

SYSTEMS CONTAINING MIXTURES OF EXTENDED SURFACTANTS AND CONVENTIONAL NONIONICS. PHASE BEHAVIOR AND SOLUBILIZATION IN MICROEMULSION

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Abstract

The concept of lipophilic linker action recently allowed to develop the so-called extended surfactants in which an intermediate polarity poly-propylene oxide chain is inserted in between the conventional lipophilic and hydrophilic groups. These extended surfactants are found to enhance considerably the interaction on the oil side of the interface up to the point that the formation of microemulsion is now possible with natural and synthetic triglyceride oils, or very long chain hydrocarbons. Extended surfactants of the alkyl poly-propylene-oxide-ethoxy-sulfate type are mixed with conventional ethoxylated alkyl phenol nonionics and the phase behavior and formation of microemulsion is analyzed by changing several formulation variables such as: mixture composition, number of propylene oxide groups, aqueous phase salinity etc..

Résumé

Systèmes contenant des mélanges de tensioactifs rallongés et de tensioactifs nonioniques conventionnels. Comportement de phase et solubilisation en microémulsion: Le concept d'intermédiaire lipophile a récemment permis de développer de nouveaux tensioactifs, qualifiés de rallongés parce qu'ils contiennent une chaîne poly-oxyde de propylène de polarité intermédiaire entre les groupes hydrophile et lipophile conventionnels. Ces tensioactifs rallongés produisent une augmentation notable des interactions du côté huile de l'interface, au point de permettre la solubilisation en microémulsion d'huiles polaires naturelles et synthétiques de type triglycéride ou d'hydrocarbures longs. Les tensioactifs rallongés du type alkyl poly-oxyde de propylène ethoxy sulfate, sont mélangés à des tensioactifs conventionnels du type alkylphénols ethoxylés, pour étudier le comportement de phase et la solubilisation en microémulsion dans différents cas de formulation où changent les variables suivantes: composition du mélange, nombre de groupes oxyde de propylène, salinité de la phase aqueuse etc...

Zusammenfassung

Systeme welche mischungen von Tenside und vertragsmässigen nicht-ionische Tenside enthalten. Phase benehem und löslichkeit in Mikroemulsion: Der Begriff von der Vermittlung der Lipophilen hat in letzter Zeit erlaubt neue Tenside zu entwickeln, die sogenannten ausgedehnten Tenside, weil sie eine Kette Polarität Poly-Propylen Oxid enthalten die zwischen den Gruppen vertragsmässiger Hydrphilen und Lipophilen eingeführt werden. Diese ausgedehnten Tensiden entwickeln wichtige Interaktionen auf der Seite des Oels und syntetischen Triglyceriden-Oele oder auch in langen Kohlenwasserstoff-Ketten. Die ausgedehnten Tenside, die der Poly-Propylen-Oxid Ethoxid-Sulpaten Gattung angehören, werden mit vertrasmässigen nicht-ionischen Tensiden, der Klass Alkyl Phenol mit Ethylen Oxid gemischt und man analysiert das Phase Benehem und die Bildung der Mikroemulsion beim Tauschen verschiedener, Salsbestand der Wasserphase etc.

1. INTRODUCTION: WINSOR'S APPROACH TO SOLUBILIZATION

In his pioneering work back in the fifties, Winsor's [1] established that the phase behavior of surfactant-oil-water SOW systems depended not upon specific values of the formulation variables, but upon the physico-chemical situation at interface. He introduced the R ratio of the interaction energy between the surfactant and the oil phase on one side, to the interaction energy between the surfactant and the water phase on the other side, as a yardstick to measure the effect of the formulation. Since then, Winsor's R ratio has been used as the best pedagogical way to understand the concept of physico-chemical formulation at interface [2]. In Figure 1, A_{CO} , and A_{CW} indicate the interactions between the surfactant on the one hand and the oil and water molecules on the other hand. Other interactions are illustrated in Figure 1. In the modified definition of the R ratio, the interaction between alike molecules are substrated, so that only the neat interaction is taken into account. Unfortunately, in Winsor's time the state of modelling molecular interaction was not, and by the way is not yet, ready for an accurate calculation of the interaction energies. As a consequence the R ratio is not amenable to numerical calculations, and it is only used to estimate trends, a serious drawback as far as formulation predictive forecasts are concerned.

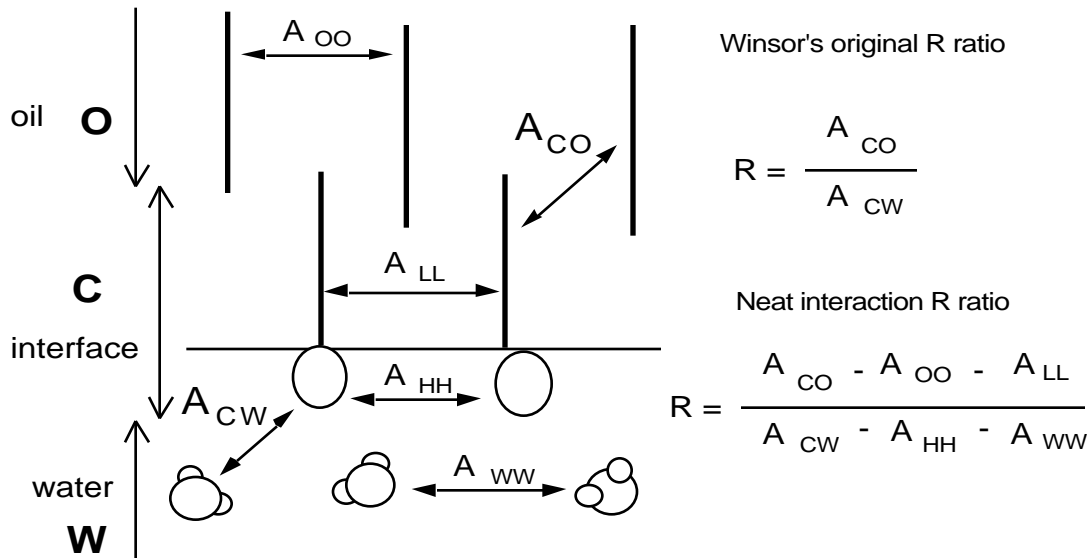


Figure 1: Winsor's R ratio of interaction between the interfacial layer and both phases

In the seventies, a lot of research was dedicated to the phase behavior of SOW systems [3-5] by academic and industry laboratories dealing with the enhanced oil recovery processes. The formulation was quantified by means of down-to-the-bench variables such as the brine salinity, oil alkane carbon number (ACN), surfactant characteristic parameters, as well as temperature.

Empirical correlations [6-7] for the attainment of ultra-low interfacial tension minimum for best oil recovery, at the so-called optimum formulation, were established for both anionic and nonionic surfactants. It was also shown that the occurrence of optimum formulation was associated with a maximum solubilization of oil and water in the microemulsion middle phase [8] of a three-phase system.

In Winsor's terminology the maximum solubilization of a formulation scan occurs whenever $R = 1$, a standard situation that is to be attained for comparison purposes. On the other, the extend of the solubilization, i.e., the amount of both water and oil co-solubilized into the middle phase microemulsion, is directly related to the absolute value of the dual interactions, i.e., the R ratio

numerator (or denominator since they are equal at optimum) [1-2]. Extensive experimental evidence gathered in the next 15 years showed that Winsor's assumption was correct [9-10], and a review book [2] has reported the different ways to improve the solubilization.

The interactions may be increased on both sides of the interface by using a surfactant with both a larger hydrophilic group and a larger hydrocarbon "tail"; the word larger actually means that a greater interaction results from it as expected from a simple length increase. This so-called Winsor's approach to enhanced solubilization is illustrated in Figure 2 left graph, in which a concurrent increase in hydrophile and lipophile sizes produces an extra zone (shaded) of interaction with oil.

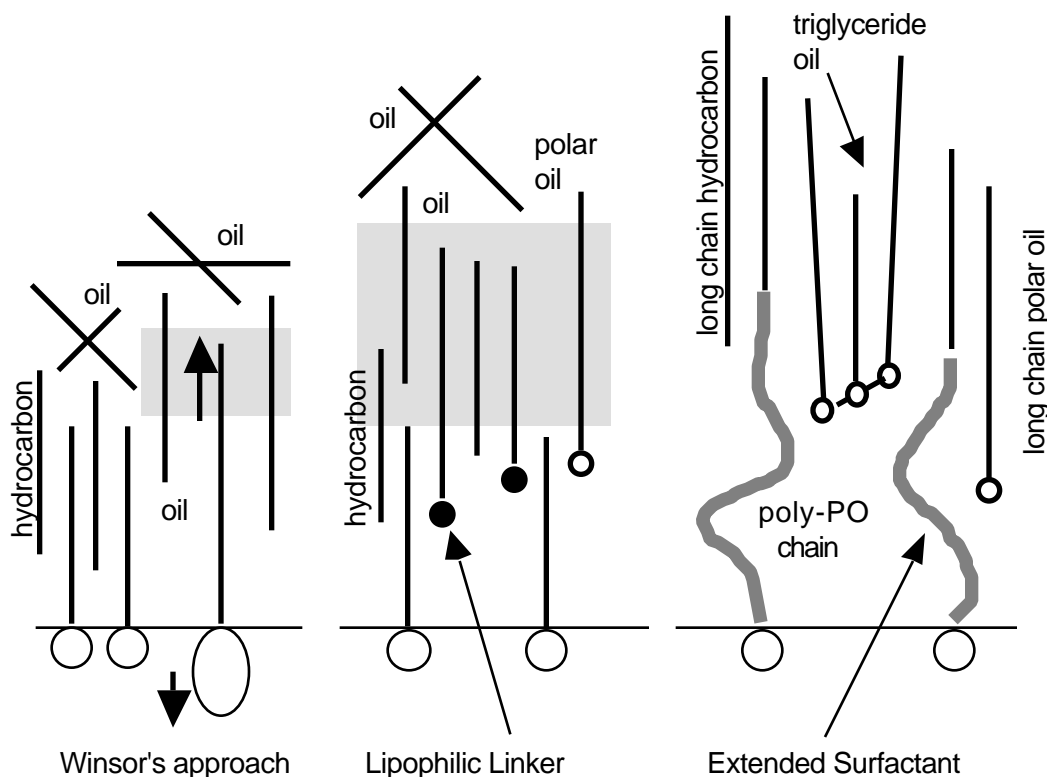


Figure 2: Different mechanisms for enhancing solubilization

This can be readily done on the water side of the interface, by increasing the number of ethylene oxide group or EON (nonionic surfactants) or by decreasing the brine salinity (ionics), two variables which are easy to handle and to monitor. However this is not the case on the oil side, because a larger interaction between the surfactant lipophilic group and the oil phase is almost always associated with an increase in length and/or an increase in linearity of the lipophilic group, a requirement with some consequential drawbacks. In effect, longer tail surfactants are less soluble in water, and at some point the solubility becomes lower than the critical micelle concentration [11], and the surfactant actually precipitates before forming any micelle nor microemulsion. On the other hand a longer tail results in more organized solubilization structures such as liquid crystals, rather than microemulsions. Liquid crystals can be molten or disorganized without changing temperature by adding short chain alcohols, but in both cases a decrease in solubilization is exhibited, because of the decrease of surfactant adsorption per unit interface area [2]. As a consequence Winsor's approach is useful in general to start with, but it is always limited, says to a tail size made of 16-20 carbon atoms, depending of the structure.

The solubilization is measured at optimum formulation, when equal amount of oil and water are cosolubilized in the microemulsion, as the amount (weight or volume) of oil or water solubilized per unit (weight or volume of surfactant), or of amphiphile mixture, i. e. surfactant plus alcohol. For comparison purposes, it may be said that typical solubilization values with conventional surfactants can be as high as 30 ml/ml or ml/g with short alkanes, 10 ml/g with hexadecane, while less than 5 ml/g with monochain polar oils such as ethyl oleate, and essentially nil with triglyceride oils.

2. BEYOND WINSOR'S APPROACH FOR ENHANCING SOLUBILIZATION

Recently, a new approach to enhance solubilization was proposed [12]. It consists in using an additive, so-called lipophilic linker, which is essentially a polar oil, for instance a long chain (> 8 carbon atoms) alcohol. It is conjectured that such a slightly hydrophilic oil molecule tends to take an orientation perpendicular to the interface, which results in some ordering of the oil phase structure in the vicinity of the interface. Figure 2 center graph illustrates the role of the lipophilic linker. It is worth noting that the lipophilic linker is actually a polar oil, and cannot be considered as a conventional co-surfactant component of the interfacial layer, since it was found to perform better whenever it adsorbs less at interface [13]. It seems to be actually located into the oil layer adjacent to the interfacial layer, as evidenced in recent oil segregation studies [15].

The experimental evidence reported recently shows that the oil solubilization increase (indicated by the extra interaction shaded area in Figure 2 center graph) does not obey Winsor's premise, since it is not accompanied by an increase of the hydrophilic group size on the water side. The lipophilic linker is then some kind of intermediate link between the surfactant layer (adsorbed at interface) and the bulk oil phase, from which the name. Moreover it is conjectured that the presence of the lipophilic linker hydrophile nearby the interface, but in the oil phase, allows the solubilization of single chain polar oil molecules such as ethyl oleate, as recently found [13].

A very recent study [14] indicates that the best intermediate role is attained when the lipophilic linker chain length is just average between the oil and surfactant hydrophobe, an indirect evidence that steric interactions are involved.

Because of the intermediate polarity produced by the lipophilic linker group some distance away from interface, the surfactant/lipophilic linker pair can be considered as some kind of composed amphiphile that exhibits an intermediate zone of slight polarity on the oil side of the interface. At first it was first thought that this scheme was unique in allowing an extended interaction with no penalty of precipitation, since the composed amphiphile was made of two molecules that were separately soluble in the system. However the coupling could not be controlled easily, and in particular no double or triple chain polar oils could be solubilized. A single molecule with the same built-in feature, i.e., intermediate polarity zone was designed [16-18]. The new surfactants were alkyl poly propylene oxide ethoxy sulfate sodium salts, with an alkyl chain in the C12-C18 range and a number of propylene oxide units (PON) in the 5-15 range. One or two ethylene oxide units had to be added at the end of the polypropylene oxide chain before sulfatation for steric reasons.

These so-called extended surfactants are referred to according to the following symbols: Cx-POy-EO₂-SO₃Na, or simply Cx-POy-ES, where "x" is the number of carbon atoms in the alkyl group, and "y" is the average number of propylene oxide units in the intermediate polarity chain. Such surfactant molecules are likely to locate at interface with the sulfate or ethoxysulfate hydrophile in water, while the intermediate poly-propylene oxide chain and the alkyl group belong to the oil phase [16]. Figure 2 right graph illustrates this situation, in which the intermediate low polarity oil phase layer (made of polypropylene oxide units) accommodates single chain polar oil molecules such as ethyl oleate, triglyceride oils or long chain hydrocarbons, as shown by experimental data [16-18]. It is worth stressing that the solubilization of polar oils as well as long chain hydrocarbons, e. g. hexadecane, in a

polypropylene oxide thick layer is probably made possible by the mainly lipophilic but somewhat polar “solvent layer” that is anchored at the boundary of the oil phase by the location of the sulfate group on the water side of the interface. Finally, it should be remarked that if the intermediate zone is 10 PO groups thick, it can fully accommodate oil molecules with 30 or so carbon atoms.

Figure 3 illustrates some basic properties of extended surfactants[16,18]. The left graph indicates that the optimum salinity decreases as the number of propylene oxide groups per molecules (PON) increases, a very significant hint that the PO chain is part of the lipophilic group, and that Winsor’s premise may be followed, at least qualitatively. As a matter of fact, it has been calculated [18] that each propylene oxide unit is from the point of view of lipophilicity equivalent to half a methylene group, although it is of course much bulkier.

The left graph relative position of the S*-PON curves indicates that the optimum salinity increases as the oil equivalent alkane carbon number (EACN) increases, since the EACN of ethyl oleate, STG (a 25% C8-75% C10 commercial synthetic triglyceride), hexadecane and soya oil are respectively 7, 14, 16 and 18 [16]. This is an indication of the ionic character of extended surfactants. If the effect is referred to the variation of the logarithm of salinity versus EACN, the value of slope $d\ln S/dACN$ is slightly lower than the one for anionic[6] and cationic[19] surfactant systems, but it increases with PON[17]. This is obviously due to the intermediate anionic/nonionic character of these surfactants.

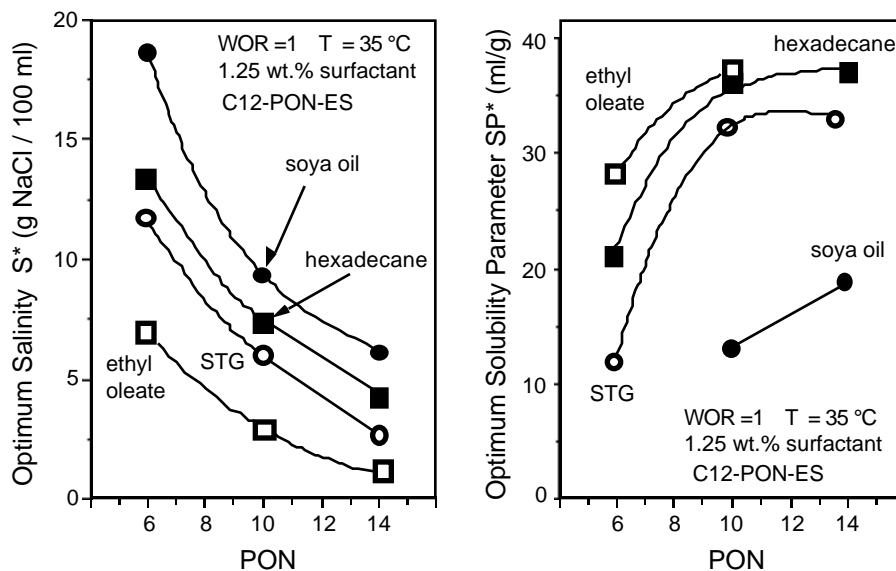


Figure 3. Properties of Extended Surfactant-Oil-Water Systems at optimum formulation

Figure 3 right graph exhibits the most important property of these new surfactants, i. e., their ability to solubilize long chain oils, either hydrocarbon (hexadecane), single chain ester ethyl oleate), synthetic triglyceride (C8-C10 triester) or natural one (soya oil). The attained solubilization of hexadecane is quite high when compared with systems containing conventional anionic or nonionic surfactants. On the other hand it is worth remarking the ability of extended surfactants to solubilize natural triglycerides such as soya oil to an outstanding 20 ml/g, a value that is high even with conventional surfactants and short alkanes.

Figure 3 right graph also indicates that the solubilization depends upon the poly-PO chain length, and that a too short poly-PO intermediate chain is less performant than a longer one, when a long chain oil is dealt with. The increasing trend seems however to level off, and it is probable that some kind of optimum is reached for each oil structure. In any case the natural triglyceride might require a poly-PO chain longer than 14 units.

3. EXTENDED AND NONIONIC SURFACTANTS MIXTURES

Nonionic surfactants of the ethoxylated alcohol or phenol type are used in many commercial products. There are well documented and exist in a variety of alkyl chain and ethoxylation degree. They provide a lot of flexibility in formulation tune up, since their mixing rules are well known. In many cases they have become relatively inexpensive. As a consequence it might be worthwhile mixing expensive extended surfactants with conventional nonionics to try to retain both the attractive cost and flexibility of use of nonionics and the solubilization performance of extended surfactants.

Used nonionic surfactants are nonylphenol ethoxylates with a number of ethylene oxide group per molecule symbolized as EON. For instance the symbol C9_EON stands for ethoxylated nonylphenol, while C12EON indicates a dodecyl alcohol ethoxylate, and C12-SORB-EO20 an ethoxylated (20 EO) sorbitan lauryl ester. In all cases the solubilization is measured at optimum formulation for three phase behavior, which is attained by adjusting the EON of the nonionic surfactant. EON* indicates the EON value at optimum and SP* the oil (or water) solubilization in the microemulsion middle phase.

Figure 4 left graph indicates the variation of optimum formulation, as EON*, when the mixture composition is changed. In both cases, the salinity is set to the optimum salinity of the pure extended surfactant for this oil. Fig 4 left shows that the nonionic surfactant EON* increases as the extended surfactant content increases. A EON* increase corresponds to an increased interaction with water, that is required to compensate an increased interaction with oil provided by the extended surfactant. The question is how the extended surfactant produces a shift in balance toward oil, if it is at its optimum salinity? The first explanation may be that the mixture of C9 and C12-PON tails produces a lipophilic interaction that does not follow a linear mixing rule. Instead the bigger groups tends to dominate, and the mixing results in an increased interaction, a well known effect [15]. On the other hand, it can be also explained by the fact that the mixture of anionic and nonionic surfactants results in a decrease in hydrophilicity due to the interaction of the polyEO chain and the anionic group [20].

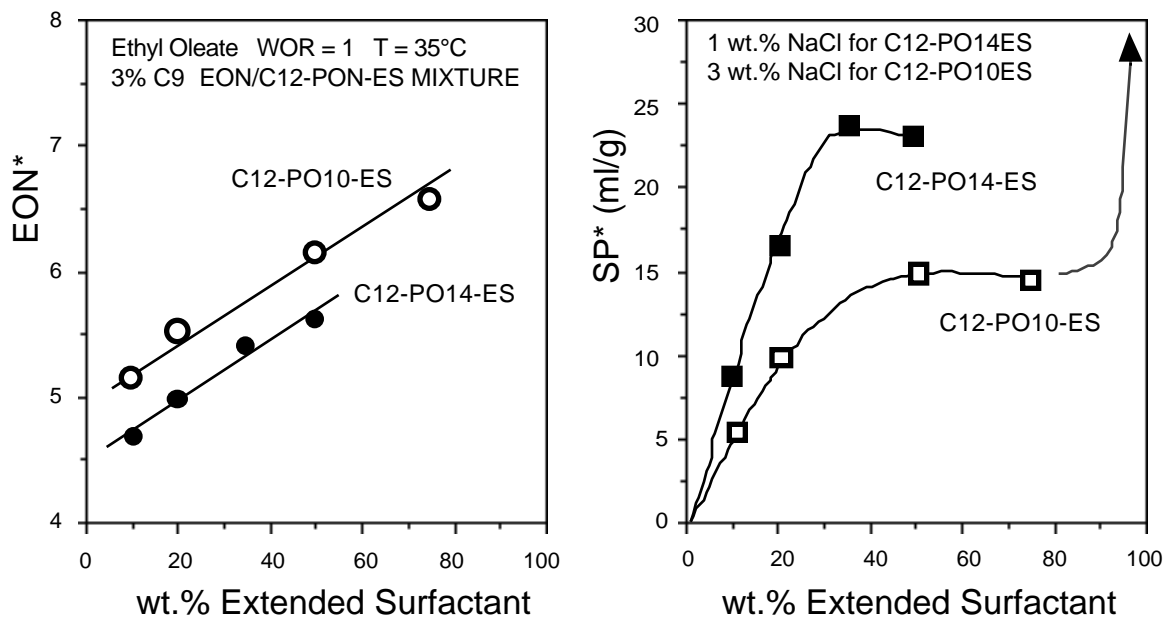


Figure 4: Optimum nonionic surfactant EON and optimum Solubilization Parameter for different mixtures of extended surfactants and ethoxylated nonylphenols.

Figure 4 right shows that the SP^* increases when the proportion of extended surfactant in the mixture increases. As a matter of fact it is essentially proportional at least until 30% of extended surfactant. This is really no surprise since it is known that ethyl oleate is essentially non solubilizable with ethoxylated nonylphenol surfactants. It is worth noting that the initial trend for C12-PO10-ES mixtures is compatible with an extrapolation to the $SP^* = 37$ ml/g value for the pure C12-PO10-ES (see Figure 3).

Three phase behavior was not attained for pure C12-PO14-ES with ethyl oleate, so that no extrapolation can be made for the second series. The initial slope is different for the two series, but this is no wonder since the difference in formulation is enough to explain it. Since the mixture with C12-PO14-ES requires a longer poly-EO chain in the nonionic surfactant (Figure 4 left) and a lower salinity, the increase of solubilization can be attributed to additional interaction both on the oil and water sides of the interface. However, these data cannot be used to calculate the compensating equivalence between EO and PO groups because the salinity is not the same.

The solubilization seems to level off beyond 30% of extended surfactant in the mixture, and the trend to pure extended surfactant performance is not recovered but very near 100% (dashed line). This non linear variation of the solubilization is in contrast with the linear formulation rule exhibited in Figure 4 left graph. This indicates that Winsor's premise is not followed quantitatively. Nevertheless, it is not known whether a lipophilic linker type of interaction, or a surfactant partitioning is responsible for such a departure.

Figure 5 shows the same kind of data for Soya oil and C12-PO14-ES, the best performer when used alone with this triglyceride oil (see Figure 3: $SP^* = 17$ ml/g at 6% NaCl), mixed with two nonionic surfactants. Figure 5 shows that the mixture of the extended surfactant with ethoxylated dinonylphenol produces a better solubilization than the mixture with ethoxylated nonyl phenol. This may be attributed to the increased interaction of the double nonyl chain with the oil. By the way, this increased interaction on the oil side is compensated by an increased interaction on the water side. In effect for the 50% mixture composition, $EON^* = 7.5$ for the dinonylphenol while it is $EON^* = 4.6$ for the nonyl phenol. Both curves converge to $SP^* = 17$ ml/g, the value for pure extended surfactant. It is worth noting

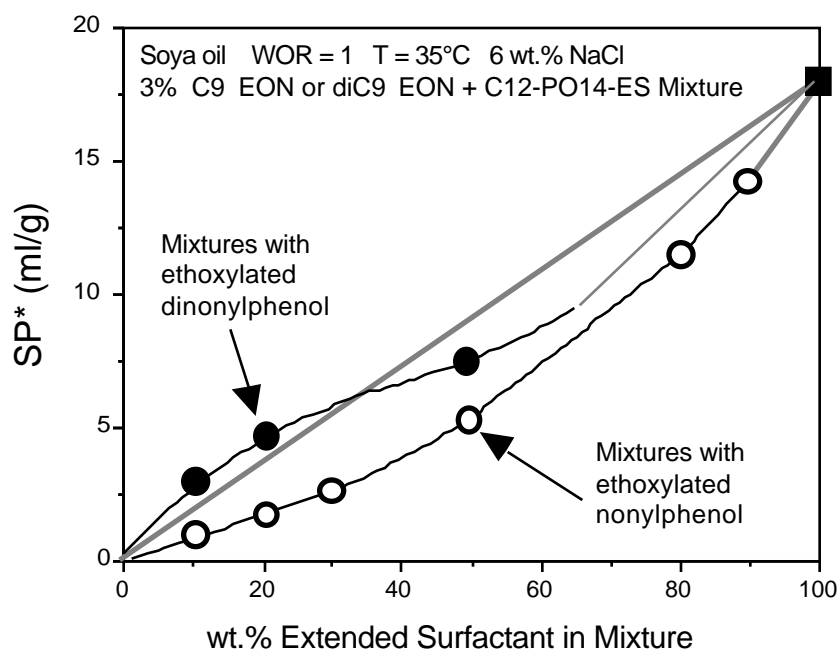


Figure 5: Solubilization parameter at optimum with mixtures of extended and single/double chain nonionic surfactants.

that the curve exhibits a variation that is smoother than in the previous case. There is no plateau but rather some departure from the dashed line that indicates what would be the linear mixing rule. These systems have not been studied enough for suggesting a straight explanation, for this effect. However, it is worth remarking that an eventual partitioning into soya oil is much less likely than into ethyl oleate, a hint that some selective partitioning might be playing some role.

In any case, the solubilization is not far from the linear mixing rule value, and it should be noted that the value (5 ml of soya oil per gram of surfactant 50%-50% mixture) is not bad, but rather better than any previous result with conventional surfactants. The question is how much the solubilization is affected by the choice of the conventional nonionic surfactant.

Figure 6 indicates the optimum solubilization parameter for systems with soya oil and surfactant mixtures containing 50% of C12-PO14-ES, and 50% of various nonionics. The white dots refer to data corresponding to optimum water phase salinity for the pure extended surfactant (6 wt.% NaCl). On the other hand the black dots correspond to a 7.5 wt.% NaCl salinity which is slightly above optimum. In that second series the extended surfactant is slightly lipophilic, so that the nonionic surfactant component needs to be more hydrophilic, i. e., with a higher EON*. In all cases, but one, the ethoxylation degree of the nonionic surfactant is adjusted so that a three phase behavior optimum formulation is reached. For the system containing a mixture of ethoxylated sorbitan esters, the formulation adjustment is carried out by mixing the mono-lauryl and mono-oleyl species. The ethoxylation degree of the nonionic surfactant can be readily deduced from the HLB scale in abscissa.

Figure 6 data show that there is little variation of SP* in spite of changing considerably the structure and the HLB of the nonionic surfactant. Even the double tail dinonyl phenol does not look very much better, actually just a little bit higher than other nonionics.

There is no the difference that could be expected from a large variation of the nonionic surfactant hydrophobe group. On the other hand the sorbitan esters, that are generally considered as poor surfactants as far as the solubilization is concerned, lead to the same result than the alkylphenol ones. This corroborates that the solubilization is essentially due to the extended surfactant, not to the nonionic one. There is however as slight systematic decrease of SP* when the salinity increases, as expected from Winsor's premise, but it is also not very significant, probably due to the partially nonionic character of the surfactant mixture.

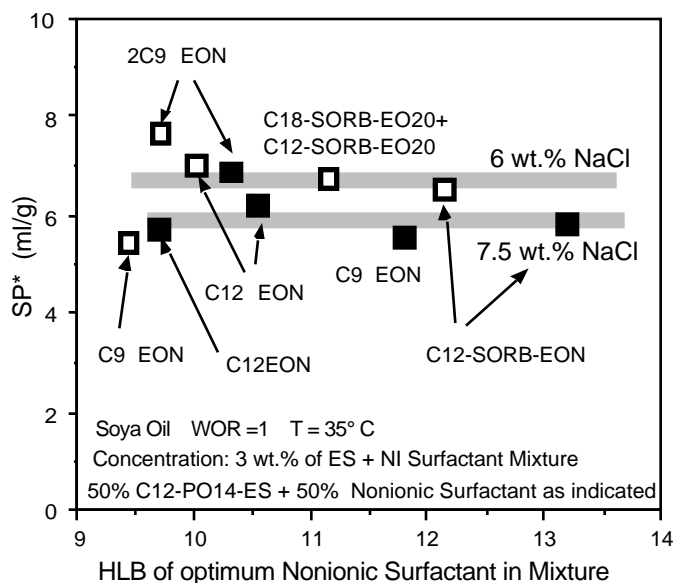


Figure 6: Solubilization parameter at optimum with mixtures of extended and various nonionic surfactants.

4 CONCLUSION

It is corroborated that extended surfactants are capable of solubilizing polar oils to a considerable extent. Extended surfactants can be mixed quite well with conventional nonionic surfactants and the mixture-oil-water phase behavior can be predicted as for anionic-nonionic mixture systems.

As far as the solubilization of polar oils, particularly triglycerides, is concerned, it is practically directly proportional to the amount of the extended surfactant component in the mixture. A departure to this trend is observed with ethyl oleate, a simple polar oil that might be suspected of favoring surfactant partitioning.

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