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Aqueous Extended-Surfactant Based Method for Vegetable Oil Extraction: Proof of Concept

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Abstract The use of hexane to extract vegetable oil from oilseeds is of growing concern due to hexane's environmental impact and because of worker exposure concerns. The goal of our work is to demonstrate that the aqueous extended-surfactant-based method is a viable alternative for vegetable oil extraction. In our method, ground oilseeds were dispersed in the aqueous surfactant solution, allowing the oil to be liberated from the seeds as a separate phase from the aqueous phase. The impact of pH, shaking intensity, shaking time and seed to liquid ratio on oil yield are presented. Extended-surfactants are a new type of surfactant with propoxylate (PO) and/or ethoxylate (EO) groups inserted between the hydrophilic head and the hydrophobic alkyl chain of the surfactant molecule. This unique structure of extended-surfactants enables them to produce ultralow interfacial tension with vegetable oils. We have found that at low aqueous concentrations (less than 0.3 wt%), extended-surfactant solutions are able to produce ultralow interfacial tension between aqueous extraction and vegetable oil phases. At optimum condition (seed to liquid ratio of 1–5, 30 min extraction at 150 shakes/min and 30 min centrifugation at 2,170×g) we achieved 93–95% extraction efficiency for peanut and canola oils at 25 °C. The oil quality produced from the aqueous extended-surfactant-based method was found to be comparable or even superior to that obtained from hexane-based extraction, further demonstrating the viability of aqueous extended-surfactant based extraction.

Keywords Surfactants · Ultralow interfacial tension · Oilseeds · Extraction · Emulsions · Triglyceride analysis

Introduction

Vegetable oils are typically produced from oilseeds by either hexane extraction or a combination of mechanical processing and hexane extraction. However, worker exposure to hexane at 15 ppm/day for 3 months has been shown to cause peripheral nerve damage, and hexane is also a potential hazardous explosive material [1]. Therefore, hexane-based extraction requires airtight, leak-proof equipment and highly-skilled labor in hexane extraction plants. In 2001, the U.S. Environmental Protection Agency (EPA) established regulations on hexane emission due to growing environmental concerns. In addition, oils produced by hexane extraction are high in free fatty acid, wax and unsaponifiable matter, and might also suffer from dark greenish-brown color [2]. Further there is a growing demand for vegetable oil to be used in biodiesel production.

In view of the disadvantages of existing extraction processes, a number of alternative technologies have been evaluated for oilseed extraction, including water-based (aqueous) extraction or use of other volatile organic

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solvents [3–7]. The aqueous extraction process (AEP) was studied in the 1950s because it was believed that this process was cheaper and safer than hexane. AEP for oilseed extraction eliminates the potential of explosion and emissions of volatile organic solvents when using hexane. Simultaneous recovery of oil and protein by AEP is possible with lower equipment costs and energy consumption than hexane extraction [8–10]. AEP is based on the water soluble components of oilseeds dissolving in the water, thereby releasing the oil which was previously bound to the cell structure [11]. AEP has consistently been reported to produce vegetable oil superior in quality to that produced by hexane-based processes [11]. However, AEP with water alone has low oil extraction efficiency (less than 70%) because water cannot effectively release the oil which is trapped in the plant cell structure by high capillary force. In addition, AEP is operated at relatively high temperatures (50–60 °C) and high water to solid ratio (20:1 to 30:1), both of which are undesirable in application [12].

Enzyme-assisted aqueous extraction has been introduced in an attempt to improve the oil yield with the AEP process. The enzyme-assisted aqueous extraction process uses an enzyme system to disrupt the cell walls, thereby improving the oil release by mechanical means alone [12]. Greater than 90% oil extraction efficiency has been achieved for various vegetable oils (e.g. canola, peanut and coconut oils) using this approach [6]. The structure of the plant cell wall, made of various strata, is very complex. The strata are composed of many compounds such as cellulose, hemicelluloses and lipids. Since each type of enzyme can only degrade a certain type of compound, an effective extraction system requires a combination of at least three types of enzymes [13]. The oil extraction efficiency of different oilseed types is greatly dependent on the combination of enzymes [13, 15]. In addition, since enzyme activity is pH and/or temperature dependent, optimization of reaction conditions for multiple enzymes can be challenging when evaluating an effective enzyme system [15]. These disadvantages make the enzyme-assisted aqueous extraction complicated and thus to date there is no versatile enzyme system that can be applied for all types of oilseeds as is true with hexane [10, 12, 14]. Another drawback of this method is the enzyme cost [15, 16]. Similar to AEP process, enzyme-assisted aqueous extraction process produce vegetable oil with superior quality to hexane. However, this method also requires long incubation time (up to 18 h) and high temperatures (30–55 °C), both of which are undesirable in application [6, 10, 17].

In this research study, we investigated the use of surfactant-microemulsion-based extraction of vegetable oil extraction from oilseeds. The goal of this work is to develop surfactant-based formulations with simplicity of operation, acceptable energy consumption and desirable extraction performance. Our group is unique in investigating the use of aqueous-surfactant-based method for oil extraction from oilseeds [18]. Past research has evaluated the efficiency of water-in-oil (W/O) microemulsions (surfactant solubilized in an oil phase, in this case) in extracting vegetable oils [19–21]. Microemulsions are thermodynamically stable dispersion of water and oil, stabilized by a film of surfactant where the microemulsion droplet size is generally smaller than 100 nm [22]. In W/O microemulsions (also referred to as Winsor II microemulsion systems), the reverse micelles (head groups in the core and the hydrophobic tails outward) solubilize water while they are dispersed in the continuous oil phase [22]. In the studies of W/O microemulsion-based extraction of sodium dioctyl sulfosuccinate (AOT)/isooctane/water or cetyltrimethylammonium bromide (CTAB)/isooctane/*n*-butanol/water, the W/O microemulsions have the same role as hexane solvent where the vegetable oil in the oilseed is solubilized. This method requires high surfactant concentrations (2–4 wt%), an organic solvent (isooctane) and relatively complicated separation processes to isolate the oil from the W/O microemulsions, both of which are undesirable and not necessary for our system [19, 20]. An aqueous-surfactant-based method is a different approach.

In the past, the use of aqueous surfactant-based processes for vegetable oil extraction was impractical since conventional surfactants proved unable to produce ultralow interfacial tension with vegetable oils, a critical factor in efficient vegetable oil extraction by this method. By definition, interfacial tension (IFT) is the surface tension caused by intermolecular interactions at the surface separating two immiscible fluids [22]. We define ultralow IFT as IFT values $\ll$0.1 mN/m (preferably $<$0.01 mN/m). In the microscopic study of aqueous oil extraction mechanisms, it was found that when employing water alone, the unextracted oil was trapped in an insoluble matrix of denatured proteins. The coalesced oil size was too large to diffuse through the disrupted cellular matrix [23]. The oil release mechanisms when using surfactant is to disrupt the oil/water interface by lowering the interfacial tension between the surfactant solution and the oil, thereby facilitating the oil droplet breakup and making it possible for the oil to diffuse through and be librated from the disrupted cell [23]. Thus, a system that produces ultralow IFT between the extracting solution, an aqueous-based surfactant system in our case, and the vegetable oil in the seeds will release the oil trapped in the disrupted cells. The high IFT that conventional surfactants produce between water and vegetable oils is due to the hydrophobicity of triglycerides, which are the main component in vegetable oils. Vegetable oils are hydrophobic oils with the equivalent alkane carbon number (EACN) ranging from 16 to 20 [24]. In order to achieve ultralow IFT, the hydrophobicity-

hydrophilicity between surfactant solution and the oil must be balanced [25]. The surfactant solution can be made more hydrophobic by increasing the alkyl chain of the surfactant molecule [25]. However, increasing the alkyl chain too much will decrease the water solubility of the surfactant. Eventually, the surfactant phase will separate from water. Therefore, an aqueous conventional surfactant solution could not achieve ultralow IFT with vegetable oils because the hydrophobic-hydrophilic balance was not achieved within the limiting solubility of the surfactants. A recently developed new class of surfactants known as extended-surfactants is able to achieve ultralow IFT. Distinct from conventional surfactants, the extended-surfactant molecule has an intermediate polar group (e.g. propoxylate group) inserted between the head and the tail of the surfactant molecule. The propoxylate groups in the surfactant molecule make the surfactant become more hydrophobic and also extend the surfactant tail [25]. Therefore, the surfactant tail segregates further into the oil phase without sacrificing the water solubility as often observed when increasing the alkyl chain [25]. Detailed studies on extended-surfactants, the dynamic interfacial tension properties of extended-surfactants with vegetable oils and the role of extended-surfactants in forming microemulsions and ultralow IFT with vegetable oils is reported in the literature [25–28].

For vegetable oil extraction, we are particularly interested in the lowest surfactant concentration capable of producing ultralow interfacial tension (IFT), which is known as the critical microemulsion concentration (CμC). Removal of oil at the CμC point due to IFT reduction is well known as the mobilization mechanism in enhanced-oil recovery (EOR). In this case, the oil is liberated as a separate phase rather than solubilized into the aqueous surfactant phase [29]. This property is desirable since vegetable oil can be effectively extracted without requiring an additional process to separate the solubilized oil from the surfactant micelles. Use of surfactant systems near the CμC was first tested by our group for extraction of oil from drill cuttings using about 0.1 wt% surfactant [29].

In this work, we evaluated the use of several extended-surfactant based systems for vegetable oil extraction. We also studied the effect of process parameters such as pH, shaking intensity and time, and seed to liquid ratio on the extraction efficiency. Assessment of the oil quality using our method is also discussed in this paper.

Materials and Methods

Materials

Two classes of anionic extended-surfactants were studied in this work: alkyl-propoxylate-ethoxylate-sulfate (APES) surfactants and alkyl-propoxylate-sulfate (APS) surfactants. The number of PO groups varied within each class of surfactant. While there is no EO group in the APS surfactants, the number of EO groups is fixed at two for APES surfactants. These surfactants are all predominantly linear in configuration. The extended-surfactants were kindly provided by Huntsman Chemical Co. (Houston, TX) and used as received. The surfactants studied, the optimum salinity and optimum interfacial tension between the aqueous surfactant solution and triolein oil are summarized in Table 1. Sodium dioctyl sulfosuccinate (Aerosol-OT or AOT), +99% anhydrous was purchased from Fisher Scientific (Fair Lawn, NJ) and used as received.

Triolein 65% practical grade and peanut oil were purchased from Sigma–Aldrich (St Louis, MO). Triolein was used as a model oil in the surfactant selection study as it is a major component in most vegetable oils. Crisco® pure canola oil (The J. M. Smucker Company, Orrville, OH) was used without modification. Sodium chloride +99% purity was purchased from the Fluka Chemical Corp. (Milwaukee, WI). Deshelled peanut seeds were purchased from Wal-Mart (Norman, OK). Canola seeds were kindly provided by Prairie Gold Oil Seeds (Okeene, OK).

Table 1 List of propoxylate and propoxylate ethoxylate surfactants studied in this work and their optimum salinity (S*) and optimum interfacial tension (IFT*) with triolein oil at 25 °C

Surfactant series	S* (wt%)	IFT* (mN/m)
1. APS[a]		
C_{16}-xPOsulfate		
C16-2.9PO	2.0	0.052 ± 0.0021
C16-4.5 PO	3.0	0.039 ± 0.0013
C16-5.5 PO	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. APES[b]		
C_{10}-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
C_{12}-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 ± 0.00060

All surfactant concentrations were at 0.1 wt%. Electrolyte used was NaCl

[a] Alkyl propoxylate surfactant

[b] Alkyl propoxylate ethoxylate surfactant

Methods

Interfacial Tension Experiments

Dynamic interfacial tension experiments were performed to evaluate the interaction of extended-surfactant systems with triolein and vegetable oils. These experiments were carried out using a spinning drop tensiometer purchased from the University of Texas (Model 500). Salinity scans were conducted by varying the NaCl concentration in surfactant solutions of 0.1 wt%. Each sample was conducted in triplicate and the IFT data were recorded every 5 min during a 20 min time frame. We define the dynamic IFT as the IFT between the freshly prepared surfactant solution with the studied oils recorded at different time interval; in contrast, the equilibrium IFT refers to the IFT between the aqueous surfactant phase and oil phase from a phase behavior study that was equilibrated for 2 weeks.

Oilseed Pretreatment

Deshelled peanut seeds were dehulled, whereas canola seeds were not since it is not economically feasible to dehull canola seeds [30]. Peanut and canola seeds were ground using a food processor. The particle size used in this study is in the range of 0.21–0.42 mm size by using US Sieve size No. 40 and No. 70, which is in the recommended range for oilseed extraction [31]. The oilseeds were then oven-dried at 104 °C for 35 min to inactivate myrosinase enzymes, gossypols and other unfavorable compounds [31, 32]. Moisture level in the oilseeds were determined by AOAC standard procedure (Method 925.40) [33]. Moisture level in both peanut and canola seeds were in the range of 4–6 wt% which is in the recommended range [31].

Oil Content

For oil content analysis, crude peanut and canola oils were extracted from seeds using hexane and a Soxhlet extraction method following AOAC standard procedure (Method 948.22) [33]. The amount of oil extracted by the Soxhlet extraction method was evaluated as the total oil present in peanut/canola seeds. In this method, the Soxhlet extractor was heated to 60 °C on a mantle and 50 mL of hexane was used. The thimble was filled with 5 g of peanut/canola seeds and extracted for 4 h. Hexane containing extracted peanut and canola oils was evaporated in a hot air oven at 70 °C until no change in mass of the oils was observed to eliminate residual hexane. In the second Soxhlet extraction step, no more oil was collected. The total oil analysis gave 42% peanut and 40% canola oil based on dry weight basis, consistent with values reported in the literature [34]. Oil extraction efficiency was calculated as weight percentage of oil extracted divided by the total oil present in the seeds as determined by this method. It is important to note that, in order to avoid the variation in oil content and removal efficiency in different batches, the total oil content was analyzed in each batch and the oil removal efficiency was calculated based on the corresponding oil content of the same batch.

Oil Extraction

Pretreated oilseeds were put into the surfactant solution in a 25-mL glass tube. Then, the tubes were put in the shaker (Ping-Pong™, model 51504-00) at varying shaking speeds in the horizontal position. The slurry was centrifuged at $2{,}170 \times g$ (IEC centrifuge, model HN) for 30 min to gravity separate into three different parts: free oil phase, meal and aqueous surfactant phase. The top oil phase was transparent and clear. The meal was dried in an oven at 104 °C overnight for oil residual analysis by Soxhlet extraction method, allowing for a complete mass balance for oil. The amount of oil extracted by aqueous extended-surfactant based method and the oil residual were summed and compared to the total oil content analyzed by Soxhlet extraction. Mass balance confirmed that the oil was not solubilized in the aqueous extended-surfactant solution but rather present as the liberated oil phase or remaining as residual oil in the seeds.

Triglyceride Composition Profile

The triglyceride composition (TGC) profile was obtained by reversed-phase high-performance liquid chromatography (RP-HPLC) with an evaporative light scattering detector (ELSD) SEDEX Model 75. The mobile phases were dichloromethane (A) and acetonitrile (B). The column used was Alltima HP C18 Hi-Load, 5 μm, 250 × 4.6 mm. Elution was performed at a solvent flowrate of 1.2 mL/min for 30 min. The mobile phase gradient condition followed the method described in Alltech application book [35]. For solvent composition program, the fraction of acetonitrile was set as follows: 0 min 70%B, 10 min 55%B, 18 min 70%B and 30 min 70%B. TGC peaks were identified based on the retention time of standards and the results in Alltech application book [35]. Triglyceride profile was detected by an ELSD with the following settings: evaporation temperature at 35 °C, air pressure at 3.2 bars and photomultiplier sensitivity at 6. Peak areas were used to quantify the components based on relative percentages. An internal normalization method was used to quantify the triglyceride compounds, assuming that the detector response is the same for all compounds. Validation of this quantification method for olive oil was reported by Cunha and Oliveira [36]. The interpretation of the triglyceride composition

profile from retention data was based on the method described in Redden et al. [37].

Oil Quality Analysis

Free fatty acid content was determined according to AOAC standard procedures [38]. The oil stability was tested by the AOCS cold test method (Method Cc 11-53) [39].

Results and Discussions

Surfactant Selection

The most important criterion for the surfactant used in vegetable oil extraction is the ability to produce ultralow interfacial tension between the surfactant solution and vegetable oils in order to liberate the oil from the seed. A number of aqueous conventional surfactant systems were evaluated in the absence of co-oils and/or alcohols, but failed to achieve low IFT at ambient temperature (see AOT in Fig. 1). However, aqueous extended-surfactant solutions were able to achieve ultralow interfacial tension with vegetable oils at ambient temperature and without the addition of co-oils and/or alcohols (see Fig. 1 for C_{10}-18PO-2EOsulfate with canola oil and peanut oil as well as previous work with other oils [24]). All the surfactant solutions contained 0.1 wt% surfactants and 5.0–6.5 wt% NaCl. As seen from Fig. 1, while the IFT of AOT and canola oil is always above 1 mN/m (peanut oil was likewise, data not shown), the IFT of extended-surfactant solution with canola and peanut oil are as low as 0.01 mN/m; i.e., two orders of magnitude lower than AOT. Another important criterion for surfactant selection is the time frame for the surfactant solution to reach equilibrium interfacial tension with vegetable oils. It can be seen that the equilibrium IFT values in Fig. 1 were achieved within 20 min, highly desirable for the scale-up of the extraction process [6, 10]. (Recall that the enzyme process is reported in the literature to require up to 18 h.)

In this study, we are interested in evaluating extended-surfactants for their potential use in vegetable oil extraction. Two classes of extended-surfactants were studied, namely alkyl-propoxylate-surfactant (APS) ($C_{16}H_{33}$ with varying number of POs), and alkyl-propoxylate-ethoxylate-surfactant (APES) ($C_{10}H_{21}$ and $C_{12}H_{25}$ with 2 EOs and varying number of POs). The APS and APES extended-surfactants studied in this work are summarized in Table 1. Given the uncertainty of biodegradation and human/animal consumption of these surfactants, vegetable oil extracted by this method is recommended for non-edible applications, such as biodiesel and lubrication, at this time. The aqueous surfactant-triolein IFT was measured for these

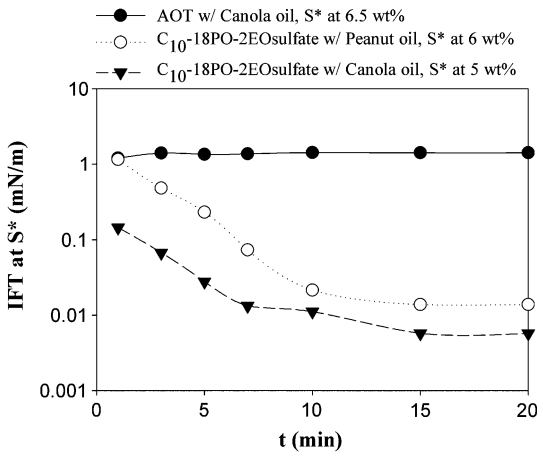

Fig. 1 Dynamic IFT versus time of C_{10}-18PO-2EOsulfate with peanut and canola oils and AOT with canola oil at optimum salinity concentrations at 25 °C. Surfactant solutions were prepared at 0.1 wt%

extended-surfactants and recorded at 20 min to choose the surfactant that produced the lowest IFT, with this surfactant to be used subsequently in vegetable oil extraction experiments. Triolein 65% practical grade has often been used in the literature as the model oil for triglycerides given that it is the most abundant triglyceride species in most vegetable oils [40].

The IFT results of these extended-surfactants with triolein are summarized in Table 1. The results suggest that APES surfactants were able to achieve IFT values with triolein an order of magnitude lower than APS surfactants The optimum salinity (S*) varied for different surfactants. Three extended-surfactants, namely C_{16}-10.7POsulfate, C_{12}-14PO-2EOsulfate and C_{10}-18PO-2EOsulfate were chosen for the subsequent vegetable oil extraction studies since they required lowest S* which is desirable in industrial application. Between C_{16}-10.7POsulfate and C_{12}-14PO-2EOsulfate, C_{10}-18POsulfate, we could compare the extraction performance of APS surfactant versus APES surfactant. C_{12}-14PO-2EOsulfate and C_{10}-18PO-2EOsulfate were produced from alcohols of different alkyl chain lengths; therefore, we would like to investigate if the alcohol sources could impact the fraction of oil extracted.

Vegetable Oil Extraction

Effect of Surfactant Types

All surfactant concentrations were prepared at 0.15 wt% and at optimum salt concentrations (refer to Table 1). The fraction of oil extracted using water alone was also evaluated. As seen in Table 2, the fraction of oil extracted for all cases is superior to water alone, consistent with the low

Table 2 Effect of surfactant types on peanut oil extraction efficiency at 25 °C

Extraction medium	S* (wt%)	IFT* (mN/m)	Fraction of oil extracted[a] (wt%)	State of liberated oil
Water	None	21	40	Emulsion
0.15 wt% C_{16}-10.7POsulfate	6.2	0.033	65	Emulsion
0.15 wt% C_{12}-14PO-2EOsulfate	6.1	0.0095	92	Emulsion
0.15 wt% C_{10}-18PO-2EOsulfate	6.0	0.0088	95	Free oil

Seed to surfactant solution liquid (S:L) ratio at 2 to 10 (g to g), 30 min extraction time, and horizontal shaking speed at 150 shakes/min

[a] Amount of oil extracted via Soxhlet extraction was used as the basis

IFT provided by surfactant-based systems. Water alone exhibited the lowest fraction of oil extracted of 40%. C_{16}-10.7POsulfate produced a somewhat higher efficiency of 65%. However, both water and C_{16}-10.7POsulfate produced stable emulsion-like phases which are not desirable in the extraction process. C_{12}-14PO-2EOsulfate and C_{10}-18PO-2EOsulfate both produced very high peanut oil extraction efficiencies of 92-95%. However, only the C_{10}-18PO-2EOsulfate produced a neat free oil phase, whereas C_{12}-14PO-2EOsulfate produced an undesirable emulsion-like phase; thus, C_{10}-18PO-2EOsulfate was chosen for study in future sections.

Effect of Surfactant Concentration

Figure 2 shows IFT values versus surfactant concentrations for C_{10}-18PO-2EOsulfate surfactant and both peanut oil and canola oil. From Fig. 2, the CμC value of C_{10}-18PO-2EOsulfate with peanut oil is 0.15 wt% and with canola oil is 0.35wt%. Based on this, in seed extractions studies we varied the surfactant concentration below and above the CμC values to study the effect of surfactant concentration on oilseed extraction as illustrated in Fig. 3. From Fig. 3 we see good agreement between the trends of the fraction of oil extracted and the CμC values reported above. With increasing surfactant concentration below the CμC, dramatic increases in both canola and peanut oil extraction efficiencies were observed. However, at surfactant concentrations higher than the CμC, the fraction of oil extracted did not change with increasing surfactant concentration. Thus, the preferred formulation for peanut oil extraction is 0.15 wt% of C_{10}-18PO-2EOsulfate and 6 wt% NaCl, and the preferred formulation for canola oil extraction is 0.35 wt% of C_{10}-18PO-2EOsulfate and 5 wt% NaCl.

Effect of Shaking Speed

The impact of mixing intensity (shaking speed) was evaluated as shown in Fig. 4. The mass of the oilseed, surfactant concentration and salt concentration were fixed at 2 g, 0.15 wt% and 6 wt%, respectively. It can be seen from

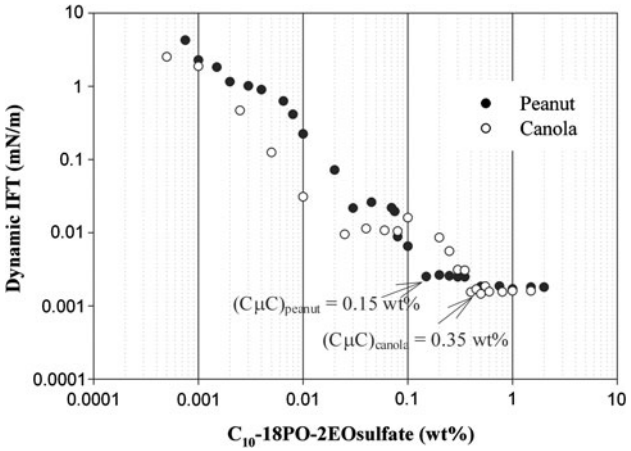

Fig. 2 Determining the critical microemulsion concentration (CμC) using the plot of dynamic interfacial tension versus surfactant concentration at optimum electrolyte concentration for the systems C_{10}-18PO-2EOsulfate/6wt% NaCl brine/peanut oil and C_{10}-18PO-2EOsulfate/5 wt% NaCl brine/canola oil. IFT data were recorded at 20 min and 25 °C

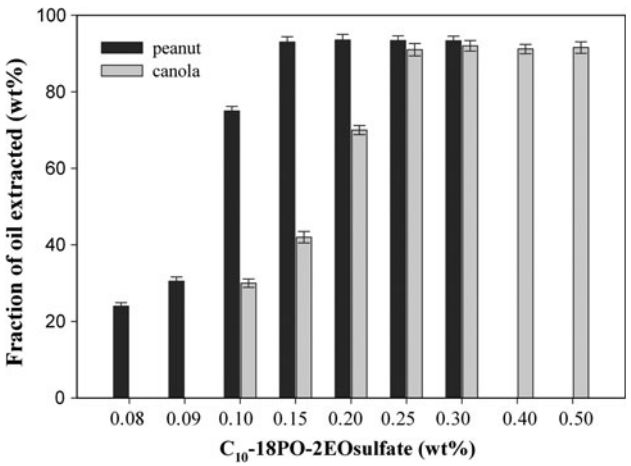

Fig. 3 Canola and peanut oil extraction efficiency versus C_{10}-18PO-2EOsulfate concentrations. Salinity was 6 wt% NaCl with peanut oil and 5 wt% NaCl with canola oil at 25 °C corresponding to S* for each. Seed to liquid ratio at 2:10 (g:g) for both oils, 30 min contact time and shaking speed at 150 shakes/min. Refer to Fig. 1 for the optimum salinity (S*) of C_{10}-18PO-2EOsulfate solution with canola and peanut oils

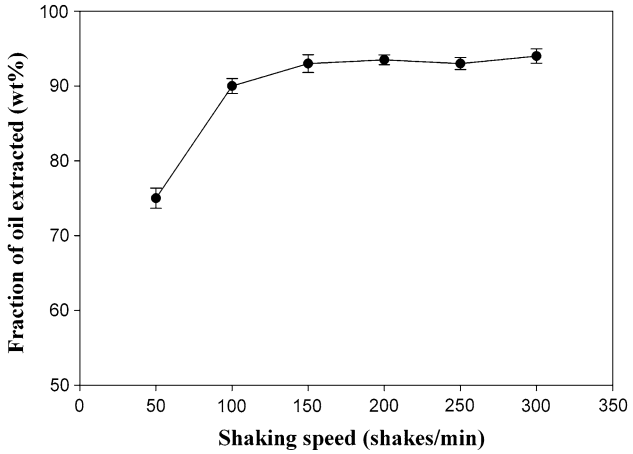

Fig. 4 Effect of shaking speed on peanut oil extraction using 0.15 wt% of C_{10}-18PO-2EOsulfate and 6 wt% NaCl at 25 °C. 30 min contact time. Seed to surfactant solution liquid ratio at 2:10 (g:g)

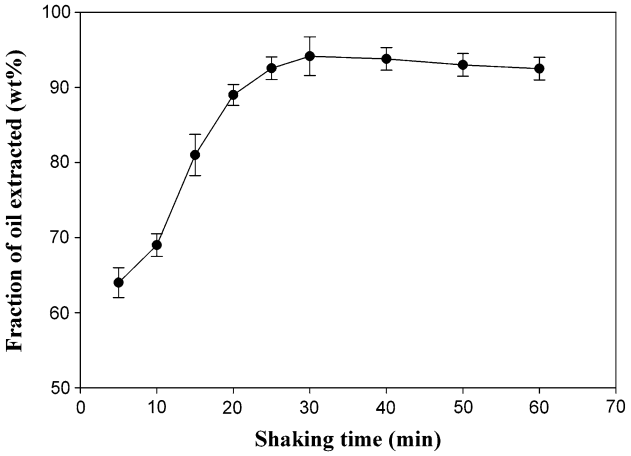

Fig. 5 Effect of shaking time on peanut oil extraction of 0.15 wt% C_{10}-18PO-2EOsulfate and 6 wt% NaCl at 25 °C. Shaking speed at 150 shakes/min. Seed to surfactant solution liquid ratio at 2:10 (g:g)

the graph that at the low agitation speed (50 shakes/min) lower fraction of extracted oil was observed. However, at shaking speeds higher than 150 shakes/min, increased shaking speed no longer had a significant effect on vegetable oil extraction. It was observed that at the highest shaking speed of 300 shakes/min, stable fine solids were formed and settled slowly which led to the problem in the separation of the fine solid from the oil phase. Based on these results, a shaking speed of 100-150 shakes/min was used in subsequent experiments.

Effect of Shaking Time

From the dynamic IFT results shown in Fig. 1, equilibrium IFT was obtained between surfactant solutions and with peanut or canola oil within 20 min. Therefore, it is expected that the amount of oil extracted will not change after 20 min at 150 shakes/min. This is in good agreement with results in Fig. 5, which shows that no further oil was extracted after 25 min. In addition, the dynamic IFT of the post wash surfactant solution taken from the aqueous phase after centrifugation still exhibits ultralow interfacial tension with fresh vegetable oil (<0.02 mN/m at 20 min, data not shown); suggesting that the surfactant solution can be easily recycled as proposed in the overall process.

Effect of Salt Concentrations

Salinity scans were performed at a fixed C_{10}-18PO-2EOsulfate concentration of 0.15 wt%, as seen in Fig. 6. Dynamic IFT results suggested that the lowest IFT occurred at the salt concentration of 6 wt%, in excellent agreement with S* reported in Table 2 and the maximum oilseed

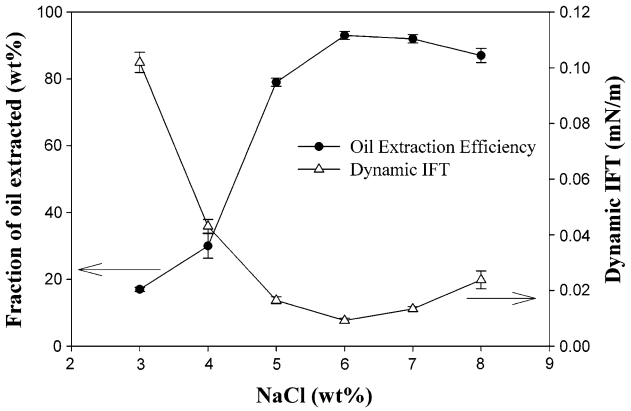

Fig. 6 Effect of salt concentration on peanut oil extraction and dynamic IFT (data recorded at 20 min) using 0.15 wt% of C_{10}-18PO-2EOsulfate at 25 °C. Shaking speed at 150 shakes/min for oil extraction experiments. Seed to surfactant solution liquid ratio at 2:10 (g:g)

extraction results in Fig. 6, respectively. However, from Fig. 6 we see that 5 and 8 wt% NaCl also show excellent oil extraction, demonstrating a degree of robustness relative to the NaCl concentrations.

Effect of Solid–Liquid Ratio on the Fraction of Oil Extracted

We next investigated different solid–liquid ratios of 1–10 to 5–10 (g to g), as shown in Fig. 7. It can be seen that at low or high solid to liquid ratio, the fraction of oil extracted decreases, with the best extraction efficiency obtained at 2:10 (g:g) for peanut oil (Fig. 7). The same trend was observed with canola oil (data not shown). The amount of oil extracted decreased at the highest solid–liquid ratios likely because the viscosity increase made it difficult to

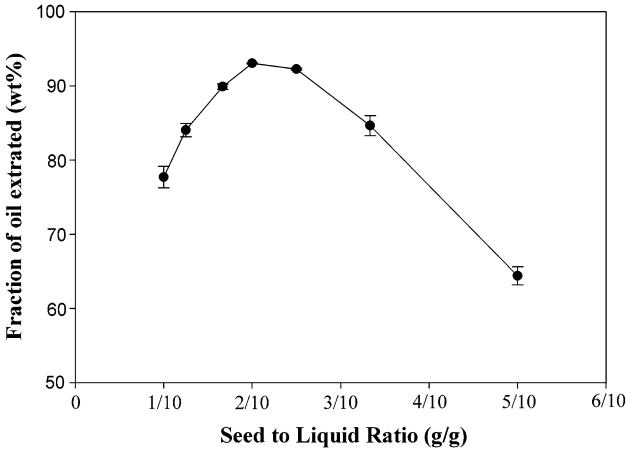

Fig. 7 Effect of seed to liquid ratio on extractability using 0.15 wt% of C_{10}-18PO-2EOsulfate and 6 wt% NaCl at 25 °C. 30 min contact time and shaking speed at 150 shakes/min

maintain effective mixing and to achieve surfactant-oilseed contact. Conversely, we speculate that too high of a liquid to solid ratio causes less particle collision, leading to poor extraction efficiency. It is important to note that compared to other aqueous extraction processes studied in the literature, we are able to employ a higher solid–liquid ratio; a solid to liquid ratio of 1:20 (g to mL) is normally observed in other studies [6, 10, 15].

Effect of pH on Fraction of Oil Extracted

Peanut and canola oil extraction efficiencies were evaluated at four different pH values; 4, 7, 9 and 11 (data not shown). In contrast to aqueous extraction methods using enzymes, pH values ranging from 4 to 9 had no significant effect on the fraction of oil extracted, which is consistent with the IFT results (data now shown). At pH 11, the solution suddenly changes into green-brownish color and the extraction drops sharply since a green-brownish emulsion was observed instead of a clear oil phase. This can be explained by the solubilization of protein in the aqueous phase at pH 11.

Oil Quality

The crude oil quality resulting from the aqueous surfactant-based extraction method was analyzed and compared to oil recovered using hexane as extractant. Parameters that were compared include free fatty acid concentration, triglyceride composition profile and oil clarity. The results are summarized in Tables 3 and 4 for peanut oil and canola oil, respectively. The hexane-extracted peanut oil has a significantly higher content of free fatty acid (0.7 wt% FFA) than aqueous surfactant-based extracted peanut oil (0.05 wt% FFA). It is important to note that the hexane extraction was performed on the same oilseed batches used in aqueous extended-surfactant extraction. It would be interesting to investigate how the triglyceride profile might change when the oil was extracted using aqueous extended-surfactant-based versus hexane. The triglyceride composition profiles for peanut and canola oils obtained by our method are also illustrated in Tables 3 and 4, respectively. Due to the aqueous extraction medium, polyunsaturated fatty acids (PUFAs) can be subject to oxidation because of the chemical active of the double bonds [41]. An analysis of the triglyceride profile would provide an insight to this degradation [42]. Tables 3 and 4 show the most abundant triglyceride content in peanut and canola oils. Other minor triglycerides were detected but not reported. It can be seen that the aqueous extended-surfactant-based method produced vegetable oil with triglyceride profiles similar to

Table 3 Analysis of extracted peanut oil

TGC profile[a]	Surfactant-based process[c]	Hexane-based process
LLO[b]	14.3	11.0
LOO	14.0	14.8
LOP	11.8	10.1
OOO	14.1	10.0
%FFA[d]	0.050	0.70
12 h cold test	Pass	Not pass

[a] Reported values are in weight percentages based on total triglycerides

[b] XYZ-hydrocarbon tail for each of three triglyceride tails; the group in each tail is shown in the abbreviation (for example, LLO has two C18:2 tails and one C18:1 tail); abbreviations: Ln: Linolenic (C18:3), L: Linoleic (C18:2), O: Oleic (C18:1), S: Stearic (C18:0), P: Palmitic (C16:0)

[c] Extraction conditions: 0.15 wt% C_{10}-18PO-2EOsulfate, 6 wt% NaCl, 25 °C, seed to liquid ratio at 1:5 (g:g), 150 shakes/min

[d] Weight percentage of free fatty acids

Table 4 Analysis of extracted canola oil

TGC Profile[a]	Surfactant-based process[c]	Hexane-based process
LnOO[b]	8.45	7.70
LOO	23.9	25.7
OOO	44.4	47.8
%FFA[d]	0.040	0.60
12 h cold test	Pass	Not pass

[a] Reported values are in weight percentages based on total triglycerides

[b] See Table 3 for abbreviations

[c] Extraction conditions: 0.35 wt% C_{10}-18PO-2EOsulfate, 5 wt% NaCl, 25 °C, seed to liquid ratio at 1:5 (g:g), 150 shakes/min

[d] Weight percentage of free fatty acids

those obtained from the conventional hexane method, indicating no significant PUFAs degradation had occurred [42]. It is worth mentioning that while the oil quality tests performed in this paper gave some information on the oil quality, more detail on oil qualities (such as information on oxidative stability, saponification value and etc.) extracted by aqueous extended-surfactant solution will be reported in a subsequent paper focusing on scale up of this work.

Conclusion

In conclusion, we have shown that, among the extended-surfactants studied in this research, the alkyl-propoxylate-ethoxylate-sulfate class of surfactants is most suitable for the vegetable oilseeds evaluated in this research since it produces the lowest interfacial tension (IFT). Additionally, the C_{10}-18PO-2EO-sulfate exhibits the best performance for vegetable oil extraction in terms of low IFT, salinity values and absence of stable macroemulsions. The aqueous extended-surfactant based method proved to be effective for extracting peanut and canola oils, being able to achieve 95 and 93% oil extraction, respectively. Although the fraction of oil extracted is not as high as that of the hexane method, which achieved 98–99% efficiency, our method offers significantly better crude oil quality in terms of free fatty acid. The amount of oil extracted by aqueous extended-surfactant-based extraction and the amount of residual oil were summed and compared to the total oil content analyzed by Soxhlet extraction. There was no statistical difference between these two values, indicating that an insignificant amount of oil was lost through solubilization in the aqueous surfactant solution.

We also looked at the effects of different processing parameters on the vegetable oil extraction efficiency, including pH, surfactant concentration, extraction time, shaking speed, solid-to-liquid ratio, and salinity levels. We found that surfactant concentrations at the CμC and optimum salt concentrations are the most important parameters for vegetable oil extraction efficiency. From the evaluation of crude oil quality, it was shown that our method offers better crude oil quality in terms of free fatty acid content compared to the hexane extraction method. The peanut and canola oils are clear and exhibit a fresh smell. Hexane extracted oils have a burnt-like smell because the oils were heated to evaporate the hexane. Thus, we have successfully demonstrated the viability of the aqueous surfactant based extraction method for seed extraction of vegetable oils; future work will explore the scale-up of this process.

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