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# Revisiting the Influence of Carboxylic Acids on Emulsions and Equilibrated SOW systems using the PIT-Slope Method

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**Abstract**

The influence of various carboxylic acids (from $C_2$ to $C_{18}$) on equilibrated and emulsified surfactant/oil/water (SOW) systems is investigated. The PIT-slope method, based on the influence of an additive on the PIT of the $C_{10}E_4$/*n*-octane/$10^{-2}$ M $NaCl_{(aq)}$ reference emulsion, shows that from butanoic to hexadecanoic acids, the PIT of the system is decreased. A breakdown on dPIT/dx (considering the molar fraction x) or a minimum on dPIT/dC (taking into account the weight percentage C) is obtained with octanoic acid. The phase behavior of the $C_{10}E_4$/carboxylic acid/*n*-octane/0.01M $NaCl_{(aq)}$ system maintaining a molar fraction of carboxylic acid $x_{CA} = 0.2$ shows that from octanoic acid, the solubility of the system is clearly enhanced explaining the breakdown obtained in the PIT-slope. The Span 80/carboxylic acid/oil/$10^{-2}$ M $NaCl_{(aq)}$ system at a water-to-oil ratio equal to 1 is able to form O/W emulsions in the presence of some carboxylic acids, of which the alkyl chain modifies the partition of the different oligomers of Span 80. Finally, the PIT-slope method is applied to mixtures of lauric acid/sodium laurate providing a linear behavior of the PIT-slope dPIT/dx as a function of the acid/salt ratio.

**Keywords:** PIT-slope method; fatty acids; carboxylic acid; sorbitan monooleate; emulsion; microemulsion.

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**INTRODUCTION**

The world production of fatty acids (FAs) from natural fats and oils represents about 4 million metric tons per year. Most fatty acids of vegetable origin have a straight-chain with an even number of carbon atoms while odd-numbered fatty acids are most commonly found in bacteria, some plants and animals [1]. Chain lengths typically range commonly from 12 to 24. FAs are simple in structure and can be saturated or unsaturated, named MUFA for the monounsaturated and PUFA for the polyunsaturated ones. In some animals, fatty acids may be more complex with branched chains or other functional groups.

Fatty acids are ultimately consumed in a wide variety of end-use industries (rubber, plastics, detergents...). They are used to modify polyesters providing alkyd resins for coatings. They are also widely introduced in pharmaceutical, food and cosmetic formulations as additives. The alkaline salts of fatty acids provide surfactant molecules which have been used in soap formulations since Roman civilization [2]. The presence of carboxylic acid groups in oil, as naphthenic and resins molecules, is at the origin of the so-called alkaline flooding process for enhanced oil recovery [3,4]. Description of aqueous phase behavior and pH dependence of these compounds has largely been described in the literature [5–8]. Because of the pH dependence of the carboxylic function, their influence on Surfactant/Oil/Water (SOW) systems is important. Indeed, under alkaline conditions, they can play the role of a surfactant with a more or less important effect at the interface while under acidic conditions, they are more lipophilic, changing thus the polarity of the oil depending on their concentration. However, as weak acids, both forms generally coexist over a certain range of pH.

Several studies dealing with S/O/W ternary systems and fatty acids and/or their salts at equilibrium have also been reported in the literature. According to the Winsor nomenclature, the behavior of microemulsions [9] can include systems with two phases (Winsors I and II), three phases (Winsor III) or one single phase behavior (Winsor IV). For the two-phase

behavior, when the microemulsion is in equilibrium with an excess oil phase, the system is called Winsor I. When the microemulsion is in equilibrium with an excess water phase, the system is Winsor II. In the early studies of S/O/W equilibrated systems, Schulman et al. [10] studied oleic acid and its salt with different cations using alkanes, benzene or kerosene as oily phases. Ekwall et al. [11,12] published detailed phase diagrams of sodium octanoate/oil/water systems, using alcohol or fatty acids as third component. Mendez et al. [3] have shown that some fatty acid (FA)/O/W systems exhibit an unusual retrograde transition, i.e. WII □ WIII □ WI □ WIII □ WII when NaOH is added. Indeed, pH raises first increases the proportion of fatty acid sodium salt (i.e. hydrophilic surfactant) at the interface thus promotes WII□WIII□WI transitions. Then, a further pH increase does not change the acid/carboxylate equilibrium and the rise of $Na^+$ concentration results in the classical salinity driven WI□WIII□WII transitions. Bravo et al. [13] have studied the influence of pH and alkyl chain length on the phase behavior of FA/oil/alcohol/$NaCl_{aq}$ systems. They have shown that it is possible to obtain a three-phase behavior, maintaining a constant quantity of NaOH in the system, by changing the concentration of the fatty acid. For each fatty acid, it is possible to determine the pH to achieve the so-called optimal formulation, i.e. the formulation at which the minimum interfacial tension and the maximal solubilization occurs. The longer the alkyl chain of the acid is, the higher the pH of the aqueous phase must be to obtain the optimal formulation. In addition, when the system is triphasic, i.e. Winsor III, for an equal amount of FA, the microemulsion middle phase increases in volume when the alkyl chain increases. Thus, the longer the alkyl chain, the more the FA solubilizes both water and oil. Researches concerning carboxylic acids have not been limited to equilibrated systems and several studies have also been published on emulsions [14–18], most of them related to formulations for pharmaceutical, cosmetics or food applications.

Recently, Ontiveros et al. have proposed a simple and convenient method for the

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classification of surfactants [19,20]. The method is based on the perturbation of the Phase Inversion Temperature (PIT) through addition of a second surfactant. The concept of PIT, introduced by Shinoda et *al.* [21,22], characterizes the change of the affinity of polyethoxylated fatty alcohol surfactants, noted C$i$E$j$, towards water, oil and interface when they are heated or cooled. Starting from the $C_{10}E_4$/*n*-octane/water reference system, with a PIT close to 25 °C, the linear decrease or increase evolution of the PIT through addition of a second surfactant is quantified through the so-called PIT-slope which affords a robust classification of surfactants compared to the reference $C_{10}E_4$.

Based on these previous studies, we have investigated the influence of the alkyl chain length of a series of saturated carboxylic acids from $C_2$ to to $C_{18}$ and oleic acid $C_{18:1}$ on the PIT-slope, dPIT/dx$_{CA}$ (*i.e.*, the PIT variation versus the molar fraction of the acid). The effect of the lauric acid/sodium laurate ratio on dPIT/dx$_{CA}$ has also been studied using the same method. The discussion is completed with the phase behavior of $C_{10}E_4$/CA/*n*-octane/water systems, in order to verify the data obtained with the emulsified system and to evaluate the impact of carboxylic acids into the solubility capacity of microemulsion.  Finally the influence of the carboxylic acids into the morphology of Span 80/CA/oil/water model emulsion is studied. In this emulsion, both surfactant (Span 80) and oil phase (Creasil IH CG) are mixtures, a model system with ingredients often used in cosmetics to point-out the complex behavior of these formulations.

**MATERIALS AND METHODS**

**1. Chemicals**

Pure tetraethyleneglycol monodecyl ether ($C_{10}E_4$) reference surfactant was synthesized according to a method described elsewhere [23,24]. Its purity was assessed by NMR and GC analyses (> 99%) and by comparing its cloud point temperature [25] (20.4 °C at 2.6 wt.%)

with the reference value (20.56 °C at 2.6 wt.%). *n*-Octane (99%) was obtained from Sigma-Aldrich. Sodium chloride NaCl (≥ 99.5%) was supplied by Acros Organics. The carboxylic acids: acetic acid $C_2$ (99%), propionic acid $C_3$ (99.5%), hexanoic acid $C_6$ (99.5%), heptanoic acid $C_7$ (99%), octanoic acid $C_8$ (99%), decanoic acid $C_{10}$ (99%), lauric acid $C_{12}$ (98%), myristic acid $C_{14}$ (99.5%), palmitic acid $C_{16}$ (99%) and oleic acid (≥ 99%) were obtained from Sigma-Aldrich. Butyric acid $C_4$ (+99%) was obtained by Alfa Aesar. Creasil IH CG (iso-hexadecane) was supplied by Créations couleurs.

**2. PIT-slope method**

The method has been described in our previous papers [6,7] (see Supporting Information). It consists in measuring the PIT deviation of the $C_{10}E_4$/*n*-octane/water reference system through addition of small amounts of an additive, *i.e.* the carboxylic acids (CAs) in the present work. The results are interpreted in terms of the PIT-slope which can be expressed in molar fraction $dPIT/dX_{CA}$ or in weight percentage $dPIT/dC_{CA}$. The carboxylic acid molar fraction $X_{CA}$ in the surfactant/carboxylic acid mixture is given by Eq.1:

$$X_{CA} = \frac{\frac{m_{CA}}{MW_{CA}}}{\frac{m_{CA}}{MW_{CA}} + \frac{m_{C10E4}}{MW_{C10E4}}} \qquad (1)$$

where $m_{CA}$ and $MW_{CA}$ are the mass and molecular weight of the carboylic acid respectively and $m_{C10E4}$ and $MW_{C10E4}$ are the mass and molecular weight of the surfactant of the reference system, *i.e.* $C_{10}E_4$. The water weight fraction $f_w$ is equal to 0.5 in all systems. For the experiments carried out with mixtures of carboxylic acid and sodium salt, the molar fraction is defined as:

$$X = \frac{\frac{m_{CA}}{MW_{CA}} + \frac{m_{NaA}}{MW_{NaA}}}{\frac{m_{CA}}{MW_{CA}} + \frac{m_{NaA}}{MW_{NaA}} + \frac{m_{C10E4}}{MW_{C10E4}}} \qquad (2)$$

**3. Phase behavior of equilibrated $C_{10}E_4$/carboxylic acid/*n*-octane/NaCl$_{aq}$ systems**

1.5 g samples were prepared in 2 mL vials by weighing successively the compounds. NaCl aqueous solution and $n$-octane had the same weight ($f_w = 0.5$) in each sample, carboxylic acid was added until reaching a molar fraction $X_{CA} = 0.2$ and the surfactant total concentration was 3% wt. The resulting 3 wt.% $C_{10}E_4$/carboxylic acid/$n$-octane/$10^{-2}$ M $NaCl_{aq}$ systems were gently mixed to maximize the water/oil contact while avoiding emulsification. The vials were then placed in a thermostated bath at the required temperatures T $\pm$ 0.1 °C until phase separation and equilibrium were reached, at least for one day and up to several days in the vicinity of transition zones. Visual inspection of the vials allowed the determination of the phase behavior in order to classify them in Winsor scale.

## 4. Emulsification of the Span 80/carboxylic acid/oil/$NaCl_{aq}$ systems

8.5g samples were prepared in 20 mL vials by weighing successively the compounds. Span 80 was preliminary dissolved into the oily phase, either octane or Creasil IH CG (isohexadecane). the NaCl ($10^{-2}$ M) aqueous solution and the oil (octane or Creasil IH CG) had the same weight ($f_w = 0.5$) in each sample. Hexanoic, octanoic, decanoic, lauric, tetradecanoic and hexadecanoic acids were used at 0.5 wt.%. The 0.5 wt.% Span 80/0.5% carboxylic acid/oil/$10^{-2}$ M $NaCl_{(aq)}$ resulting systems were gently mixed to maximize the water/oil contact while avoiding emulsification All systems were prepared and left to equilibrate at least for 18h. The samples were then emulsified using an Ultra-Turrax at 6000 rpm for 30 s and their conductivity was measured simultaneously. The alkane carbon number for octane is 8. For the Creasil IH CG, the Equivalent Alkane Carbon Number (EACN = 13.5) was experimentally previously determined by Queste et *al.* [26] (See supporting information).

## RESULTS AND DISCUSSION

## 1. Effect of carboxylic acids chain length on SOW systems

The influence of carboxylic acids (CAs) at the interface as a function of the CA chain length was determined using the PIT-slope method. Thus, the PIT of the 3 wt.% $C_{10}E_4$/$n$-octane/$10^{-2}$ M $NaCl_{(aq)}$ reference system was measured in the presence of increasing amounts of 12 linear carboxylic acids (CAs) from acetic acid ($C_2$) to stearic acid ($C_{18}$) and one unsaturated compound, *i.e.* oleic acid. **Figure 1** describes the linear evolution of the PIT values as a function of the weight concentrations for some acids in the studied range of concentrations (< 1 wt.%), limited by the solubility of the acids and by the practical lowest temperature ($\approx$ 10 °C) that can be experimentally reached. Results for all the acids are given in Supporting Information.
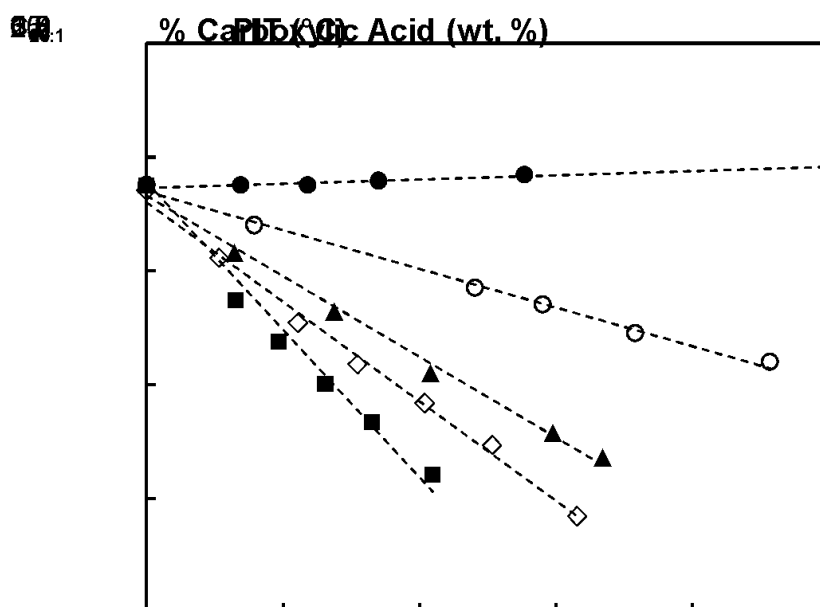


**Figure 1.** Phase inversion temperature (PIT) of the 3 wt.% $C_{10}E_4$ /$n$-octane/$10^{-2}$M $NaCl_{(aq)}$ system as a function of weight percentage of carboxylic acid (CA). Acetic acid ($C_2$), butyric acid ($C_4$), octanoic acid ($C_8$), tetradecanoic acid ($C_{14}$) and oleic acid ($C_{18:1}$). Dotted lines indicate the linear fitting.

Acetic acid $C_2$ is water-soluble and slightly increases the PIT, it enhances the hydrophilicity of the system as expected. For longer CAs from $C_4$ to $C_8$, the PIT significantly decreases with

the chain length. From decanoic acid $C_{10}$, the PIT value still diminishes but this decrease is less important than the strongest effect observed until $C_8$. In the range of the studied concentrations, *i.e.* below 1 wt.%, there is a linear dependence between the PIT and the concentration.
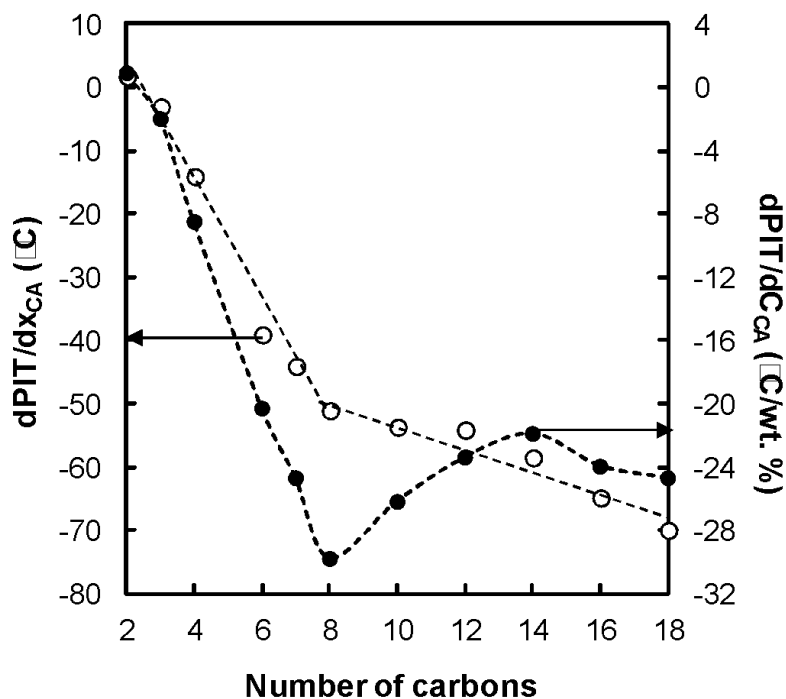


**Fig. 2** Evolution of $dPIT/dX_{CA}$ (°C) and $dPIT/dC_{CA}$ (°C/wt. %) with increasing alkyl chain length of carboxylic acid CA for the 3 wt.% $C_{10}E_4$ /CA/*n*-octane/$10^{-2}$M $NaCl_{(aq)}$ system.

The slope of PIT with $dPIT/dC_{CA}$ (weight percentage) or $dPIT/dX_{CA}$ (molar fraction) corresponds to the ability of the carboxylic acid CA to modify the phase inversion temperature of the reference system. If the slope is negative, the acid decreases the PIT, at contrary a positive slope reflects an increase of the PIT. **Figure 2** shows a rapid fall of $dPIT/dC_{CA}$ as a function of the total number of carbon atoms of the acid, the lowest $dPIT/dC$ corresponding to the $C_8$. When the slope is represented by considering the molar fraction $X_{CA}$, there is not a minimum value with $C_8$ but a discontinuity in the tendency. The slopes determined from the PIT *versus* CA concentration plots for the 11 investigated acids are

reported in the supplementary material.

The change of the PIT reflects the activity of the carboxylic acids at or near the interfacial layer, modifying the spontaneous curvature and the rigidity of the interfacial film formed by the $C_{10}E_4$ surfactant molecules. For short CAs like acetic and propionic acids, the influence on the interfacial film is weak leading to slightly positive and negative values of dPIT/dC or dPIT/dX$_{CA}$, respectively. Other CAs increase the lipophilicity of the system, however octanoic acid establishes a boundary in the effect of these compounds on the PIT. We have already reported such a similar evolution of the PIT with linear alcohols, using both the 7 wt.% Brij30/$n$-octane/$10^{-2}$ M NaCl$_{(aq)}$ [27] and the 7 wt.% $C_{10}E_4$/$n$-octane/$10^{-2}$ M NaCl$_{(aq)}$ systems [28]. In both cases, the minimum observed for dPIT/dC was reached with heptanol, and this alcohol defines the zone in which the alcohols act as lipophilic linkers. That means that its polar head is not enough efficient to lead the alcohol to the interface but it contributes to create an order between the alkyl chain of the surfactant and the alkane [29,30]. Compared to alcohols, the carboxylic acids are more polar and the fact that the minimum for dPIT/dC for acids is obtained with the $C_8$ is not casual. The additional carbon in the alkyl chain compensates for the higher polarity of the carboxylic group compared to the OH in alcohols. From the values of their dPIT/dx$_{CA}$, most acids are more hydrophobic than $C_{10}E_4$, $i.e$ the interfacial activity of lauric acid is comprised between that of dodecyl isosorbide (dPIT/dx = -54) and dodecyl glycerol (dPIT/dx = -43) [20]. The weight concentration values dPIT/dC$_{CA}$ indicate a lipophilic tendency higher than the values obtained for all surfactants of the sorbitan alkanoates which are commercial lipophilic surfactants (*i.e.* Span).

## 2. Phase behavior of the $C_{10}E_4$/carboxylic acid/$n$-octane/water systems

In order to go deeper into the influence of carboxylic acids on SOW systems, the phase

behavior evolution of the $C_{10}E_4$/$n$-octane/water system through addition of the carboxylic acids was also investigated at equilibrium. The phase behavior of the $C_{10}E_4$/$n$-octane/water system is well-known with a critical temperature (noted T*) and concentration (noted C*) at $f_w$ = 0.5 equal to 25.6 °C and 10.8 wt.% respectively [26,31,32]. When the concentration of the surfactant is lower than C* and the surfactant is not pure, the temperature at which the ethoxylated surfactant presents the same affinity for oil and water in a S/O/W equilibrated system is called $T_{HLB}$ and differs from T* [33–35].

A temperature scan for the 3 wt.% $C_{10}E_4$/$n$-octane/water system has thus been carried out without CA and in the presence of the $C_6$ to $C_{14}$ acids at a molar fraction $x_{CA}$ of 0.2, under equilibrated conditions using temperature as a scan variable.

As shown previously, the PIT of the $C_{10}E_4$/$n$-octane/water system is impacted by the presence of CAs. The behavior at equilibrium when adding a carboxylic acid is also affected and the temperature needed to obtain a three-phase system (*i.e.* WIII) shifts to lower values. In order to compare all the studied CAs, we have plotted, on **Figure 3**, the volume fraction of the different phases as a function of the difference T-$T_{HLB}$, where $T_{HLB}$ is the temperature of the three phase system with the same weights of oil and water in the middle phase microemulsion.
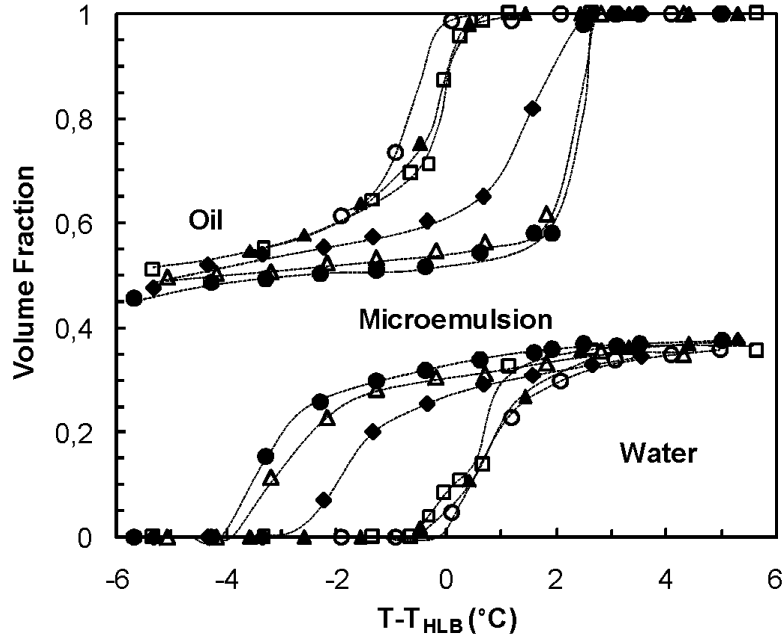
**Figure 3**. Volume fraction of the oil, microemulsion and water phases as a function of T-$T_{HLB}$ for the 3 wt.% $C_{10}E_4$/carboxylic acid/$n$-octane/water system at a constant molar fraction of carboxylic acid $x_{CA} = 0.2$. ● = no CA, △ = $C_6$, ◇ = $C_8$, □ = $C_{10}$, ▲ = $C_{12}$, ○ = $C_{14}$.

Addition of carboxylic acids from $C_6$ to $C_{14}$ to the $C_{10}E_4$/$n$-octane/water system changes not only the temperature but also the shape of the volume fraction- temperature difference diagram of the reference system. At $T_{HLB}$, the presence of carboxylic acids increases the microemulsion phase volume of the systems in the following order $C_{14} > C_{12} > C_{10} > C_8$. Conversely, hexanoic acid does not change the limits of the volume fraction- temperature difference diagram of the reference system. At temperatures far away from $T_{HLB,}$ the frontiers of acid systems converge with the reference system (in both WI and WII phase behaviors). Temperature range in which the WIII systems are obtained dramatically decreases for longer acids, from 6 °C for the reference system to less than 0.5 °C for the $C_{14}$. This decrease on the temperature extent of the WIII behavior and the significant increase of the volume of the microemulsion phase for $C_{12}$ and $C_{14}$ shows that the reference system tends to a monophasic WIV microemulsion in the presence of these acids. It is noteworthy that to attain the Winsor

IV system with the $C_{10}E_4$/$n$-octane/water system, 10 wt.%. of $C_{10}E_4$ is required. Hence, a similar effect is obtained by addition of only 0.2 molar fraction of long chain fatty acids (> $C_8$) with only 3 wt.% $C_{10}E_4$ instead of 10 wt.%.

As described for alcohols in the earliest 90's by Graciaa et *al.* [30], the addition of some carboxylic acids generate a synergistic effect that allows to increase the water/oil interfacial activity of the surfactant. This increase is probably due to the segregation of the fatty acid between the alkyl chain of the surfactant and octane, inducing a more organized transition from the surfactant palisade to the oil bulk phase. This is the so-called lipophilic linker effect [29,30]. Such a behavior matches well with the change on the dPIT/d$x_{CA}$ tendency observed in **Figure 2** from octanoic acid. In that sense, our findings complete the behavior reported by Lohateeraparp et *al.* [36] with the sodium dodecyl sulfate (SDS)/carboxylic acid (CA)/$n$-hexane/NaCl$_{(aq)}$ system, using the salinity as a formulation variable. The increase of alkyl chain decreases the salinity required to achieve WIII systems, analogous to the temperature decrease observed for the $C_{10}E_4$/CA/$n$-octane/W system. Alcohols can be easily replaced by CA not only when using ionic surfactant systems (SDS) but also with non-ionic surfactants ($C_iE_j$). Contrary to the continuous increase of solubility with the alkyl chain reported in Figure 3, in the SDS/CA/$n$-hexane/NaCl$_{(aq)}$ system, the increase of solubility with the alkyl chain of CA is asymptotic, probably "because gel formation prevents further enrichment in the solubilization" [36].


## 3. Influence of carboxylic acids on the emulsification of the Span 80/oil/water systems

Fatty carboxylic acids are not able to form stable emulsions by themselves but strongly influence the behavior of SOW emulsified systems. Their influence has thus also been studied as additives on Span 80/oil/water systems (0.5 wt.% of span 80, $f_w$ = 0.5). Two oils were selected: $n$-octane and the commercial Creasil-IH CG, a mixture of isohexadecane isomers,

used in cosmetic formulations. The systems without carboxylic acid produce O/W emulsions at low concentrations of surfactant (0.5% wt.) with both oils. Even if Span 80 is a lipophilic surfactant, at low concentrations, the partition of the different molecules is enhanced and a net hydrophilic behavior is obtained as described in the literature for ethoxylated surfactants [35,37,38]. Indeed, for a Span/Cod Liver + sec-butanol/water (1 wt.% NaCl) system, Salager et *al.* [39] reported an O/W emulsion at $f_w$ = 0.5, using 2 wt.% of the sorbitan surfactant. To study the effect of the CAs, the conductivity of the emulsions were measured (**Figure 4**).
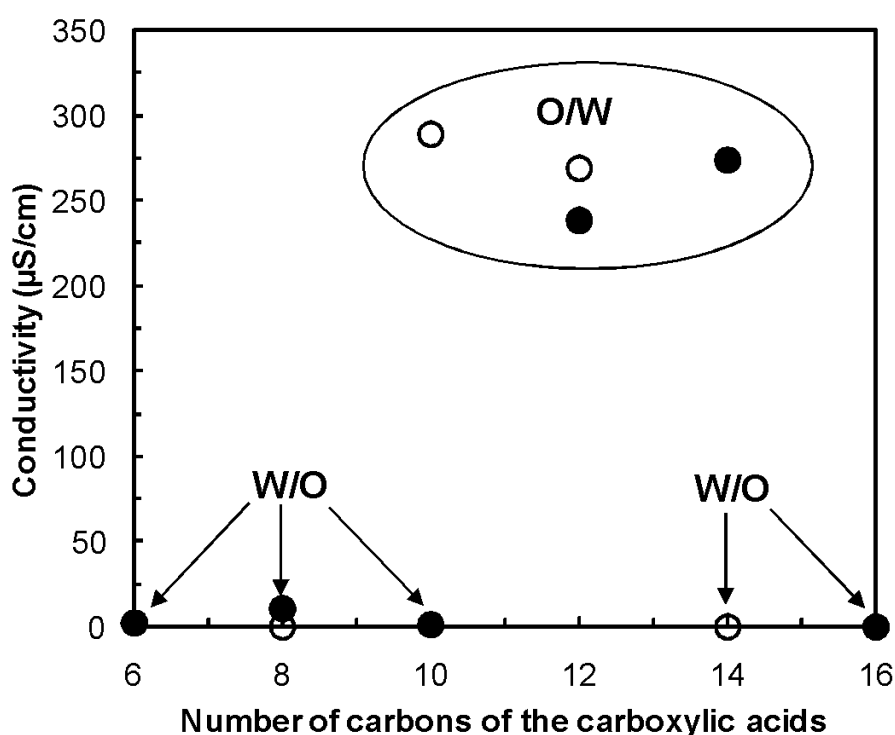


**Figure 4**. Conductivity and emulsion type of the Span 80/oil/water system in the presence of carboxylic acid as a function of the CA chain length. Conditions: 0.5 wt.% Span 80, carboxylic acid 0.5 wt.%, 0.01 M NaCl in the aqueous phase. ● : octane, ◯ : isohexadecane isomers mixture.

Addition of 0.5% wt. of carboxylic acid clearly changes the morphology of the emulsions. For *n*-octane, all systems produce W/O emulsions except lauric and tetradecanoic acids. The "hydrophobicity" of the oily phase can be quantified by the Equivalent Alkane Carbon

Number (EACN), the number of carbon atoms of the linear alkane that has its optimal formulation at the same conditions of the studied oil [40,41]. The increase of the CA chain length from 6 to 16 should produce a monotonic change of the EACN with an inversion of the emulsion from W/O to O/W when the EACN of the system reaches the initial value without carboxylic acid. When the alkyl chain of CA increases up to 12, an O/W emulsion is obtained. However, the fact that Span 80 is not a well-defined surfactant but a mixture (as most of commercially available surfactants) increases the complexity of its behavior. Span 80 contains fatty acid mono, di and tri-esters of sorbitan and the alkyl chain is a mixture of oleic, linoleic, linolenic and palmitic acid [42]. Partitioning of all these compounds between the oily phase and the interface, when the carboxylic acid changes, appears to be determinant to re-obtain W/O emulsions. This hypothesis is schematized in **Figure 5**, from the system without carboxylic acid **(5A)** and in the presence of different carboxylic acids **(5B, 5C and 5D)**.



|  |  |  |  |
|---|---|---|---|
| **A (O/W)** | **B (W/O)** | **C (O/W)** | **D (W/O)** |
| No carboxylic acid | Increasing the alkyl chain of carboxylic acids | | |

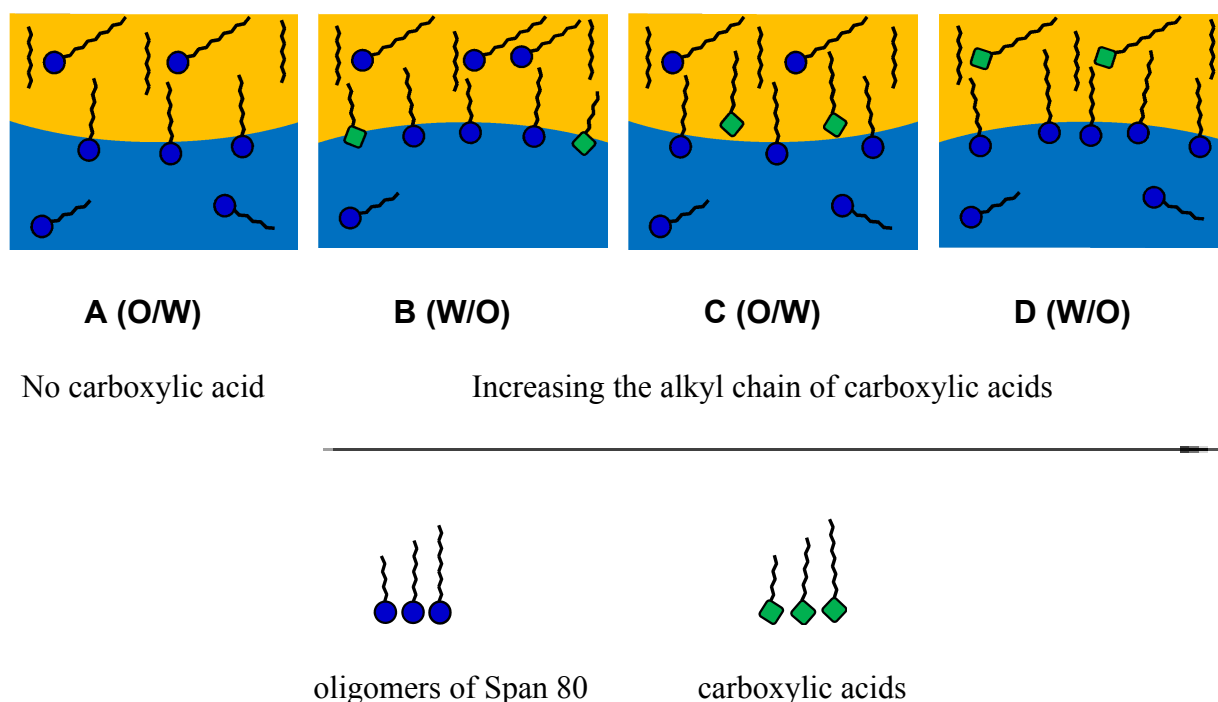oligomers of Span 80          carboxylic acids

**Figure 5.** Schematic representation of droplet interface for different carboxylic acids added to the Span 80/oil/water emulsion systems.

When the balance between the polar head and the alkyl chain of the carboxylic acid is reached, the CA preferentially localizes at the interface (as *n*-butanol for alcohols), changing the Span 80 partition (**Figure 5A and B**). When the alkyl chain of the carboxylic acid increases, the CA plays the role of a linker between the alkyl chain of the oil and the surfactant. The most lipophilic oligomers of Span 80 are segregated into the bulk oily phase and the O/W system is obtained (**Figure 5C**). Longer alkyl chains are solubilized into the oily phase and the lipophilic oligomers of Span 80 are preferentially distributed in the interfacial film, thus accounting for the formation of W/O emulsions observed when adding 0.5% wt. hexadecanoic acid to the 0.5% wt. Span 80/octane/water (**Figure 5D**).

This "retrograde" inversion has already been reported for ethoxylated surfactants when using alcohol concentration [43] or oil nature [44] as formulation scan variables. Salager [43] and Ysambertt [44] have shown that the partitioning of the surfactant produces anomalous inversions in S/O/W equilibrated systems. Furthermore, the partitioning of Span 80 would be affected by its concentration and by the carboxylic acid concentration as well.

It is well known that an increase of EACN enhances the hydrophilicity of the system producing a WII→WI transition [45,46]. The behavior obtained with the mixture of isohexadecane isomers is similar except that O/W emulsions are observed for decanoic and lauric acids. This result agrees with the main hypothesis: as the iso-hexadecane has a higher EACN (13.5) than that of *n*-octane (8), the O/W emulsion is easily obtained (the alkyl chain of the CA required is smaller). The retrograde inversion is observed for the iso-hexadecane emulsion when adding the tetradecanoic acid, even if it will be expected that this system need a higher carboxylic acid chain that that observed for octane emulsion (hexadecanoic acid). This behavior could be promoted by the different isomers of hexadecane present at the Creasil-IH CG.

## 4. Influence of the carboxylic acid/sodium carboxylate ratio on dPIT/dx$_{CA}$

As carboxylic acids are weak acids, there is always a mixture of the acid and the carboxylate forms in solution depending on the pK$_a$ of the acid and on the pH of the solution. The pK$_a$ of shorter carboxylic acids is near to 5 (4.79 for acetic acid) and increase until 8.1-8.2 for tetradecanoic acid [47]. It was thus of interest to assess the influence of the sodium salt of the carboxylic acid as well as of its amount on the PIT of the reference system. Two methods have been used. The first one consisted in mixing directly the acid and its corresponding sodium salt and measuring the resulting dPIT/dx$_{CA}$ of the mixture at different ratios. The second one was to change progressively the pH of the aqueous phase by addition of NaOH until one equivalent in order to form the carboxylate *in situ*. **Figure 6** shows the influence of the lauric acid/sodium laurate ratio on the PIT evolution of the 3wt.% C$_{10}$E$_4$/*n*-octane/10$^{-2}$ M NaCl$_{(aq)}$ system. As expected, the higher the molar fraction of sodium salt, the higher the dPIT/dx$_{CA}$ is.
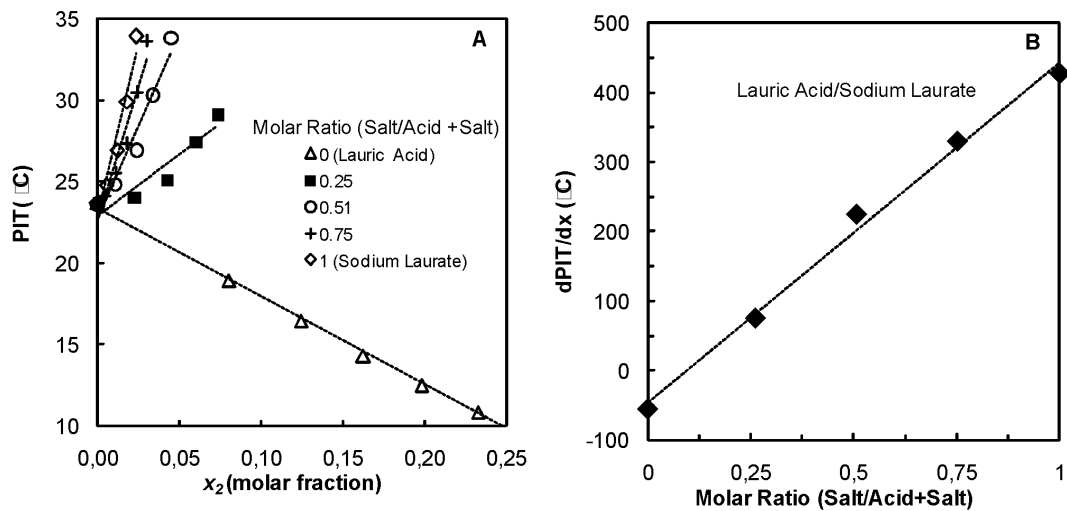


**Figure 6. A)** Phase inversion temperature (PIT) *vs.* molar fraction x of lauric acid + sodium laurate at different salt/acid + salt molar ratios for the 3 wt.% C$_{10}$E$_4$/lauric acid/sodium laurate/*n*-octane/10$^{-2}$M NaCl$_{(aq)}$ system at $f_w$ = 0.5. **B)** Evolution of dPIT/dx (°C) with increasing sodium laurate/lauric acid + sodium laurate molar ratios.

The last point on molar fraction on **Figure 6A** (for every molar ratio different to zero) is the maximal molar fraction of the acid/salt mixture that allows the phase inversion by heating/cooling. Indeed, addition of sodium laurate, even at a molar ratio of 0.25, induces at some critical concentration the formation of O/W emulsions insensitive to temperature, as expected for ionic surfactants-$C_iE_j$ mixtures [20]. When the salt ratio increases, the limit of the molar fraction to obtain the temperature insensivity decreases. Independently of the ratio of the mixture salt/acid, the quantity of sodium laurate to obtain the temperature insensitivity is approximately the same. Indeed, when the molar fraction of sodium laurate is higher than 0.026, an O/W emulsion is produced no matter the temperature of the system or the salt/acid ratio. **Figures 6B** shows a very good linearity of dPIT/dx as a function of the molar ratio of lauric acid/sodium laurate. If the linearity between mixtures of a same family of non-ionic surfactants could be expected, it was not obvious for mixtures of a carboxylic acid and its salt as it complicates the patterns in phase behavior [3,13] and, as mentioned before, their mixtures with the $C_{10}E_4$/$n$-octane/$10^{-2}$M $NaCl_{(aq)}$ system produces at some critical concentration O/W emulsions insensitive to temperatures variations. Results from **Figure 6B** suggest that acid and salt effects are independent and dPIT/dx quantifies both effects at the same time. Lauric acid acts as a lipophilic additive of the mixture, and the non-ideal behavior with $C_{10}E_4$ is only due to the presence of the ionic surfactant. **Table 1** shows the values of the PIT for the $C_{10}E_4$/$n$-octane/water system when the molar fraction of lauric acid and sodium laurate is equal to 0.02 at different mixture ratios.

**Table 1**. PIT of the 3 wt.% $C_{10}E_4$/sodium laurate/lauric acid/$n$-octane/$10^{-2}$M $NaCl_{(aq)}$ system in the presence of different molar ratios of the lauric acid/sodium laurate mixtures determined 1) by mixing directly lauric acid and sodium laurate and 2) by adding NaOH to the lauric acid-based system. In all cases the molar fraction of lauric acid and sodium laurate mixture is

0.02.

| $\dfrac{Sodium\ laurate}{Sodium\ laurate + Lauric\ acid}$ | 0 | 0.25 | 0.5 | 0.75 | 1 |
|---|---|---|---|---|---|
| PIT (°C) (sodium laurate + lauric acid) | 22.6 | 24.4 | 27.2 | 29.2 | 31.4 |
| PIT (°C) (addition of NaOH) | 22.6 | 24.1 | 25.7 | 27.0 | 28.2 |

It is noteworthy that the PIT linearly increases by adding directly NaOH as well as by mixing directly the salt and the acid. However, by comparing the PIT values obtained by the two methods, there are some discrepancies. The values obtained when mixing the acid and the salt are slightly higher than the values obtained by adding sodium hydroxide, and the difference is higher when the ratio increases. Lauric acid is predominantly in the oil phase of the system $C_{10}E_4$/$n$-octane/water and the real sodium laurate/lauric acid ratio is difficult to predict as reported by Mendez et *al.* [3]. In order to reduce the PIT difference, the addition of NaOH must be followed by an additional time of equilibration that allows the complete reaction and partition of reactants and products. Irrespective of the method, interaction of sodium laurate and lauric acid on the PIT of the reference system is complementary. Higher hydrophilicity of the systems using the sodium salt can be adjusted by changing the salt/acid ratio. Linearity of the dPIT/dx is analogous to the hydrophilic lipophilic balance (HLB) linearity [48] observed with the Tween/Span mixtures.

**CONCLUSION**

The role of carboxylic acids in SOW systems is complex and it can be compared in some aspects to the alcohols effect. They are able to modify both the polarity of the oil phase and also the interfacial layer behavior. PIT-slope experiments allow to demonstrate that most of them (except acetic acid) enhances the lipophilicity of the $C_{10}E_4$/$n$-octane/water emulsion. The temperature scan for equilibrated systems at a fixed molar fraction of carboxylic acid of 0.2

confirms the PIT-slope results. Even if all acids modify the temperature at which the three phase behavior is obtained, hexanoic acid changes only slightly the third phase volume of the reference system while from octanoic to tetradecanoic acid, there is a dramatic increase of solubility. Alcohols can thus be easily replaced by fatty acids, not only in ionic SOW formulations as pointed out by Lohateeraparp et *al.* [36] but also in nonionic systems.

Emulsification of the Span 80/0.5% CA/octane or isohexadecane/water systems at $f_w = 0.5$ shows that different carboxylic acids are able to modify not only the EACN of the oily phase but also the partition of the surfactant, producing an unexpected inversion behavior. Finally, the influence of mixtures of lauric acid and sodium laurate at different ratios on the PIT of the reference $C_{10}E_4$/*n*-octane/water emulsion exhibits a linear behavior. Temperature insensitive O/W emulsions are obtained when the fraction of sodium laurate is higher than 0.026.

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