-phase behavior at optimum formulation, with hexadecane, ethyl oleate, and, as reported for the first time, with triglyceride oils, such as soya oil. Outstanding values of the optimum solubilization parameter are reached (in the 10-30 ml g range).

Keywords: Extended surfactants; Polar oils; Solubilization

1. Introduction

By definition, the oil and water phases of a surfactant-oil-water (SOW) system are immiscible, and the role of the amphiphile is to reduce the miscibility gap, until the three components are eventually cosolubilized into a so-called microemulsion.

Pioneering work by Winsor [1] established that the phase behavior of SOW systems depended not upon specific values of the formulation variables, but upon the physicochemical situation at the interface, which he described in terms of the ratio of the interaction energy between the surfactant and the oil phase on one side, and the interaction energy between the surfactant and the water

phase on the other side. This is the so-called Winsor's R ratio, which has since been used as the best pedagogical way to understand the concept of physicochemical formulation at an interface [2].

In the 1970s, the Enhanced Oil Recovery research drive boosted knowledge concerning the phase behavior of SOW systems [3-5], and the concept of a generalized formulation was expressed in terms of numerical relationships between practical formulation variables such as brine salinity, oil alkane carbon number, surfactant average number of ethylene oxide groups per molecule (EON), temperature, etc.

The so-called empirical correlations [6,7] for the attainment of an optimum formulation that produce a low interfacial tension were esta-

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blished for both anionic and nonionic surfactants. Simultaneous works showed that the minimum interfacial tension was associated with a maximum solubilization of oil and water in the microemulsion phase [8,9]. In Winsor's terminology, maximum solubilization corresponded to $R = 1$. The fundamental premise [1,2] to be used to understand the solubilization phenomena was that the extent of solubilization, i.e. the amount of both water and oil co-solubilized in the middle phase microemulsion, was directly related to the R ratio numerator (or denominator, since they are equal under optimum conditions).

Over the past 15 years, research has progressed on several fronts. First, the empirical correlations to attain an optimum formulation, from which the maximum solubilization can be found, have been interpreted in terms of thermodynamic arguments [10,11]. It was shown that the empirical correlations traduce numerically the free energy contributions of the different variables to the overall energy summation; in other words, the generalized formulation is written as a difference (which is optimally zero) instead of a ratio in Winsor's R theory (which is optimally unity).

Second, the scope and range of the empirical correlations have been extended to other surfactants, oil phases, electrolytes, etc., as well as mixtures of them and even other polar protic phases [12]. The results have been discussed in terms of Winsor's R theory [13-20], as well as according to the ratio of the effective cross-sectional areas of the tail and head groups of the surfactant and its relationship with the surfactant film bending properties, and the viscoelastic properties of surfactant monolayers [21-32].

Third, extensive experimental evidence gathered by Bourrel and other authors has shown that Winsor's assumption that the solubilization was directly linked to the value of the numerator or denominator of the R ratio under optimum conditions was correct [33,34]. A review of the work carried out before 1987 has been published [2], and explains different ways to improve solubilization. At equal interfacial coverage, the best way to enhance the interactions on both sides of the interface is to use a surfactant with both a larger hydrocarbon

"tail" and a larger hydrophilic group; the word "larger" actually means that a greater interaction results from it, as expected from a simple length increase. There is neither a theoretical nor an experimental problem on the water side of the interface, since the EON and the salinity formulation variables allow precise monitoring of what is happening in nonionic and ionic surfactant systems, respectively. The problem is on the oil side, i.e. with the surfactant lipophilic "tail". In effect, a larger interaction between this lipophilic group and the oil phase is expected to result from an increase in length and/or an increase in linearity (if it is branched). However, such an increase has two direct effects on the system. On the one hand, longer tail surfactants are less soluble in water, and at some point the solubility becomes lower than the critical micelle concentration (CMC) and the so-called Kraft point of the ionic surfactant is reached [35]; if no micelle can form, no microemulsion can form, and the surfactant actually precipitates. On the other hand, a longer tail tends to produce more organized solubilization structures, so-called mesophases or liquid crystals, rather than microemulsions. The melting of the liquid crystals can be achieved without changing the temperature by adding short chain alcohols, but this results in general in a decrease in solubilization, since the alcohol molecules adsorbed at the interface displace the surfactant molecules, and reduce the overall number of interactions per unit area [2].

As a matter of fact, the solubilization at optimum formulation with conventional surfactants has been found to reach values as high as 30 ml ml⁻¹ or ml g⁻¹ with short alkanes and may be 10 ml g⁻¹ with hexadecane, while it is essentially less than 4 ml g⁻¹ with monochain polar oils, and much less with triglyceride oils. The solubilization of polar oils remained an unsolved problem until the recent introduction of the lipophilic linker additive.

2. Lipophilic linker and extended surfactant

In order to overcome the dilemma between a longer tail that increases the solubilization and lesser solubility of the surfactant, which places an upper limit at say 20 methylene groups per molecule, the so-called lipophilic linker feature

was proposed [36,37]. This consists of forming an apparently longer tail surfactant at the interface by linking the surfactant and a lipophilic additive that is introduced separately into the system, and thus does not affect the surfactant solubility. In order to avoid gel-like structures, a proper but not-so-good fit is found between the surfactant tail and the additive, for instance by mixing linear and branched chains.

Fig. 1 indicates the role of the lipophilic linker, which is a slightly polar oil, such as a long-chain alcohol (more than 8 carbon atoms), or phenol. It cannot be considered as a conventional co-surfactant component of the interfacial layer, since it was found to perform better when it adsorbed less at the interface [37]. It seems to be located in the oil layer adjacent to the interfacial layer, as evidenced in recent oil segregation studies [38]. As a consequence of their polar group, the lipophilic linker molecules are likely to have an average orientation perpendicular to the interface. This preferred orientation tends to organize the oil layers located next to the interface (as illustrated in Fig. 1), thus providing extra interactions with the surfactant molecules. The lipophilic linker is then some kind of intermediate between the surfactant layer (adsorbed at the interface) and the bulk oil phase, where molecules are oriented at random.

Fig. 2 shows the multiple role of n-alkanols, depending upon their chain length. Short alcohols (up to C3) tend to adsorb more and more at the interface, with a maximum absorption found between propyl and butyl alcohols; as a

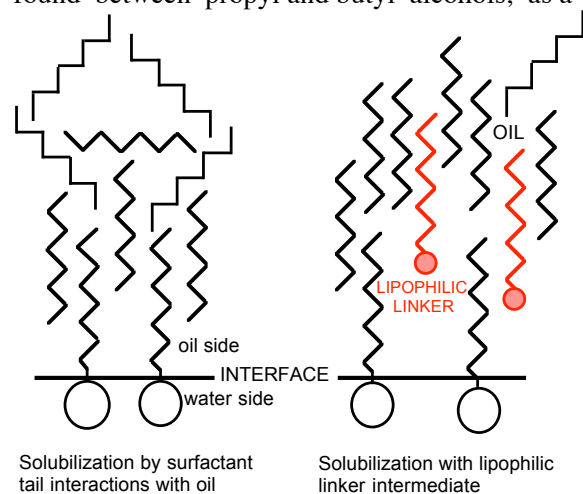


Fig. 1. Illustration of the role of the lipophilic linker in improving solubilization

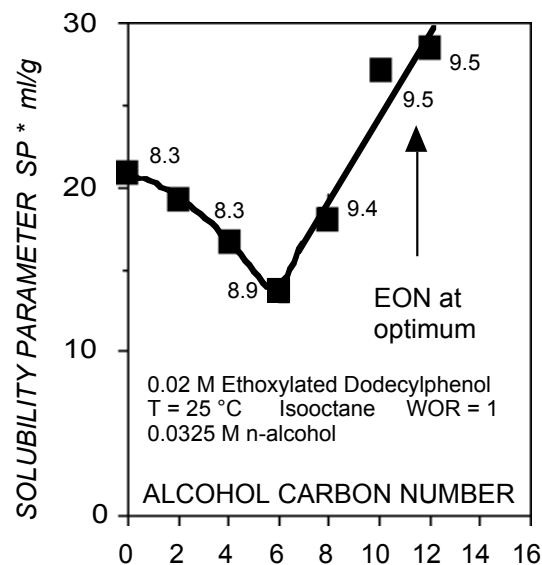


Fig. 2. Variation in optimum solubility parameter SP* for dodecyl phenol ethoxylates in the presence of different n-alkanols.

consequence, they pull apart the surfactant molecules and a lesser interaction per unit area results, as deduced from the decreasing solubilization parameter. As the chain length increases (C4-C6), the alcohol is known to play the role of co-surfactant, i.e. it changes the interfacial hydrophile-lipophile balance to a more lipophilic one. In order to compensate for this extra lipophilicity, the hydrophilic group has to be increased (from 8.3 to 8.9 and up to 9.4) to keep the optimum formulation. This results in a better interaction with the oil phase, which is, however, limited at first by the previous effect (so that a minimum occurs). Finally, from octanol up, the alcohol adsorbs less and less at the interface, and its role is expected to vanish eventually. This is not the situation observed in Fig. 2; indeed, the increase in alcohol chain length considerably increases the solubilization, but without affecting the formulation, since the EON remains at the same value. This means that the balance of affinities is not changed at interface, according to Winsor. As a consequence, the lipophilic linker role is out of the scope of Winsor's R, since the increase in interaction on the oil side is not compensated on the water side. This increase is believed to be due to the extension of the

surfactant interaction with oil through the intermediary role of the lipophilic linker.

Following this finding, the lipophilic linker additive was seen as a substance able to produce a layer of intermediate polarity and of some thickness in the oil phase located in the neighborhood of the interface. It was then conjectured that such an intermediate polarity region could be incorporated intramolecularly, i.e. inside the surfactant molecule, without precipitation. This idea gave birth to the so-called extended surfactants, which contain an intermediate polarity part located between the conventional hydrophile and lipophile groups.

Fig. 3 indicates the average molecular formulae of the used extended surfactants kindly prepared for us by Seppic, a French surfactant manufacturer. They can be defined as alkyl polypropylene oxide ether sulfates. The polypropylene oxide chain length ranges from 6 to 14 propylene oxide units, and is defined by the average number of units, symbolized as propylene oxide number (PON). Because of the Markovnikov rule, the propylene oxide chain is branched, and a 10 PON intermediate zone is likely to exhibit a thickness in the 30-40 Å range, which is quite an "extension" compared to the dodecyl chain length (say 15-25 Å). Two ethylene oxide groups are inserted to facilitate the sulfatation reaction which cannot be carried out directly on the propylene oxide end group because of steric hindrance.

3. Chemicals and experimental procedures

The extended surfactants were used as received. Hexadecane was a pure grade reagent from Fluka, and ethyl oleate was a pharmaceu-

$\text{C}_{12}\text{H}_{25} - (\text{PO})_n - (\text{EO})_2 - \text{O} - \text{SO}_3^- \text{Na}^+$	
SURFACTANT LABEL	n
712 SN	6
713 SN	10
714 SN	14

Fig. 3. Characteristics of used extended surfactants.

tical grade product made by Laserson-Sabetay; Mygliol 812 was a synthetic triglyceride oil containing 75% octanoic and 25% decanoic acids made by Hüls; soya oil was provided by Touzart and Matignon. Sodium chloride was an analytical reagent from Merck.

The CMC in water was determined at 25°C from the break point in the surface tension versus concentration semi-log plot. A Fisher De Nouy tensiometer was used for carrying out the tension measurements.

The cloud point was determined by the visual observation of the transition from clear to turbid on heating (1 - 2°C min⁻¹ a 10 wt.% surfactant solution sample).

Phase behavior experiments were carried out according to a standard procedure [2] by scanning a single formulation variable, i.e. salinity of the aqueous phase, surfactant PON, etc. The optimum formulation of the scan is denoted by an asterisk, e.g. S* (where the salinity is expressed in wt.% NaCl in the aqueous phase). It corresponds to the system for which equal amounts of water and oil are solubilized in the microemulsion middle phase.

For each scan, appropriate amounts of surfactant, oil and NaCl brine were introduced into elongated graduated test tubes, which were sealed and placed in a constant temperature bath at 35 °C, unless otherwise specified. They were gently shaken twice a day for a week and then left until complete equilibration was assured e.g. when the phase volumes became constant.

The phase behavior was then observed, and the phase volumes were recorded in order to calculate the solubilization parameters as the ratio of the amount of oil or water (ml) to the amount of surfactant (g). Since both solubilization parameters are equal at optimum formulation, there is a single common value denoted by SP* (ml of oil or water per g of surfactant in the system).

4. Properties of extended surfactants

The variation in surface tension versus the logarithm of the surfactant concentration exhibits the typical break point feature, symptomatic of a CMC, for the three tested extended surfactants.

The change in the location of this CMC-like point with formulation variables such as salinity and temperature will be dealt with elsewhere; however, it is assumed in the following (without direct proof) that these new surfactants associate themselves into micellar aggregates as do other surfactants.

Fig. 4 indicates the variation in CMC as a function of the number of propylene oxide groups per molecule, for the dodecyl series. It is found that the CMC decreases as the PON increases, as expected from the fact that the polypropylene oxide chain is globally lipophilic. The variation in log CMC with PON tends to indicate that the decrease in hydrophilicity is roughly proportional to the number of propylene oxide groups. This variation can be expressed as a decrease by a factor of 1.2 in the surfactant CMC per added propylene oxide group.

Extended surfactants have a dual anionic and nonionic character, and are expected to exhibit an intermediate change in hydrophilicity with temperature as do ethoxylated sulfates and sulfonates [13]. Nevertheless, the effect on the polypropylene oxide chain is not well known.

For each of the surfactants, the cloud point was determined as the temperature at which a 10 wt.% solution in pure water became turbid. Fig. 5 indicates that the cloud point temperature decreases when the number of propylene oxide groups

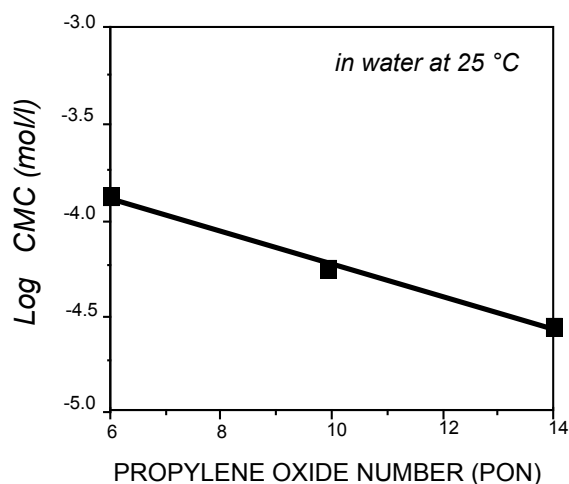


Fig. 4. CMC of extended surfactant as a function of propylene oxide number (PON).

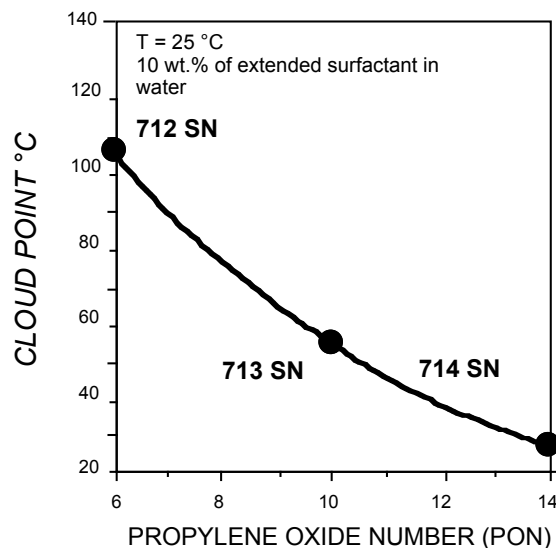


Fig. 5. Cloud point of extended surfactants as a function of PON.

increases; the cloud point decrease is approximately 10°C per PO group. This is clearly an indication that the surfactant is becoming more lipophilic with the increase in PON, a trend which is consistent with the CMC decrease noted previously.

As a matter of fact, there are two effects that could be held responsible for the decrease in cloud point as PON increases: first, the increase in the lipophilic part of the surfactant (longer PO chain), which tends to make it more lipophilic; second, the eventual dehydration of propylene oxide units located near the interface. The first effect is probably the main one, since the intermediate polarity part is built up on the oil side of the interface and inside the oil phase, so that the dehydration is probably negligible.

5. Three-phase microemulsion-oil-water phase behaviour with extended surfactants

Salinity scans were carried out to detect the eventual occurrence of a three-phase system at optimum formulation. Because of the strong hydrophilic nature of the sulfate group, a high salinity was required to attain optimum formula-

tion with short polypropylene oxide chain length, whereas the increase in PON resulted in all cases in a decrease in optimum salinity.

As a matter of fact, three-phase behavior was found to occur with long n-alkane (n-hexadecane), monochain polar oil (ethyl oleate), as well as triglyceride polar oils. It is worth remarking that this latter occurrence is reported here for the first time. Fig. 6 shows the decrease in optimum salinity (as $\ln S^*$) as a function of PON for different oil phases, which can be compared with the decrease in optimum salinity as a function of the number of methylene groups in the surfactant lipophile [2,39].

As shown recently [39], the $\ln S$ -ACN correlation for optimum formulation is a straight line for this kind of surfactant, as for other anionics [6]; however, the slope was found to decrease as the PON increased, as does the nonionic nature of this kind of surfactant. As a consequence, the variation in optimum salinity versus PON is actually dependent upon the nature of the oil phase. The variation extracted from Fig. 6 ranges from $\Delta \ln S = -0.14$ for soya oil (EACN = 18) to $\Delta \ln S = -0.12$ for ethyl oleate (EACN = 6) per added propylene oxide

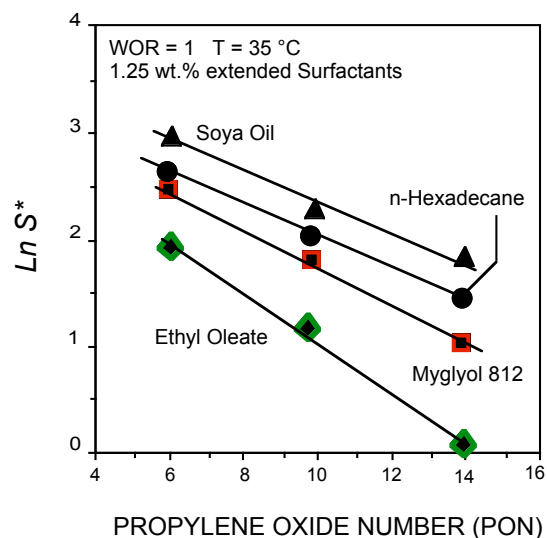


Fig. 6. Variation in optimum salinity ($\ln S^*$) of extended surfactants as a function of PON for different oils.

Table 1:
Chemical structure and experimental EACN of used Oils

OIL	CHEMICAL STRUCTURE	EACN
HEXADECANE	ALKANE	16
ETHYL OLEATE	MONOESTER (C18)	6-7
MIGLYOL 812	TRIESTER (C8-C10)	14
SOJA OIL	TRIESTER (mostly C18)	18
ETHYL MYRISTATE *	MONOESTER (C14)	5
MIGLYOL 840 *	DIESTER (C8-C10)	9

* added data (not in original paper)

group, as compared to $\Delta \ln S = -0.22$ per added methylene group in anionic surfactants [6]; this results in the expected equivalence between half a methylene group and one propylene oxide group [35].

Fig. 6 shows other interesting results. First, the oil phases can be located above and below hexadecane according to some EACN ranking, which is reported elsewhere [36]. Under these conditions, the following values (Table 1) are consistent with this and other data [37].

These results clearly show that the presence of a polar portion in an oil molecule is able to reduce its EACN considerably. The EACN can thus be viewed as a measurement of the overall lipophile-polar balance of the oil molecule.

Not shown is the fact that three-phase behavior was not found to occur with the tested extended surfactants and short alkanes, e.g. octane and decane. It is well known [6] that at a given salinity and alcohol concentration the system is optimum for an alkane carbon number (ACN*) that depends upon the length of the surfactant lipophilic chain. For alcohol-free systems at unit salinity ($1 \text{ g dl}^{-1} \text{ NaCl}$) the corresponding ACN* value has been called both the EPACNUS [6] and N_{\min} [40].

The final point to be noted from Fig. 6 is that the decrease in optimum salinity as PON increases means that interactions on both the water and oil sides are likely to increase, a fact that should result in an increase in solubilization whenever Winsor's approach is globally correct.

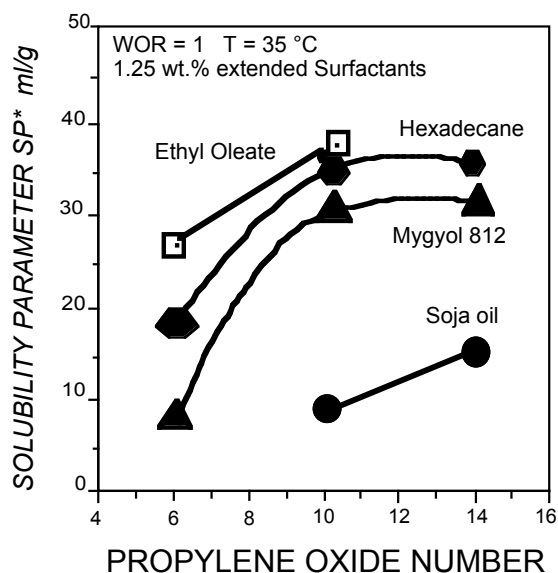


Fig. 7. Variation in SP* as a function of PON of extended Surfactants for different oils.

6. Solubilization with extended surfactants

Fig. 7 shows the value of the optimum solubilization parameters as a function of PON for different oil phases. First, it should be noted that the solubilization increases as PON increases (and the salinity decreases), as expected from Winsor's reasoning. However, the increase occurs essentially in the 6-10 PON range.

Second, the solubilization parameter attains outstanding values with hexadecane, i.e. a long-chain alkane, and ethyl oleate, i.e. a long single-chain polar oil. Previous data [36] indicate solubilization parameter values in the 3-7 ml g⁻¹ range for ethyl oleate, i.e. five or more times lower.

Further, the solubilization is much higher than any reported value for di- and triglyceride oils. This can lead to breakthrough formulations in the cleansing action and health-related products. In effect, a solubilization parameter in the 20 ml g⁻¹ range means that only 2-3 g of surfactant is required to co-solubilize 50 ml of water and 50 ml of oil.

The final comment to be made on the data in Fig. 7 is that it is obviously more difficult to solubilize three-chain oils than single-chain oils. In any case, the difference between Miglyol 812

(C8-C10 triglyceride) and soya oil (mostly C18 triglyceride) might be due not only to the number of ester chains, but also to their length [41].

7. Conclusions

Alkyl polypropylene oxide ether sulfates, so-called extended surfactants, are found to exhibit intermediate behavior between anionic and nonionic surfactants. They show three-phase behavior at optimum formulation with a variety of longchain oils, in particular mono-, and triglyceride esters. The values of the optimum solubilization parameters are extremely high.

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