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REVIEW OPEN ACCESS

Extended surfactants and their tailored applications for vegetable oils extraction: An overview☆

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Abstract – The vegetable oil extraction process from seeds and nuts depends on mechanical and solvent (usually n-hexane) extractions. Despite the efficiency of n-hexane, its use is nowadays questioned due to health, environmental, and technological issues. As an alternative to hexane extraction, several greener solvents and extraction techniques have been developed and tested during the last decades. Among these alternatives, the Surfactant-Aqueous Extraction Process (SAEP) appears as a promising method. Initially developed for the petroleum sector, this method was then tested and optimized for vegetable oil extraction. Successful implementations at the laboratory scale led to slightly more than 90% oil yield, mainly by using so-called “extended surfactants”. Compare to conventional surfactants, these surfactants can efficiently solubilize a large amount of vegetable oil in water, despite the structural diversity and the bulkiness of vegetable oil molecules. The present review is devoted to extended surfactant applications to SAEP. This review summarizes and discusses the main findings related to the extended surfactant structures and properties, as well as the main experimental results on the SAEP, and the advantages and the current limitations towards a scaling-up of this promising process.

Keywords: Extended surfactants / aqueous extraction / vegetable oils / microemulsions

Résumé – Les tensio-actifs rallongés, alternative prometteuse pour l’extraction des huiles des végétales : Revue. Le procédé d’extraction d’huile végétale, à partir de graines oléagineuses et de noix, dépend de deux méthodes d’extraction : mécanique et par solvant (généralement le n-hexane). Malgré l’efficacité de l’hexane, son utilisation est associée à des risques pour la santé, des enjeux environnementaux et des contraintes technologiques. Pour trouver une alternative à l’extraction à l’hexane, plusieurs solvants et techniques d’extraction plus écologiques ont été développés et testés au cours des dernières décennies. Parmi ces alternatives, le procédé d’extraction aqueuse assitée par des tensioactifs (SAEP) apparaît comme une méthode prometteuse. Initialement développée pour le secteur pétrolier, cette méthode a ensuite été testée et optimisée pour l’extraction d’huile végétale. Des expériences réussies à l’échelle laboratoire ont conduit à un peu plus de 90 % de rendement en huile, principalement en utilisant des tensioactifs « rallongés ». Comparés aux tensioactifs conventionnels, ces tensioactifs peuvent solubiliser efficacement une grande quantité d’huile végétale dans l’eau, malgré la diversité structurelle et l’encombrement stérique des molécules constitutives des huiles végétales. La présente revue est consacrée aux tensioactifs étendus appliqués au SAEP. Cette revue résume et discute des principales conclusions rapportées dans la littérature concernant les structures et propriétés des tensioactifs rallongés ainsi que les principaux résultats expérimentaux sur le SAEP et, enfin, les avantages et les limites actuelles vers une intensification de ce processus prometteur.

Mots clès : Tensioactifs rallongés / extraction aqueuse / huiles végétales / microemulsions

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☆ Contribution to the Topical Issue “Technological challenges in oilseed crushing and refining / Défis technologiques de la trituration et du raffinage des oléagineux”.

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1 Introduction

Several industrial sectors, such as oleo-chemistry, cosmetics, energy, and food, use vegetable oils. Nowadays, to obtain vegetable oils from oilseeds and nuts, mechanical extraction and hexane extraction are industrially used. Mechanical extraction is generally considered the most efficient technique to recover virgin oil from high oil content seeds ($> 20\%$) (Ionescu *et al.*, 2013; Bogaert *et al.*, 2018). The resulting pressed cake is usually defatted by the subsequent n-hexane extraction to dissolve the remaining oil, generating a low oil-content meal (Mhemdi *et al.*, 2016). Industrially, n-hexane is the most widely used solvent for oil extraction despite the health, environmental and qualitative issues linked to its use. Such drawbacks have encouraged both researchers and crushing industries to investigate and evaluate novel methods that meet the requirements of a green process concept. In this context, the literature proposes many alternatives, such as the use of greener organic solvents (*e.g.* isopropanol, ethanol) (Baümler *et al.*, 2016; Toda *et al.*, 2016; Capellini *et al.*, 2019), the use of supercritical fluid (sc-CO_2) (Marrone *et al.*, 1998; Bravi *et al.*, 2002; Han *et al.*, 2009; Koubaa *et al.*, 2016; Mhemdi and Vorobiev, 2019), or the implementation of aqueous extraction assisted either by enzymes (Rosenthal *et al.*, 1996; Jiang *et al.*, 2010; Yusoff *et al.*, 2015; Campbell *et al.*, 2016; Liu *et al.*, 2016a, b; Casas and González 2017) or surfactants (Do and Sabatini 2010; Kadioglu *et al.*, 2011; Petts *et al.*, 2017).

The use of an aqueous solution was first pointed out as a promising alternative to n-hexane by researchers 50 years ago (Cater *et al.*, 1974). Those works have shown that aqueous extraction could overcome the drawbacks mentioned above while maintaining a low capital cost. However, simple aqueous extraction presents some limitations. Among them is the low extraction yield, which blocks the development of this technology (Cater *et al.*, 1974). The limited extractability of oil by water results from the immiscibility of water and oil: the high interfacial tension (IFT) between oil and water (around 19–24 mN/m) keeps them apart (Gaonkar, 1989). Consequently, decreasing the IFT seems an effective solution in order to make the aqueous extraction possible. Surface-active agents, also known as surfactants, decrease the IFT thanks to their amphiphilic structure that confers them the property to adsorb to the oil/water interface. Although the originality and the interest of the concept, the implementation of this extraction method is very challenging because many constraints should be considered. The first difficulty is to find the right surfactant molecule able to solubilize vegetable oils in the water at a sufficiently high level. Vegetable oils are mostly mixtures of triglycerides molecules that are composed of three fatty acids bound to a glycerol molecule. Triglycerides are highly hydrophobic, due to medium to long alkyl chains (8 to 22 carbons) of their constitutive fatty acids, but with a dual light hydrophily associated with the glycerol region (Fig. 1). Besides, within the same oil species, the fatty acids can be saturated or not, branched or not, which leads to a large variety of molecular structures. In other words, vegetable oils are made of various bulky molecules not easily solubilized in water.

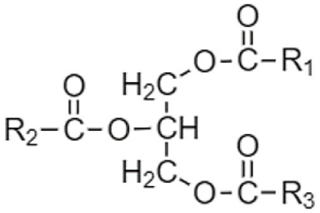

Fig. 1. Triglyceride semi-structural formula with three fatty acid chains ($R_{1,2,3}$).

Due to their varied chemical structure and their bulkiness, triglycerides interact less easily with the tail of surfactants than short-chain oils like alkanes (Raman *et al.*, 2003; Gadhave and Waghmare, 2014). Thereby, conventional surfactants cannot solubilize vegetable oils to a high level due to their preferential interaction with the side of the water at the interface. Increasing the interaction of the surfactants with the oil side could be achieved by increasing the length of their lipophilic chain (Joubran *et al.*, 1993; Doan *et al.*, 2003). However, such an elongation decreases their water solubility and thus weakens their ability to decrease the IFT.

To increase the lipophilic character of a surfactant without sacrificing its water solubility, Miñana-Perez *et al.* proposed in 1995 a new class of surfactants named “Extended surfactants”. These surfactants include an intermediate polarity spacer between the hydrophilic head and the lipophilic tail. The innovation followed around twelve years of research work aiming at attaining high solubilization of natural bulky oils, like mono/di/triacylglycerols, for veterinary preparations that should be soluble in the blood (Salager *et al.*, 2019). Such a molecular structure provides the surfactants the capacity to achieve an ultralow IFT ($\leq 10^{-2}$ mN/m) between the water and a wide range of oils, including triglycerides. Reducing the IFT to such low values enables the formation of so-called “microemulsions”, which are ideal systems for a co-solubilization of the oil and the water (Salager *et al.*, 2001). Today, the Scopus database references more than 3000 scientific papers related to extended surfactants, among which only about 30 deal with vegetable oils.

In 2010, Do and coworkers published the first paper proving that vegetable oil extraction with an aqueous medium was achievable with a satisfying oil yield (at least 93% oil yield from peanut and canola) at lab-scale thanks to the use of extended surfactants. The surfactants used were principally sulfated molecules. These results were possible only with formulations leading to the lowest IFT between water phase and vegetable oil *i.e.* microemulsions. Furthermore, the method led to a significantly better oil quality in terms of clearness, odor, and free fatty acids content, without any additional purification or refining steps, compared to the conventional n-hexane extraction method. During these last ten years, only a few studies dealing with the use of extended surfactants for vegetable oil aqueous extraction were published (Naksuk *et al.*, 2009; Phan *et al.*, 2010a, b; Kadioglu *et al.*, 2011; Do and Sabatini 2011; Do *et al.*, 2014a, b; Petts *et al.*, 2017). In this line, this review presents (1) the characteristics and properties of extended surfactants, especially their interfacial properties in water/vegetable oils systems,

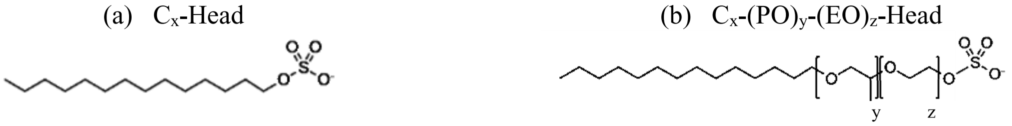

Fig. 2. Typical formulas of conventional (a) and extended (b) surfactant molecules. Case of sulfate headed C_{12} surfactants.

(2) the current insights on Surfactant-Aqueous Extraction Processes (SAEP) of vegetable oils, and finally (3) the limits to be overcome towards the industrialization of this novel extraction method.

2 Extended surfactants and their interfacial properties

2.1 Chemical structure, nomenclature and main functions of the chemical extension

2.1.1 Chemical structure and nomenclature

Conventional surfactants are amphiphilic molecules made of a lipophilic hydrocarbon chain (having typically 10 to 20 $-CH_2-$ units) directly connected to a hydrophilic polar head group (Fig. 2a). Depending on the charge of the polar head, surfactants are classified into nonionic, anionic, cationic, or zwitterionic. In comparison to conventional surfactants, extended surfactants contain intermediate polar groups, such as polypropylene oxide $(PO)_y$ and/or polyethylene oxide $(EO)_z$, inserted between the hydrophilic head and the lipophilic tail as illustrated in Figure 2b.

The concept suggests that PO and EO groups increase the oil/water interaction on each side of the interface. The literature review shows that *x, y*, and *z* vary considerably in number from one paper to another, going respectively from generally 10 to 18 for the carbon number (x), from 2.9 to 18 for the PO groups (y), and from 0 to 5 for the EO groups (z). On the contrary, the polar head is much less varied: it can be nonionic, *i.e.* with an alcohol ethoxylate at the end (*i.e.* EO_z–Head, with Head = OH), but in most of the papers related to SAEP, it is sulfated (Tab. 1).

2.1.2 Main functions of the PO/EO intermediate groups

When the polar head of the surfactant is nonionic, it was shown that an increase of the number of EO groups swells the hydrophilic structure of the molecule, and therefore, increases its attraction for the water phase (Miñana-Perez *et al.*, 1996). The cosmetics commonly use such nonionic extended surfactants as skin conditioning or emulsifying agents. More frequently, an ionic group (typically sulfate) is added to the terminal EO group (Tab. 1), conferring to the surfactant a dual nonionic and anionic character (Miñana-Perez *et al.*, 1995) but minimizing the hydrophilic function of EO groups.

Regarding the intermediate PO units, they enlarge the lipophilic character of the surfactant without sacrificing its water solubility. Their role is not limited indeed to an extension of the chain length; the addition of intermediate PO groups provides three beneficial properties compared to the simple addition of $-CH_2-$ groups to the alkyl chain: (i) addition of polarity, (ii) increase of mobility, and (iii) diversification of the 3D conformation:

- With one heteroatom of oxygen for three carbons in a PO unit, the $(PO)_y$ part of the surfactant becomes more accessible to the water than a simple $(-CH_2-)y$ chain. In addition, this part of the surfactant can interact more easily with triglycerides which are both hydrophobic and polar as mentioned above. As a result, the triglycerides can organize themselves with the ester region near the interface, while the three highly lipophilic chains follow the rest of the very lipophilic alkyl chain of the surfactant (Miñana-Perez *et al.*, 1996).
- The oxygen atoms of the first PO groups also tend to be hydrated. This promotes a nonlinear structure (coiling or zig-zag effect) of this part of the surfactant and blurs the interface (He *et al.*, 2014). By this, a much better transition connects the oil and the water compared to the use of conventional surfactants (Klaus *et al.*, 2011). More precisely, PO units thicken the interface (about 30–40 Å for 10 PO units) in comparison to a direct transition, as observed between the very lipophilic tail and the very hydrophilic head of a conventional surfactant (Miñana-Perez *et al.*, 1995).
- The hydrated region of the surfactant tail allows different surfactant conformations at the interface. The various conformations of the surfactants at the same interface simulate a mixture of surfactants, which is known as having higher performances on the decrease of IFT than the use of a solo surfactant (Larpent 1995). For instance, the concentration of surfactant needed to attain the same IFT value is generally lower for a system containing two surfactants compared to a single surfactant (Muherei and Junin 2007). According to Muherei and Junin (2007), this effect is due to synergism mechanisms and conformation adaptation (Muherei and Junin 2007). In addition, in the special case of ionic surfactants, the presence of intermediate PO units increases the bulkiness of the molecules and thus helps to decrease the charge density of the polar heads and the repulsive effects of the same charges (Larpent 1995).

2.2 Surface properties and micellization

The solubility of a surfactant in water depends on its type, structure, and operating conditions such as the temperature. According to Davies (1957), the solubility of anionic surfactants depends on both temperature and salinity, whereas only the temperature significantly changes the solubility of nonionic surfactants. From a structural point of view, the solubility of surfactants in water is inversely correlated to the length of the alkyl chain: the longer the chain, the less water-soluble the surfactant. On this basis, the HLB parameter has been proposed for characterizing this aspect (Davies 1957; Griffin 1949). However, owing to their

Table 1. Extended surfactants investigated in the scientific literature relative to vegetable oils solubilization.

x	*y*	*z*	Head	Oils	References
10	10, 14, 18	2	Sodium sulfate	Triolein, Canola, Peanut, Olive, Corn, Soybean	Do *et al.* (2009)
12	10, 12, 14	2			
16	2.9, 4.5, 5.5, 8.2, 10.7	0			
10	10, 14, 18	2	Sodium sulfate	Triolein, Canola, Peanut	Do and Sabatini (2010)
12	10, 12, 14	2			
16	2.9, 4.5, 5.5, 8.2, 10.7	0			
10	18	2	Sodium sulfate	Peanut, Canola	Do and Sabatini (2011) and Do *et al.* (2014a, b)
10	18	2	Sodium sulfate	Corn	Kadioglu *et al.* (2011)
12–14	10	2			
10	18	2	Sodium sulfate	Cottonseed	Petts *et al.* (2017)
12	6, 10, 14	2	Sodium sulfate	Soy	Miñana-Perez *et al.* (1995)
12	14	2	Sodium sulfate	Canola, Peanut, Triolein	Witthayapanyanon *et al.* (2006)
12–13	8	0			
14–15	8	0			
12–13	4, 8	0	Sodium sulfate	Tricaprylin, Canola	Phan *et al.* (2010a, b)
14–15					
14–15	5, 8	0	Sodium sulfate	Palm kernel	Naksuk *et al.* (2009)
14–15	8	0	Sodium sulfate	Canola	Phan *et al.* (2010a, b)
14–15	8	0	Sodium sulfate	Canola, Peanut, Olive	Phan *et al.* (2010a, b)
14–15	4, 8	0	Sodium sulfate	Canola	Attaphong and Sabatini (2017)
16–17	4	2, 5	Sodium carboxylate	Canola	Attaphong *et al.* (2012)
16–18	4	2, 5			

Table 2. Surface activity parameters of surfactants at 25 °C.

Surfactant	CMC (mmol. l^{-1})	γ_{cmc} (mN.m^{-1})	Γ_{max} x 10^{10} (mol.cm^{-2})	pC_{20}	CMC/C_{20}	A_{min} ($Å^2$)
C_{12}–Sulfate[a]	8.200	39.5	3.16	2.51	2.6	53
$C_{12\text{-}14}$–EO_2–Sulfate[b]	0.349	26.5	3.51	4.70	17.5[c]	47
C_{12}–PO_4–Sulfate[a]	0.420	40.0	1.00	4.44	11.6	166
C_{12}–PO_8–Sulfate[a]	0.078	35.5	1.08	5.47	23.0	154
C_{12}–PO_{12}–Sulfate[a]	0.043	33.7	1.01	5.99	42.2	164

[a] Liu *et al.* (2016a, b).
[b] Lv *et al.* (2018).
[c] calculated from the original data of Lv *et al.* (2018).

specific chemical structure and their resulting complex behavior at interfaces, as previously described, the HLB concept proves to be hardly relevant for extended surfactants in practice.

Beyond that point, structural variations such as the addition of an extension structure into a surfactant molecule impact its surface properties. In particular, this modifies molecular interactions at the interface, and thus affects the two main

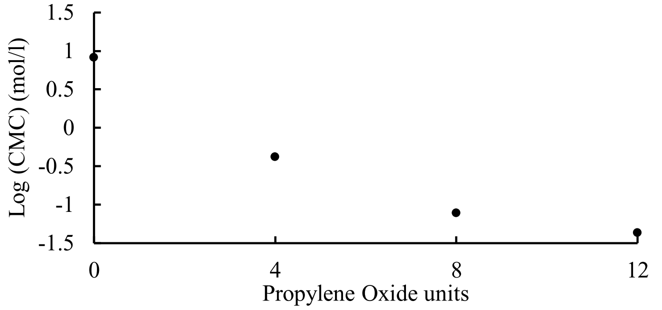

Fig. 3. Log of the molar CMC *vs*. the number of PO units for sulfate headed C_{12} surfactants (adapted from Liu *et al.*, 2016a, b).

properties of surfactants in solution: (i) adsorption at the interface, which at this place provides a decrease of the IFT, and (ii) micellization, which governs the solubilization of non-soluble components over the critical micelle concentration (CMC). For instance, Table 2 details a list of surface properties deduced from the curves of surface tension *versus* the log of the molar concentration of different surfactants. All those properties are detailed below.

2.2.1 Critical micelle concentration (CMC)

The CMC is the concentration of surfactants in a solution above which micelles form. As shown in Table 2, the addition of extension (PO or EO) units into a surfactant molecule generally decreases the CMC (He *et al.*, 2014; Liu *et al.*, 2016a, b; Lv *et al.*, 2018). For instance, Liu *et al.* (2016a, b) have observed a decrease in CMC from 8.2 mmol.L^{-1} for the conventional SDS (C_{12}-Sulfate) to 0.42 mmol.L^{-1} for C_{12}–PO_4–Sulfate (addition of 4 PO units) and down to 0.043 for C_{12}–PO_{12}–Sulfate (addition of 12 PO units). The CMC of surfactants is inversely correlated to the lipophilicity of the molecule (Miñana-Perez *et al.*, 1995). Figure 3 illustrates an example of the $(PO)_y$ contribution to the decrease of the CMC for an extended sodium sulfate surfactant. This figure shows that the decrease of the CMC is the deepest with the addition of the four first PO units and becomes less and less pronounced with the following additions.

2.2.2 Surface tension at CMC

Table 2 also presents the impact of PO and/or EO units' addition on the surface tension at CMC, γ_{cmc}. It is interesting to mention that adding PO units to the surfactant does not change drastically the surface tension at CMC. γ_{cmc} remains practically constant after adding 4 PO and then slightly decreases with the addition of 8 or 12 PO units. In contrast, the addition of EO units to a conventional surfactant affects γ_{cmc}. For instance, adding 2 first EO units to the C_{12}-sulfate greatly reduces the surface tension at CMC from 39.5 to 26.5 mN.m^{-1} (Tab. 2).

2.2.3 Surface excess concentration

Strictly speaking, the surface excess concentration (Γ_{max}) is the difference between the surfactant's interfacial concentration at CMC (saturated surface) or above, and the concentration at a virtual interface inside the bulk phase. Γ_{max} (mol.cm^{-2}) is obtained from a derivate formula of Gibbs equation of energy-isotherm (Eq. (1)):

$$\Gamma_{max} = -\frac{1}{2.303 \cdot n \cdot R \cdot T}\left(\frac{d\gamma}{dlogC}\right)_T, \quad (1)$$

where n refers to the number of species at the surface (2 for univalent ionic surfactants), R is the gas constant (8.314 J.mol^{-1}.K^{-1}), T is the temperature (K), and dγ/dlogC is the slope of the surface tension, γ (mN.m^{-1}), *versus* the log of the surfactant concentration, C (mol.L^{-1}), close to the CMC.

A sharp decrease in surface tension with increasing surfactant concentration (dγ/dlogC) results in a high Γ_{max}. As can be seen in Table 2, the addition of EO units inside the conventional sulfated surfactant molecule does not significantly modify Γ_{max} compared to the addition of PO units. The addition of PO units tends to lower the Γ_{max} due to a smoother decrease of the surface tension. As previously mentioned, the addition of PO groups provides mobility and variability of conformations of the middle part of the surfactant. Therefore, this increases the bulkiness of the molecule. The result is a lower value of Γ_{max}. That means that a lower amount of surfactant is necessary to saturate the interface compared to the conventional surfactant (like SDS). Conventional surfactants require more molecules to complete this process. However, according to Table 2, the effect of PO insertion on Γ_{max} is only noticeable for the first 4 added units. This observation suggests that only the first PO groups would impact the steric hindrance at an interface, while the additional PO units might play a greater role on the nonpolar side of the interface.

2.2.4 Minimal cross-sectional molecular area

Another surface property impacted by adding PO groups is A_{min}, the minimal cross-sectional area of the molecule at the interface. A_{min} is obtained from Γ_{max}, using equation (2):

$$A_{min} = \frac{1}{N_A \cdot \Gamma_{max}}, \quad (2)$$

where N_A is the Avogadro's constant (6.022×10^{23} mol^{-1}).

The insertion of PO units increases the molecule size but also its cross-sectional area (Tab. 2). This is following the observed decrease of Γ_{max}. As previously mentioned, this is due to the increased mobility at the interface and the resulting disordered conformations induced by the presence of the intermediate PO groups. However, adding 4 PO units seems enough to ensure this effect (Tab. 2). Over that number, increasing the number of PO units does not affect A_{min}. The longer length of such extended surfactants means that they are likely to penetrate more deeply into oil and water phases.

2.2.5 "pC_{20}" and CMC/C_{20}

The pC_{20} is a surface activity parameter defined as the log of the surfactant concentration needed to reduce by 20 mN.m^{-1} the surface tension of the water, C_{20} (Liu *et al.*, 2016a, b) (Eq. (3)):

$$pC_{20} = -logC_{20}. \quad (3)$$

Table 3. CMC and A_{min} of surfactants with different extensions and ionic heads (adapted from Forgiarini *et al.* (2010)).

C12 (PO_7/EO_7) Head	$PO_7 + EO_7$ Sequential distribution		$PO_7 + EO_7$ Homogenous distribution	
	CMC (mmol/L)	A_{min} ($Å^2$)	CMC (mmol/L)	A_{min} ($Å^2$)
–	0.11	65	0.23	80
Carboxylate	0.19	170	0.30	200
Sulfate	0.30	230	0.46	270
Disodium phosphate	2.0	720	4.0	710
Disodium phosphate with 0.5 mol/liter NaCl	0.22	85	0.20	83

As depicted in Table 2, adding EO or PO units increases the pC_{20}. This indicates that extended surfactants are more effective than conventional ones for decreasing the surface tension.

The CMC/C_{20} ratio is a parameter that indicates if the surfactant preferably adsorbs to the surface or aggregates into micelles. A high CMC/C_{20} ratio reflects a high adsorption capacity of the surfactant to the interface. On the contrary, a small ratio indicates a high micellization capacity of the surfactant. Table 2 shows that the CMC/C_{20} increases quasi-proportionally with the increase of PO units. This increase indicates stronger adsorption to the surface than micellization capacity in the case of extended surfactants, as mentioned by Liu *et al.* (2016a, b). The result will be a higher cohesion of the immiscible phases, especially in the case of liquid/liquid systems.

2.2.6 Influence of the polar head and the EO/PO distribution in the molecule

Forgiarini *et al.* (2010) have determined the CMC and the surface cross-sectional area, A_{min}, of different extended surfactants. They showed that the CMC depends on the surfactant size, the number of PO and EO units, but also on the polar head type (Tab. 3). A larger head increases the CMC, whereas a longer tail decreases it, as widely observed with conventional surfactants. On the other hand, a carboxyl head which is more oil-soluble than a sulfate head appears to be more suitable to increase the hydrophobicity of a surfactant (lower CMC) than a sulfate head. This is in accordance with the work of Attaphong *et al.* (2012).

Forgiarini *et al.* (2010) also studied the impact of the distribution (homogenous *versus* sequential) of PO and EO units in the intermediate section (Fig. 4). They reported that homogenous species have a higher cross-sectional molecular area than their sequential counterpart. The authors explained this result by stronger interactions with water in the case of the homogenous arrangement. Since the water can hydrate a greater proportion of the tail, this would compress the tail further onto the interface, creating a larger surface aggregate.

2.3 Aqueous phase formulation for oil solubilization

2.3.1 Role of salts and alcohols

Finding the optimal formulation of the aqueous phase containing the surfactant is the first step to successfully solubilize the oil. In practice, salts and alcohols are often added to surfactant solutions to improve their interfacial properties and thus decrease both the CMC (Larpent, 1995) and the surface or interfacial tension (He *et al.*, 2014). The principal salts used are NaCl, $CaCl_2$, and KCl. Monovalent salts are, however, preferred since divalent ions can cause surfactant precipitation (Negin *et al.*, 2017). Salts impact the electrostatic repulsions of the head groups in the case of ionic surfactants (Doan *et al.*, 2003) but also the steric repulsion between tails (He *et al.*, 2014). They also stretch the carbon chains further into the lipophilic phase (salt-out effect) (He *et al.*, 2014). In addition, salt solubilization in an aqueous solution decreases its water activity and consequently the ability of the water to interact with the surfactant (Salager *et al.*, 2001). All that induces a more lipophilic behavior of the surfactant by pushing it out of the aqueous phase. However, in practice, adding a high amount of salts in an industrial process may be very problematic owing to their corrosive effect, cost, and mainly the complexity of their elimination during the downstream purification process.

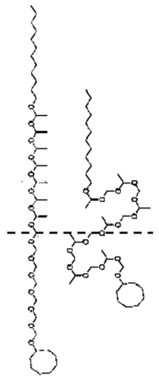

Fig. 4. Extended surfactants adsorbed at the interface: C_{12}–PO/EO-sulfate with sequential (left) and homogeneous (right) PO/EO distribution (adapted from Forgiarini *et al.* (2010)).

Alcohols are also frequently used with surfactants in formulations. Those ranges more often from ethanol to medium chain length alcohols like octanol and decanol (Melo-Espinosa *et al.*, 2015; Salager *et al.*, 2001; Abbasi and Mohsen, 2016). Generally, short-chain alcohols are easily solubilized in the water, while long-chain alcohols have a reverse behavior, in favor of the lipophilic phase. The medium-chain alcohols are located at the interface, where they can more efficiently soften the interfacial film (Salager *et al.*, 2001). In other words, alcohols play the role of co-surfactants. However, alcohols do not have a direct impact on IFT (Salager *et al.*, 2001).

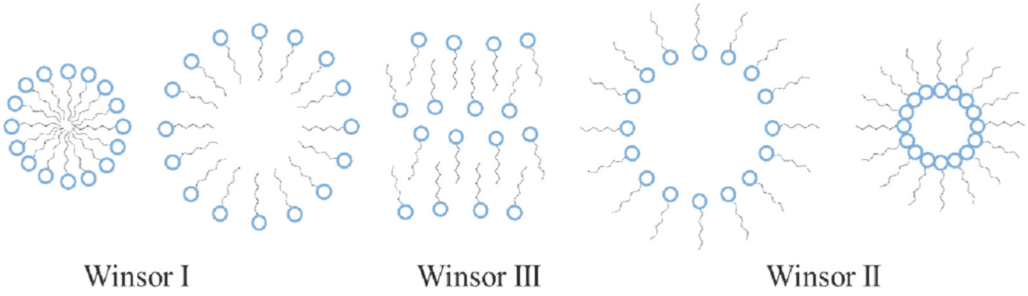

Fig. 5. Schematization of the Winsor transition at one micelle scale.

The addition of alcohol favors the deconstruction of the interfacial film and avoids some undesirable phenomena like crystallization and gelling (Doan *et al.*, 2003; Tongcumpou *et al.*, 2006). Moreover, alcohol can reinforce the effect of salts and increase the solubility of the surfactants in the lipophilic phase.

2.3.2 Formulation methods

Many formulation methods have an interest in reducing the concentration of salt, alcohol, and surfactant while attaining ultralow IFT ($< 10^{-2}$ mN.m^{-1}). At such low IFT, systems of oil and water are named "microemulsions" (Salager, 2000). Microemulsions can be oil in water (Winsor type I) or water in oil (Winsor type II) but only at a very special formulation of the water phase (giving the lowest IFT) the oil-water system is bicontinuous and is called "Winsor type III microemulsions" (Winsor, 1954; Martellucci and Chester, 1989; Salager, 2000). Winsor III microemulsions are characterized by the coexistence of oil and water phases at a quasi-molecular scale, in nanodomains of typically 5 to 50 nm (Salager *et al.*, 2001). In this case, oil and water phases mix themselves spontaneously without any external energy supply (Nishimi, 2008). Thus, the obtained homogeneous and transparent system is thermodynamically stable. It was soon found that the best conditions to attain an ultralow IFT coincide with the Winsor type III physicochemical situation in which a bicontinuous microemulsion is obtained. Such a case was called "optimum formulation" since it was associated with the successful mobilization of petroleum (Salager, 2000). As a rule, the choice of salt, alcohol, and surfactant type, and their optimal concentration depend on the physicochemical characteristics of the target microemulsion (Gadhave and Waghmare, 2014). Since the Bancroft rule of surfactant solubility in the continuous phase, five empirical correlations have been proposed to formulate microemulsions: Winsor R-ratio, Hydrophilic-Lipophilic Balance (HLB), Phase Inversion Temperature (PIT), Net-Average Curvature model (NAC), and Hydrophilic-Lipophilic Deviation (HLD) (Salager *et al.*, 2001; Witthayapanyanon *et al.*, 2008). However, most of the empirical correlations have their limitations. Nowadays, the most complete method is the latest one, *i.e.* HLD, based on a summation of every contributing part of the system (Salager *et al.*, 2001).

2.3.3 Hydrophilic-Lipophilic Deviation (HLD) formulation concept

The HLD concept has been developed based on many experimental "formulation sweeps" in the domain of alkanes and crude oils. The objectives were to better understand and model the impacts of every formulation variable and eventual compensation between each other. This concept is summarized in two algebraic summations (Eqs. (4) and (5), for ionic and nonionic surfactant, respectively) that have been proved relevant in many cases for around forty years, especially in the petroleum application field (Salager *et al.*, 2019):

$$HLD_i = \sigma + \ln Salt - k \cdot EACN + t \cdot \Delta T + a \cdot A, \tag{4}$$

$$HLD_n = \alpha - EON + \mathrm{b} \cdot Salt - k \cdot EACN + t \cdot \Delta T + a \cdot A, \tag{5}$$

with:
- i, n: Ionic, nonionic
- σ, α, k, t: Surfactant parameters
- Salt: Mass percentage of salt
- EACN: Equivalent Alkane Carbon Number of the oil phase
- a: Alcohol constant
- A: Mass percentage of alcohol
- ΔT: Temperature deviation from 25 °C
- EON: Number of ethylene oxide groups in nonionic surfactants
- b: Salt constant

(The variable EACN will be discussed more deeply in the next part of the paper).

Winsor type III bicontinuous microemulsions correspond to HLD = 0 whereas HLD < 0 indicates a Winsor type I microemulsion (oil in water), and HLD > 0, a Winsor type II (water in oil microemulsion). The HLD equation shows that an increase of the variables: Salt, ΔT or A, or a decrease of the variable EACN, causes an increase of HLD. Thus a transition from a Winsor Type I (oil in water microemulsion, HLD < 0) to a Winsor Type III (bi-continuous microemulsion, HLD = 0), and finally to a Winsor Type II (water in oil microemulsion, HLD > 0) system can be observed by varying one single formulation variable (Fig. 5). Ionic surfactants generally react more significantly to electrolyte variations. Nonionic surfactants are more likely to exhibit noticeable transitions over temperature variations, as predicted by the PIT theory. According to the concept, the deviation of HLD from 0 means a deviation from the optimal formulation where the IFT is minimal and the curvature of the interface is zero (Fig. 5). Optimum also means equal quantities of oil and water mutually solubilized into the microemulsion.

Each surfactant at a given concentration, with given salt and alcohol, has its optimal formulation for a given oil.

However, the HLD equations (4) and (5) do not consider the dependency on the surfactant concentration yet.

In practice, the optimal formulation is generally achieved thanks to formulation sweeps that means a progressive increase (or decrease) of one formulation variable at a time in a series of formulations (Salager, 2000). Salt (NaCl) is frequently used as the main experimental variable when the formulation allows it. The optimal salinity (S*) is then defined as the salt concentration needed to give a Winsor type III microemulsion (*i.e.* minimal IFT). According to Miñana-Perez *et al.* (1995) increasing the number of PO units in a surfactant molecule decreases the optimal salinity. Thus, PO-extended surfactants appear more suitable at an industrial level because of the lesser needs in salinity to decrease the IFT.

2.4 Optimal formulation and related interfacial properties with vegetable oils

2.4.1 Optimal formulation from the HLD concept

At the interface between oil and water, the surfactant properties, interactions, and conformation are affected by different parameters. Depending on the oil chemical composition, interactions with the surfactant chain (especially London-type interactions) determine the oil ability to integrate into a micelle. In the case of vegetable oils, those properties mainly depend on the length and the saturation of the fatty acids, but also the presence of branched groups that could improve or deteriorate the interactions with the surfactant. In the HLD method, the equivalent alkane carbon number (EACN) of the oil considers all those chemical variations. EACN of oil corresponds to the carbon number of the n-alkane exhibiting a hydrophobicity equivalent to that of the oil under study. Thanks to formulation sweeps, correlations have been established for triglycerides between EACN and the main structural characteristics of their fatty acids (Witthayapanyanon *et al.*, 2006) (Eq. (6)):

$$EACN_{triglycerides} = 2.05 \cdot ASC + 0.071 \cdot UC - 24, \qquad (6)$$

where ASC is the average length of saturated chain and UC is the percentage of unsaturated chains.

The negative constant term in equation (6) (−24) comes from the presence of the glycerol group which provides the polarity to the molecule (Witthayapanyanon *et al.*, 2006). EACN of vegetable oils ranges from 13 (palm oil) to 22 (peanut oil), as shown in Table 4. Compared to the carbon number of standard alkanes, the high EACN values observed for triglycerides result from the high hydrophobicity of long fatty acids, characteristic of vegetable oils (Do *et al.*, 2009).

According to the HLD method, the optimal concentration of salt (S*) needed to obtain a microemulsion with the lowest IFT (Winsor type III, HLD = 0) is directly correlated with the EACN. In the case of ionic surfactants, the relationship is shown in equation (7):

$$\ln S^* = k \cdot EACN - \sigma, \qquad (7)$$

where k and σ are parameters of the surfactant, for a solution without alcohol at 25 °C.

Figure 6 shows the correlations between lnS* and EACN for a conventional surfactant (dihexyl sulfosuccinate (Aerosol-MA)) and two extended surfactants. This figure further illustrates the relevance of using extended surfactants instead of conventional ones for solubilizing vegetable oils whose EACN are generally high (13 to 22). Extrapolation of the line corresponding to the conventional surfactant indicates that such a surfactant would require theoretically a very high salt concentration (in the range 24%–114%) for attaining the optimal formulation (minimal IFT), which is industrially inapplicable. On the contrary, extended surfactants allow bi-continuous microemulsion formation *i.e.* minimal IFT with vegetable oils using salt concentrations comparable to those required for alkanes with conventional surfactants.

Table 4. Calculated EACN of vegetable oils according to their average length of saturated chain (ASC) and percentage of unsaturated chains (UC) according to equation (6) (adapted from Witthayapanyanon *et al.* (2006)).

Oils	ASC	UC (%)	EACN calculated
Soy oil	16.5	85	16
Corn oil	16.3	87	16
Canola oil	16.6	94	17
Sunflower oil	16.8	88	17
Peanut oil	19.5	82	22
Palm oil	16.1	50	13

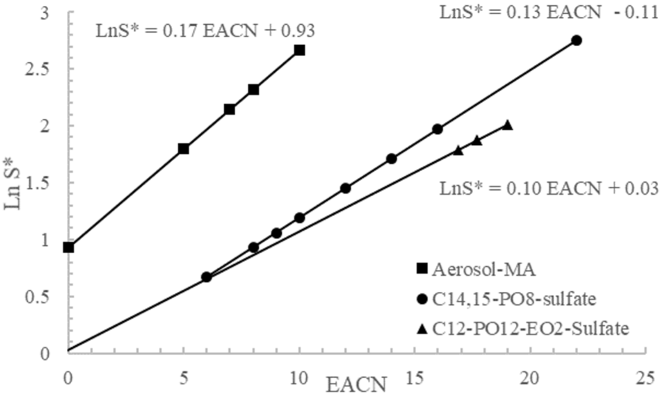

Fig. 6. HLD correlation between EACN and optimum salinity of conventional Aerosol-MA surfactant (adapted from Witthayapanyanon *et al.*, 2008), $C_{14,15}$–PO_8–sulfate (adapted from Phan *et al.*, 2010a, b), and C_{12}–PO_{12}–EO_2–sulfate (adapted from Do *et al.*, 2009).

Concerning the slope of the lines in Figure 6, *i.e.* the *k* surfactant parameter (Eq. (7)), it is 0.17 for the conventional surfactant and 0.10–0.13 for the extended ones. Conventional surfactants have generally a *k* value ranging from 0.10 to 0.19 (Salager *et al.*, 2001). That means that optimal salinity increases generally more quickly with an increase of EACN in the presence of conventional surfactants than in the presence of extended ones. Besides, according to the Figure 6, the lines in the case of extended surfactants experienced a downward translation. This indicates a lower value of the other surfactant parameter, σ, for the extended surfactants compared to conventional surfactants.

Table 5. Optimal NaCl concentration (S*) and optimal interfacial tension (IFT*) with triolein oil at 25 °C for three homologous series of extended surfactants at 0.1 wt% (adapted from Do and Sabatini, 2010).

Surfactant series	S* (wt%)	IFT* (mN.m^{-1})
1. Alkyl propoxylate surfactant		
C_{16}-xPOsulfate		
C16–2.9PO	2.0	0.052 ± 0.0021
C16–4.5PO	3.0	0.039 ± 0.0013
C16–5.5PO	2.0	0.033 ± 0.0033
C16–8.2PO	1.3	0.13 ± 0.0026
C16–10.7PO	0.60	0.043 ± 0.0009
2. Alkyl propoxylate ethoxylate surfactant		
C10–xPO–2EOsulfate		
C10–10PO–2EO	2.5	0.0090 ± 0.0004
C10–14PO–2EO	2.0	0.0037 ± 0.0011
C10–18PO–2EO	0.50	0.0014 ± 0.0015
C12–xPO–2EOsulfate		
C12–10PO–2EO	3.5	0.0031 ± 0.0014
C12–12PO–2EO	2.5	0.0023 ± 0.0018
C12–14PO–2EO	0.50	0.0017 ± 0.0006

2.4.2 Interfacial properties of optimal aqueous formulations-vegetable oils systems

Do and Sabatini (2010) have measured the IFT of the optimal formulation for a large series of extended surfactants (Tab. 5). Table 5 shows a general decrease in IFT with increasing the number of PO units. However, in the case of the non-ethoxylated extended surfactant with the longest alkyl chain, the decrease of IFT is not anymore possible beyond 5.5 PO units, even by adding more PO units. In addition, even though the IFT decreases somewhat, it is not in the range of ultra-low IFT. However, decreasing the chain length to 12 or 10 carbons and adding PO units allows attaining such low optimal values. That confirms the benefits of surfactant extension with intermediate PO units.

3 Extended surfactants and vegetable oil extraction

3.1 Surfactant-assisted aqueous extraction process

Using surfactants for oil extraction was first studied and implemented at the beginning of the 20th century in the petroleum sector to enhance oil recovery (EOR) (Negin *et al.*, 2017). In the petroleum extraction process, chemicals are commonly used to enhance the pumping capacity of the oil field. The injection of a chemical solution made of detergent-type compounds improves the displacement efficiency and minimizes the capillary forces by lowering the IFT to ultra-low levels (Donaldson *et al.*, 1985; Santanna *et al.*, 2009; Negin *et al.*, 2017).

The success of surfactant-assisted aqueous extraction in the petroleum field has inspired researchers to test this process for the extraction of vegetable oils. To lower the IFT, the first works have used conventional surfactants, which led to high surfactant and salt concentrations, and co-surfactant (like organic solvent) requirements. Different improvements were then suggested. The main improvement has been to achieve ultra-low IFT by using extended surfactants instead of conventional ones as proposed by Do and Sabatini (2010).

The surfactant-aqueous extraction process (SAEP) applied to vegetable oils is a multi-stage process, as depicted in Figure 7. The multi-stage counts two main steps, which are the (1) extraction and (2) separation (Radi *et al.*, 2013). For the extraction step, the surfactant solution completely floods the pretreated-oil-bearing materials. The type of added surfactant depends on the composition of the oil to be extracted. The extraction involves the solubilization of the oil into the optimal surfactant solution thanks to the ultra-low IFT, as previously defined. To extend the mobilization of the oil, the system is stirred for a given period (2 h maximum). This extraction time is considered short by comparison to the Enzyme-Assisted Aqueous Extraction Process (EAEP) duration (up to 36 h) (Yusoff *et al.*, 2015). The oil and the water form a cloudy mixture that should be separated and purified to obtain a free oil phase. For the separation step, the first stage aims to separate the solid and the liquid phases. This first separation is generally performed by centrifugation. The two separated products are: an insoluble fraction made of solid residue and a liquid supernatant. The liquid contains the extracted oil and the surfactant solution. Three layers are generally observed in the liquid phase, based on the density: (i) a free oil layer, (ii) an emulsion of the oil and the aqueous solution, and (iii) the surfactant solution. Nevertheless, both fractions (liquid and solid) need a second separation step, which enables the determination of the yield of the process thanks to the mass balance.

3.2 Operating conditions

The process efficiency depends on many parameters, such as the type of surfactant, the raw material, and the extraction

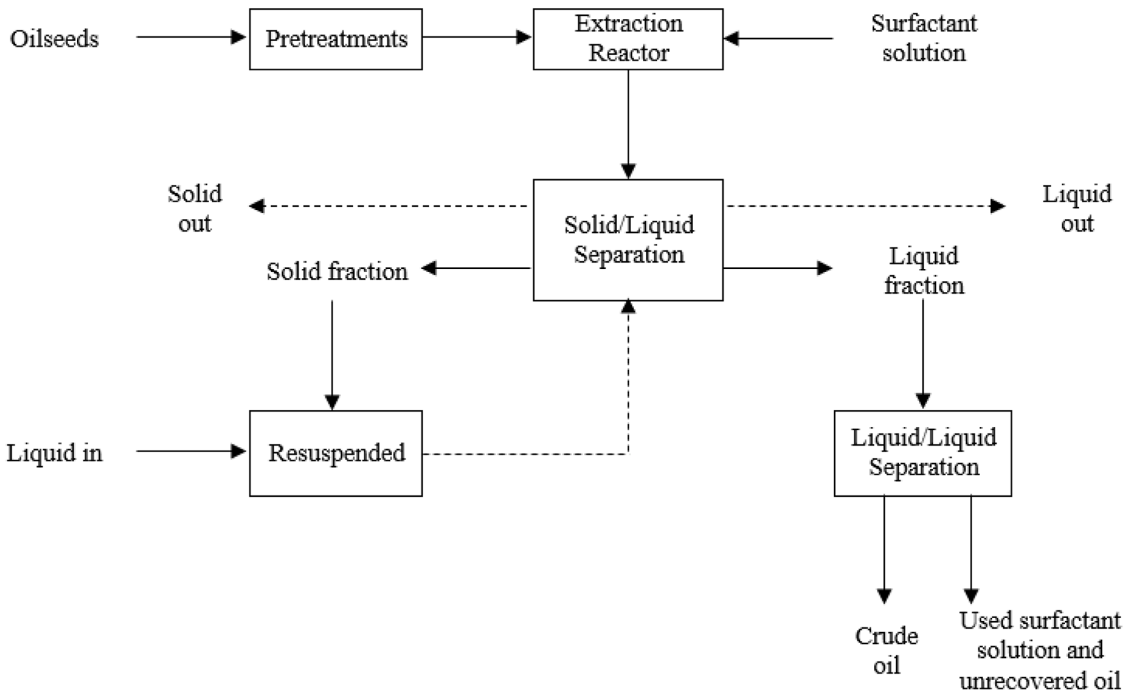

Fig. 7. Example of a typical SAEP (adapted from Do and Sabatini (2011)).

Table 6. Characteristics of studied raw materials.

Oil-bearing material	Pretreatments	Type of oil	Initial oil content (%)	References
Whole seeds	Deshelled, dehulled, grounded, dried, de-linter, steamed, flaked, extruded, and/or crushed	Peanuts	42–47	Do and Sabatini (2010, 2011), Nguyen *et al.* (2010) and Pauzan *et al.* (2013)
		Canola	40–52	Do and Sabatini (2010, 2011), Tuntiwiwattanapun *et al.* (2013) and Radi *et al.* (2013)
		Corn	17	Kadioglu *et al.* (2011)
		Soy	18.9 wt	Do *et al.* (2014a, b)
		Palm kernel seeds	48–59	Pauzan *et al.* (2013) and Naksuk *et al.* (2009)
		Shale sludge	40.54	Qin *et al.* (2015)
		Walnuts	–	Chen *et al.* (2018)
		Cottonseeds	33	Petts *et al.* (2017)
White fabric	Pre-washed in deionized water, ironed, cut, soiled with oil by complete submersion (1 min), hung to dry and equilibrate overnight	Jojoba	26	Do *et al.* (2014a, b)
		Canola	0.2–24	Phan *et al.* (2010a, b) and Do *et al.* (2014a, b)
		Coconut	0.3–25	Phaodee *et al.* (2019) and Do *et al.* (2014a, b)
		Palm kernel	24	Do *et al.* (2014a, b)
Press cake	Grounded and pressed	Palm mesocarp fiber	5–11	Ramly *et al.* (2017)

operating conditions (solid to liquid ratio (SLR), shaking speed, and extraction time). Most of the published works concerns process optimization using single-factor experiments mainly.

3.2.1 Raw material

The literature review shows that oil extraction using SAEP was performed from crude seeds or pressed cake obtained after

Table 7. Characteristics of optimal surfactant formulations.

Surfactant		Other components	References
Structure	Concentration (%)		
C_{10}–PO_{18}–EO_2–SO_4Na	0.5	–	Petts *et al.* (2017)
	0.4	1% NaCl	Kadioglu *et al.* (2011)
	0.15	5–6% NaCl	Do and Sabatini (2010, 2011)
0.26 C_{10}–PO_{18}–EO_2–SO_4Na/0.74 SDOSS	1	0.5% NaCl	Do *et al.* (2014a, b)
$C_{14\text{-}15}$–PO_8–SO_4Na	0.1	14% NaCl	Phan *et al.* (2010a, b)
	0.1	4% NaCl 90 mM 1-octanol	Phaodee *et al.* (2019)
0.03 $C_{14\text{-}15}$–PO_8–SO_4Na/0.97 Comperlan KD	3.1	20% NaCl	Naksuk *et al.* (2009)
Brij 30	0.5	–	Pauzan *et al.* (2013)
SDS	0.6	–	Tuntiwiwattanapun *et al.* (2013) and Qin *et al.* (2015)
Tween 80	1	6% NaCl	Ramly *et al.* (2017)
Span 20	1.9	1 mol/L sugar	Chen *et al.* (2018)
Lecithin	40	20% Propanol	Radi *et al.* (2013)
0.24 Rhamnolipid/0.38 Lecithin/0.38 Sophorolipid	1.31	2.5% NaCl	Nguyen *et al.* (2010)
0.21 Oleyl alcohol/0.35 SBDHS/0.44 Rhamnolipid	1.62	9% NaCl	Nguyen *et al.* (2010)

mechanical extraction (Naksuk *et al.*, 2009; Do and Sabatini, 2010, 2011; Nguyen *et al.*, 2010; Kadioglu *et al.*, 2011; Tuntiwiwattanapun *et al.*, 2013; Radi *et al.*, 2013; Pauzan *et al.*, 2013; Do *et al.*, 2014a, b; Qin *et al.*, 2015; Petts *et al.*, 2017; Chen *et al.*, 2018). Moreover, some authors tested the applicability of the SAEP to clean white fabrics soiled with different vegetable oils. Table 6 presents the most relevant works. Generally, seeds are first grinded in order to facilitate the oil release during the extraction step. The grinded seeds have generally a 21 to 42 µm particle size based on the US standards of vegetable oilseed size (Kadioglu *et al.*, 2011). The soiled fabrics (3 to 4 inches in size) represent laundry experiments from which the agent to clean is the vegetable oils (Phan *et al.*, 2010a, b; Do *et al.*, 2014a, b). Even though the soiled fabrics have a lower initial oil content, it is interesting to mention that the last oil residue remaining in the material was also accessible and extracted by this process (Phan *et al.*, 2010a, b; Do *et al.*, 2014a, b). The studies experiences with soiled fabrics showed an average oil yield of 93.4 ± 2%. Finally, only Ramly *et al.* (2017) used a pressed cake as raw material. As mentioned earlier, mechanical extraction produces a high-quality oil with efficiency and in an environmentally friendly manner. Therefore, there is no need to eliminate this step from the process. In this case, to prepare the pressed cake, a simple crushing step reduces the material to several millimeters in size.

3.2.2 The surfactant solutions

Table 7 shows the different surfactant solutions used in the literature. Those can be splitted into four classes depending on the type of surfactant used. Several authors have chosen to use conventional surfactants for their eco-friendly quality or their easy-to-find advantage since they are already commercialized: Pauzan *et al.* (2013), Radi *et al.* (2013), Tuntiwiwattanapun *et al.* (2013), Qin *et al.* (2015) Ramly *et al.* (2017) and Chen *et al.* (2018) used conventional surfactants alone whereas Nguyen *et al.* (2010) used them in mixture. A few authors used extended surfactants, either alone (Do and Sabatini, 2010, 2011; Kadioglu *et al.*, 2011; Do *et al.*, 2014a, b; Petts *et al.*, 2017; Phaodee *et al.*, 2019) or in mixture with conventional surfactants (Naksuk *et al.*, 2009; Do *et al.*, 2014a, b). According to the surfactant solution type, a classification based on the obtained average oil yield is possible from the lowest to the highest: 65 ± 21% for the conventional surfactants alone, 88 ± 5% for the extended surfactants alone, 89 ± 7% for conventional surfactant mixtures, and 93 ± 2% for the extended and conventional surfactant mixtures. These results are in accordance with the previous literature review about micellization (see Sect. 2.2). Mixed surfactant systems are more efficient than solo surfactant systems (Salager *et al.*, 2019).

In the surfactant solutions, another point to note is the presence of salt (NaCl). Salts are major components for the IFT reduction and the micellization process (see Sect. 2.3.1). For example, Do and Sabatini (2010, 2011) and Kadioglu *et al.* (2011) added NaCl, at 1 and 5–6% respectively, to the C_{10}–PO_{18}–EO_2–SO_4Na, which allowed the decrease of the optimal surfactant concentration down to respectively 0.4 and 0.15% by comparison with the optimal surfactant solution alone at 0.5% in C_{10}–PO_{18}–EO_2–SO_4Na (Petts *et al.*, 2017).

Table 8. Optimized SLR operation conditions.

SLR	Batch size (g)	References
0.04	8	Ramly *et al.* (2017)
0.05	1	Petts *et al.* (2017)
0.10	1	Naksuk *et al.* (2009) and Tuntiwiwattanapun *et al.* (2013)
0.10	3	Nguyen *et al.* (2010)
0.10	4	Kadioglu *et al.* (2011)
0.14	50	Qin *et al.* (2015)
0.20	2	Do and Sabatini (2010)
0.20	4	Radi *et al.* (2013)
0.20	150	Do and Sabatini (2011)
0.25	10	Chen *et al.* (2018)

The salt is also essential for increasing the oil yield. Extractions performed in the presence of salt gave an average oil yield of 87 ± 8% compared to 72 ± 16% without salt. However, high salt concentrations are not desired in the industry, as mentioned before.

Furthermore, as already explained in Section 2.3.1, alcohol is a recurrent ingredient acting as a co-surfactant in the microemulsion. However, only two studies have performed aqueous extraction experiments in the presence of alcohol (Radi *et al.*, 2013; Phaodee *et al.*, 2019). Phaodee and coworkers used 1-octanol, which allowed the extraction of more than 95% of canola oil from soiled fabrics. In the study of Radi, the use of propanol, as a cosurfactant, helped to extract 82.5% of canola oil from the seeds. In extraction, alcohol like ethanol could also play a role in the solubilization of the proteins (Hanjun and Dachuan 2007). Since the proteins are major components of the cell wall of oilseeds, this could facilitate the release of the oil (Yusoff *et al.*, 2015), but in return, it also facilitates the co-extraction of the proteins with the oil.

Other formulation parameters such as pH and sugar addition are reported as influencing the extraction efficiency. However, according to Do and Sabatini (2010) and Chen *et al.* (2018), the pH variation between 4 and 9 had no impact on the oil yield. Above pH 9, the oil yield decreased (Do and Sabatini, 2010; Chen *et al.*, 2018). Below pH 4, a protonation occurs since sulfate surfactants have low stability in an acidic medium. Ramly *et al.* (2017) have added fructose, up to 10%. Sugars act like salts by making the water less disponible for surfactant and then, in theory, would help the surfactants in the IFT reduction. However, fructose did not increase the surfactant efficiency in the study of Ramly *et al.* (2017).

3.2.3 Solid to Liquid Ratio

The Solid to Liquid Ratio (SLR) represents the quantity of raw materials that the surfactant solution can handle to produce the highest oil yield. The industry prefers a high SLR in order to lower the solution needs. Table 8 summarizes the optimized SLR operational conditions for the extraction step.

Counterintuitively, the studies showed that a greater SLR also refers to a higher oil yield. The highest SLR of 0.2–0.25 led to 82.5 to 95% oil yields, whereas the lowest SLR of 0.04 and 0.05 led to 77% (“oil recovery”) and 47.4% (“oil removed”) oil yield respectively.

According to this review of literature, one last point to be noticed is that the studies on this subject are still laboratory-scale studies, with small batch sizes (0.5 to 150 g).

3.2.4 Extraction equipements and conditions

Concerning the type of reactor used for the extraction experiments, all the apparatuses were similar (Tab. 9). For the majority, it was a shaking system that mixes the slurry of seeds and aqueous solution, uniformly. Petts *et al.* (2017) and Pauzan *et al.* (2013) have preferred an orbital device, whereas Radi *et al.* (2013) have chosen to let the extraction operate spontaneously, leaving the slurry in a tube without any agitation.

Regardless the apparatus, the extractions were in majority performed at ambient temperature, but some studies were performed at higher temperatures (60–80 °C). Radi *et al.* (2013) explained the use of high temperatures to ease the liquid-liquid separation step (Sect. 3.4). According to Radi, when a surfactant system only reduces the IFT at high temperature, decreasing the temperature, after extraction, should release the oil from the emulsion by getting away from the optimal parameters. However, high temperatures increase the energy cost of the process without improving its performance. Considering all the studies, high temperatures gave on average 62 ± 25% oil yield by comparison to 87 ± 7% at ambient temperature.

Table 8 presents the different optimized contact times. The extraction duration was ranging from 20 minutes to 2 h, with a majority of 30 minutes. Concerning the shaking speed, it was varied from 100 to 1000 rpm, but the majority of the studies have used a low agitation speed of 150 rpm on average. Based on the studies, no correlation was observed between the shaking speed and the oil yield. Finally, another operational parameter, the number of extraction stages, impact the extraction yield. The processes proposed in detergency studies operate through one extraction step with the surfactant solution, followed by rinsing stages with deionized water (Do and Sabatini, 2011). The rinse steps facilitate the detachment of the oil (Phaodee *et al.*, 2019). Besides, Tuntiwiwattanapun *et al.* (2013) reported that the use of three stages, each with a fresh surfactant solution, increased the extraction yield for high SLR. As a result, the oil recovery was increased from 20–30% after the 1st extraction stage to 60–80% after 3 extraction stages.

3.3 Solid-liquid separation

The separative process is mainly operated by centrifugation to obtain the liquid fraction, containing the extraction medium and the oil, and the solid fraction (meal rich in water) (Tab. 10). The rotation speed and the time of centrifugation were varied in the range 784–8000 g and 10–60 min, respectively. Experiments were oftenly performed in batch, but Do and Sabatini (2011) have operated centrifugation in semi-continuous flow. Ramly *et al.* (2017) and Radi *et al.* (2013) added a cooling step to facilitate the separation of the free oil phase. Finally, Qin *et al.* (2015) preferred decantation for solid-liquid separation.

Table 9. Optimized extraction reactor parameters.

Apparatus	Temperature (°C)	Time	Shaking rate	References
Barnstead Thermolyne Big Bill orbital shaker	–	2 h	150 rpm	Petts *et al.* (2017)
Rotary shaker	20–25	30 min	150 rpm	Pauzan *et al.* (2013)
Four-blade 1-inch mixer and a Talboys light-duty mixer overhead	25	30 min	500 rpm	Do and Sabatini (2011)
PMC Data Plate digital hot plate/stirrer	20	45 min	1000 rpm	Tuntiwiwattanapun *et al.* (2013)
Shaker Cole-Parmer Ping-Pong™	25	45 min	200 horizontal oscillations/min	Kadioglu *et al.* (2011)
Cole-Parmer Ping-Pong horizontal shaker	–	30 min	300 rpm	Do *et al.* (2014a, b)
Horizontal Shaker Ping-Pong™	25	20 min	100–150 shakes/min	Do and Sabatini (2010)
Horizontal thermo shaker	60	30 min	185 rpm	Ramly *et al.* (2017)
Mechanical shaking	23	1 h	200 rpm	Nguyen *et al.* (2010)
Screw capped plastic centrifuge tubes	60	1 h	–	Radi *et al.* (2013)
Shaker SHA-C	80	1 h	160 rpm	Chen *et al.* (2018)
HH-2 digital thermostatic water bath + TA-2 programmed coagulating stirrer	80	30 min	250 rpm	Qin *et al.* (2015)
Tergi-O-Tometer	10–20	3 cycles: 20 min, 3 min, and 2 min	120 rpm	Do *et al.* (2014a, b), Phaodee *et al.* (2019) and Phan *et al.* (2010a, b)

Table 10. Optimized solid-liquid separation parameters.

S/L	Parameters	References
Centrifugation	784 g, 15 min 2170 g, 30 min 3500 rpm, 20 min 4000 rpm, 30 min 2000 g, 20 min 2368 g, 15 min 4000 rpm, 30 min	Petts *et al.* (2017) Do and Sabatini (2010) Kadioglu *et al.* (2011) Do *et al.* (2014a, b) Tuntiwiwattanapun *et al.* (2013) Chen *et al.* (2018) Nguyen *et al.* (2010)
Semi-continuous S/L centrifuge	4116 g, 8 ml/min	Do and Sabatini (2011)
Centrifuge + Freezer/Cooling	3500 rpm, 1 h + 2 h freezing Cooling to room temperature + 8000 g, 10 min	Ramly *et al.* (2017) Radi *et al.* (2013)
Decantation	30 min	Qin *et al.* (2015)

3.4 Liquid-liquid separation

After solid-liquid separation, the liquid fraction containing water, surfactant and oil should be fractionated to recover the free oil. As mentioned earlier, the IFT reduction ensures oil extraction through a micro-emulsification process. Thereby, the liquid fraction is a relatively stable water-oil-surfactant system. To recover the oil from this liquid fraction, it is essential to destabilize the system. However, there is no universal method yet. Tuntiwiwattanapun *et al.* (2013) and Kadioglu *et al.* (2011) have successively used three destabilization processes: temperature variation, chemical interactions and mechanical stress. At first, the cooling step aimed at freezing the water fraction to scrap the top free oil. Successive addition of hexane to the emulsified remaining layer solubilized the oil. Finally, the aqueous (water) and organic (hexane + oil) phases were separated by centrifugation followed by hexane evaporation to obtain free oil. However, this process is non-sustainable regarding hexane removal. Thus, Do and Sabatini (2011) only used mechanical stress to recover the oil by applying a continuous L/L centrifugation with a flowrate varying from 1 to 5 ml/min. Besides, Petts *et al.* (2017) only used a thermal variation by drying the solution at 35 °C overnight.

3.5 Oil yield determination

Several calculation processes were used to give the oil extraction yield. However, they are different in meanings: the oil recovery, the oil removed, and the extraction efficiency.

The method used to calculate the oil recovery is related to the oil fully recovered in the liquid fraction. The oil recovery is then calculated as a summation of the free oil and the oil in the emulsion regarding the initial oil content (Kadioglu *et al.*, 2011):

Table 11. Characteristics of vegetable oils from conventional extraction process and SAEP.

Quality factors	Hexane extraction	SAEP
Water content (v%)[a]	0.036	0.033
Acidic value (mg KOH/g)[a]	0.41	0.33
Peroxide value (meq O_2/kg)[b]	2.75	0.67
FFA%[c]	0.6–0.7	0.04–0.05

[a] Tuntiwiwattanapun *et al.* (2013).
[b] Radi *et al.* (2013).
[c] Do and Sabatini (2010).

$$Oil\ recovery(\%) = \frac{free\ oil + oil\ in\ emulsion}{initial\ oil} \cdot 100. \quad (8)$$

In contrast, the percentage of oil removed compares the remaining oil in the solid fraction after extraction to the initial oil content. Both contents are obtained thanks to the n-hexane extraction method (Do *et al.*, 2014a, b):

$$Oil\ removed(\%) = \frac{initial\ oil - remaining\ oil\ after\ extraction}{initial\ oil} \cdot 100. \quad (9)$$

Oil removed and oil recovery should not be confused. The oil removed is not necessarily all recovered. Indeed, the emulsified layer needs to be separated once more to fully separate the oil from the surfactant solution. Also, as known, n-hexane extraction leads to an oil recovery of 99% from the initial oil content. Then, the oil removed calculation introduces uncertainty estimated to ± 2% (Kadioglu *et al.*, 2011).

The third method of calculation is based on the comparison between the conventional and the novel extraction processes. It mixes the two previous calculation methods (Tuntiwiwattanapun *et al.*, 2013):

$$Extraction\ efficiency(\%) = \frac{free\ oil\ + oil\ in\ emulsion}{free\ oil + oil\ in\ emulsion + remaining\ oil} \cdot 100. \quad (10)$$

Owing to the various methods of calculation and the limited number of studies, the oil yield comparison between the various studies is hazardous yet.

3.6 Impact of SAEP on the quality of products

In the field of extraction, the process efficiency also depends on the quality of the products. For the oilseeds transformation process, it requires strict control of the liquid (oil) and the solid (meal) quality because their market values vary according to their composition.

For the oil, the fatty acids profile, the peroxide, the iodine value, the free fatty acids (FFA) content the color, and the content of the polar compounds are the most important parameters to evaluate the quality of oil and its oxidative status. On the other hand, the meal is mainly used for animal feed. Thus, the meal value is closely linked to its nutritional value and especially to its protein content and quality. Unfortunately, only a few data are available on this point in the literature. Tuntiwiwattanapun *et al.* (2013) have compared the oil obtained by SAEP and conventional oil obtained with n-hexane extraction (Tab. 11). They showed that both oils present a similar water content (0.036 *vs.* 0.033%), but the acid value for the SAEP oil was significantly lower (0.33 *vs.* 0.41 mg KOH/g of oil). In another study, Radi *et al.* (2013) reported that the peroxide value of SAEP oil was about 4 times lower than the one of n-hexane extraction oil (Tab. 11). This lower peroxide value (0.67 meqO_2/kg) evidences lower rancidity and more oxidative stability during the storage step. Besides, Do and Sabatini (2010) have shown that the oil obtained by SAEP was about 10 times less concentrated in FFA than conventionally n-hexane extracted oil (Tab. 11). This result is consistent with the peroxide value and reflects lower oxidation during the extraction step.

Concerning the solid fraction (meal) quality, even if some authors have reported that the SAEP is better in terms of protein quality in the meal, no objectives results are available in the literature. This point should be studied and investigated in the future.

Regarding the quality of the SAEP, the quality of the surfactant solution should also be analyzed. This is also an important parameter because its surfactant content suggests the possibility of its recycling. However, the potential re-using of the solution has not been reported yet. Naksuk *et al.* (2009) just reported a high loss of surfactant (77 to 96%) from the water phase.

3.7 Advantages and limitations of the SAEP process

As described above, SAEP development meets the requirements to overcome the environmental and qualitative issues related to the use of hexane for oil extraction. Nowadays, according to the literature, this novel process appears as a proven technology at a laboratory-scale for different kinds of oilseeds. The first results showed its effectiveness, but many further investigations are still needed to consider its industrial implementation. These investigations should include both scientific and technical considerations. Scientifically, it is essential to understand the mechanisms occurring during the extraction and, mainly, the physicochemical interactions between the different phases. Moreover, identifying possible correlations between the surfactant properties (IFT, CMC, Γ_{max}, pC_{20}) and the extraction efficiency would allow modeling of the process and predicting its performance. More importantly, the identification of new extended-like surfactants, bio-based, biodegradable, and eco-friendlier than those mentioned in the literature is a very challenging line of investigation.

Technically, experiments were performed at a very small scale (some grams of seeds). Thus it is important to perform those experiments on a larger scale. The scale-up could validate the transferability of the tendencies observed at a laboratory scale. Moreover, the design of the reactor and the mixing equipment should be well controlled. The diffusion coefficient of water inside seeds is slower as compared to that of n-hexane. Consequently, the contact time between the solvent and the solid material should be improved in order to become similar to the one of the conventional process with hexane, where the extraction is very rapid. Thus, the reactor should perfectly stir the sludge to perform homogenous and effective extraction. After the extraction, the fractionation process of the oil/water/surfactant blend should be studied more deeply and optimized.

From an economic point of view, the energy costs of the process (extraction + downstream process) should be considered. For example, the consideration must analyze the energy demand for oil/water separation, salt removal, and residual cake dehydration after the extraction. Besides, the cost of the surfactant should be evaluated. In this line, surfactant recycling and the identification of inexpensive surfactants are major challenges for the economic profitability of the process. Finally, the quality of the liquid (oil) and solid (cake) fractions obtained by this process should be better characterized and compared to those conventionally obtained. Moreover, the extraction selectivity is an important parameter that must also be evaluated. New valorization ways may be identified depending on the composition of the obtained products.

4 Conclusion

The use of extended surfactants in water for oil extraction, named SAEP, was recently described as a promising process for vegetable oil to avoid the environmental issues related to the use of n-hexane from the conventional extraction method. In this non-exhaustive review, we have presented and explained the properties of extended surfactants and the fundamental aspects of this process, justifying their use for this application. We also have described the main works dealing with this topic according to their potential and limitations. Despite an increasing interest in extended surfactants for vegetable oil extraction in the past decades, there are still many studies to be carried out. Further investigations are necessary to understand and characterize the physical and chemical phenomena occurring during this process. Technically, the process scale-up is quite challenging because there are many constraints regarding the reactor design (contact time, mixing) and the downstream process conception (fractionation, surfactant recycling). The quality of the meal and the oil should be better characterized and compared to the ones obtained in the conventional process. Finally, economic and energy assessments are necessary to judge objectively the viability of the process.

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