

Investigation of the Surface Properties of Polymeric Soaps Obtained by Ring-Opening Polymerization of Epoxidized Soybean Oil

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ABSTRACT: Epoxidized soybean oil (ESO) was converted to a polysoap (PESO) via a two-step synthetic procedure of catalytic ring-opening polymerization, followed by hydrolysis (HPESO) with a base. Various molecular weights of PESO and HPESO were prepared by varying the reaction temperature and/or catalyst concentration. In addition, the counter ion chemistry was varied by changing the base used for saponification. The PESO and HPESO products were carefully characterized and identified using a combination of FTIR, ¹H-NMR, solid state ¹³C-NMR, and GPC. The effect of HPESO polysoaps on the surface tension of water and the interfacial tension of water-hexadecane was investigated as a function of HPESO concentration, molecular weight, and counter ion

chemistry. HPESO polysoaps were effective at lowering the surface tension of water and the interfacial tension of water-hexadecane and displayed minimum values in the range of 20–24 and 12–17 dyn/cm, respectively, at concentration of 200–250 μM. Water-hexadecane interfacial tension was also calculated from measured surface tension data using the Antonoff, harmonic mean (HM), and geometric mean (GM) methods. Measured values agreed well with those calculated using the HM and GM methods, but not the Antonoff method. © 2008 Wiley Periodicals, Inc. *J Appl Polym Sci* 108: 1976–1985, 2008

Key words: surface and interfacial tension; ring-opening polymerization; soy-based polysoaps

INTRODUCTION

Soybean is the second largest crop plant in the United States, accounting for about 28% of planted acreage, just behind corn, which accounts for about 30%, and ahead of wheat, which accounts for about 23%. In 2006, 86.9 million metric tons of soybeans were grown in the United States, far in excess of the current market demand for US soybean.¹ Thus, there is a need to develop new uses for the surplus soybeans to prevent price depression due to oversupply.

Soybean comprises (w/w), 40% protein, 30% carbohydrates, and 20% oil.^{2,3} Currently, about 95% of soy protein is used in feed and 4% in food (for human consumption) applications. On the other hand, about 94% of soybean oil is used in food and about 4% in industrial applications. Growth areas

for soybean oil industrial applications include^{2–5}: plastics, lubricants; adhesives; inks, paints and coatings; fuels/biodiesel; solvents; and surfactants.

Soybean oil is a triglyceride, which is a triester of glycerol and three fatty acids. The main fatty acid composition of soybean oil is (w/w): linoleic (54), oleic (23), and linolenic (8).⁶ These fatty acids contain 2, 1, and 3 double bonds, respectively, in their hydrocarbon chains.

Various methods are employed for developing new value-added products from soybean oil.^{7–9} Some of these methods involve the synthesis of new materials from soybean oil using chemical, enzymatic, thermal, or other methods. This is possible because soybean oil comprise two reactive sites for this purpose. These are as follows: (a) the ester linkages of the triglycerides, and (b) the double bonds on its fatty acids. A well known example of a product from soybean oil reaction at the ester linkages is biodiesel, which is obtained via trans-esterification between soybean oil and short chain alcohols.⁹

Various reactions at the double bonds are also employed for converting soybean oil to value-added products. One of the methods involves the conversion of the double bonds into the more reactive oxirane or epoxide moiety by reaction with peracids or

Names are necessary to report factually on available data; however, the USDA neither guarantees nor warrants the standard of the product, and the use of the name by the USDA implies no approval of the product to the exclusion of others that may also be suitable.

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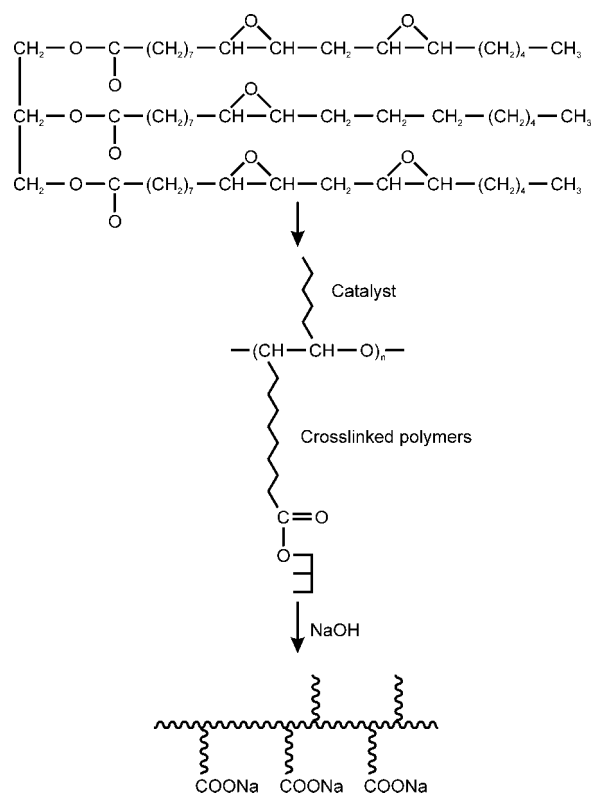


Figure 1 Synthesis of HPESO polysoaps.

peroxides. The resulting epoxidized soybean oil (ESO) has been used as plasticizer for polyvinyl chloride (PVC) compounds, chlorinated rubber, and polyvinyl alcohol (PVA) emulsions. ESO has also been used as the raw materials for the synthesis of new polymers.¹⁰⁻¹²

In this study, we prepared an ionic polymeric surfactant by ring-opening polymerization of ESO as depicted in Figure 1. After polymerization, the triglyceride group is hydrolyzed to obtain the polymer with free carboxylic acids. The polyacid is then converted into the polysoap by neutralizing it with an appropriate base. The surface-active properties of these polysoaps are the subject of this investigation.

EXPERIMENTAL

Materials

ESO was obtained from Elf Atochem (Philadelphia, PA) and used as received. Purified and redistilled boron trifluoride diethyl etherate, $(C_2H_5)_2O \cdot BF_3$, was obtained from Aldrich Chemical (Milwaukee, WI). Methylene chloride was purchased from Fisher Scientific (Fair Lawn, NJ) and used as supplied. Sodium hydroxide (97.5) was obtained from Fisher Scientific Reagent (Fair Lawn, NJ), and potassium hydroxide (A.C.S agent, 88.3% was obtained from J.T.

Baker (Phillipsburg, NJ). Triethanolamine (98%) was obtained from Sigma (St. Louis, MO). Deionized water was purified to a conductivity of 18.3 mΩ cm on a Barnstead EASYpure UV/UF water purification system (EASYpure UV/UF, Model no.: D8611, Barnstead International, Dubuque, IA). Freshly purified water was then filtered on 0.22 μm sterile disposable filter (MILLEX-GS 0.22 μm Filter Unit; Millipore Corp., Bedford, MA) prior to use in the preparation of aqueous polysoap solutions for use in surface and interfacial tension measurements. Hexadecane (99+% anhydrous) was obtained from Aldrich Chemical (Milwaukee, WI) and used as supplied.

Synthesis of polymeric surfactants

The soy based polymeric surfactants were prepared using a two-step procedure. The first step was the ring-opening polymerization of ESO using a cationic initiator. The second step was the hydrolysis of the polymerized epoxidized soybean oil (PESO). A brief description of each step is given next.

Ring-opening polymerization of ESO

In a typical procedure, 30 g ESO and 300 mL methylene chloride were added to a 500 mL round-bottomed flask fitted with a mechanical stirrer, condenser, thermometer, nitrogen line, and dropping funnel. The solution was cooled to 0°C with an ice bath, 0.396 g BF_3 (diethyl etherate) was added dropwise during 2 min, and the solution stirred at 0°C for 3 h. The methylene chloride was then removed using a rotary evaporator, the residue washed twice with hexane and dried under vacuum and 70°C to a constant weight of 29.8 g, which corresponds to a yield of 99.3%. The residue was positively identified to be pure polymerized epoxidized soybean oil (PESO) using FTIR and NMR spectroscopy as described later. PESO samples of varying molecular weights were obtained by changing the reaction temperature and the amount of catalyst. Further details about the synthesis of PESO can be found elsewhere.¹³

Hydrolysis of PESO

A solution of 2.5 g of PESO in 50 mL of 0.4M NaOH was refluxed for 24 h. The solution was then filtered with a filter paper and cooled to room temperature. The resulting gel was precipitated with 80 mL of 1.0M HCl, followed by several washings with water, and finally with two more washings with 10% (v/v) aqueous acetic acid. The resulting polymer was dried overnight at 80°C in an oven. The sample was further dried under vacuum and 70°C to a constant weight. The procedure yielded 2.1 g (84% yield) of

product, which was identified by FTIR and NMR spectroscopy (as described later), to be the hydrolyzed, polymerized, ESO or HPESO polysoap.

Structural characterization of HPESO

The structure of HPESO was characterized and confirmed using FTIR and H^1 -NMR. The molecular weights of various batches of HPESO were determined using GPC.

FTIR

FTIR spectra were recorded on a Thermo Nicolet Nexus 470 FTIR system (Madison, WI) in a scanning range of $650\text{--}4000\text{ cm}^{-1}$ for 32 scans at a spectral resolution of 4 cm^{-1} with a pair of KBr crystals in thin film.

NMR

1H and ^{13}C -NMR spectra for HPESO samples were recorded quantitatively using a Bruker AV-500 spectrometer (Bruker, Rheinstetten, Germany) operating at a frequency of 500.13 and 125.77 MHz, respectively, using a 5 mm inverse Z-gradient probe in $CDCl_3$ (Cambridge Isotope Laboratories, Andover, MA). Solid state ^{13}C -NMR spectra were recorded using a Bruker ARX-300 for PESO samples because it did not dissolve in these solvents.

GPC

GPC profiles were obtained on a PL-GPC 120 high-temperature chromatography (Polymer Laboratories, Amherst, MA) equipped with a column, autosampler, and in-built differential refractometer detector. The GPC was calibrated using a polystyrene mixture of varying molecular weights (M_w : 1700, 2450, 5050, 7000, 9200 and 10,665) in THF at 40°C . The flow rate of the mobile phase THF was 1.00 mL/min.

Preparation of HPESO salts

One percent of stock solution of HPESO— Na^+ , K^+ , and $(HOC_2H_5)_3N^+$ were prepared according to the following method: 1.0 g of HPESO sample was weighed into 50 mL beaker, the designated amount of NaOH, or KOH (to neutralize all carboxylic acid groups) was dissolved in 10 mL of deionized water, then added into the HPESO sample. The beaker containing HPESO sample and base solution was placed in a 75°C water bath. The solution was stirred with glass rod until the HPESO sample was dissolved. The solution was transferred to 100 mL volumetric flask. The beaker was rinsed three times with 10 mL of deionized water, and added to the 100 mL volu-

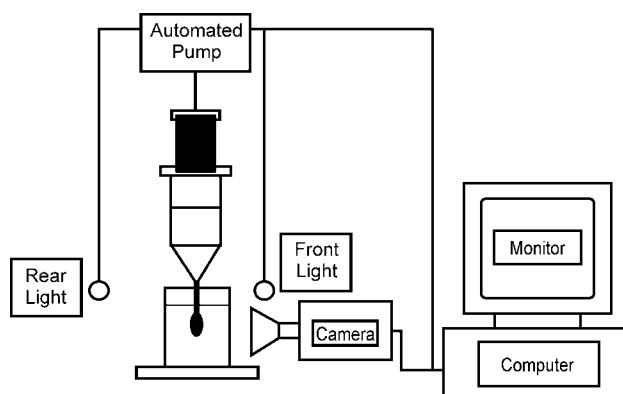


Figure 2 An automated pendant drop goniometer configured for interfacial tension measurement.

metric flask. The solution in the volumetric flask was cooled to room temperature, and then filled with deionized water to the 100 mL mark. For the preparation of the amine salt, the ratio of triethanolamine to carboxylic group in HPESO molecule was 2 to 1.

Dynamic surface and interfacial tension

Dynamic surface and interfacial tension measurements were conducted using axisymmetric drop shape analysis (ADSA) method¹⁴ on a FTA-200 automated goniometer (First Ten Angstroms, Portsmouth, VA) equipped with the fta32 v2.0 software. In ADSA, interfacial tension is obtained by analyzing the change in the shape of a pendant drop of one liquid suspended in air or a second liquid. The method is based on the Bashforth-Adams equation, which relates drop shape to interfacial tension.^{15,16} A schematic of the FTA 200 configured for dynamic interfacial tension measurement on a pendant drop is shown in Figure 2. The instrument comprises an automated pump that can be fitted with various sizes of syringes and needles to allow for control of pendant drop formation. An automated image viewing and capturing system, with various image capture triggering options, is used to capture drop image. The software allows for an automated drop shape analysis of the captured drop image, and for measuring the surface/interfacial tension. The computer hardware and software also provide the capability for data capture, storage, analysis, and transfer. All measurements were conducted at room temperature ($23^\circ\text{C} \pm 2^\circ\text{C}$). In a typical procedure, a 10-mL disposable syringe equipped with a 17-gauge (1.499 mm OD) blunt disposable needle (KDS 17-1P, Kahnetics Dispensing Systems, Bloomington, CA) was used to generate a pendant drop of the aqueous HPESO solution in air or hexadecane medium contained in a glass cuvette (10 mm). The instrument is programmed to automatically deliver a specified vol-

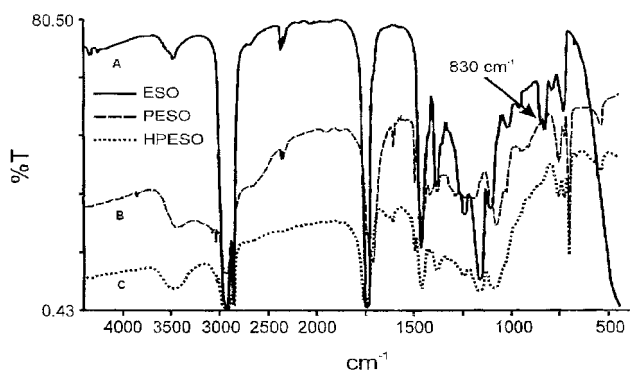


Figure 3 FTIR spectra of (A) ESO, (B) PESO, and (C) HPESO.

ume of the solution at 1 $\mu\text{L/s}$, and also to automatically trigger image capture when the pump stops. All runs were programmed to acquire images at a rate of 0.067 s/image, with a predetermined trigger period multiplier to allow for a total of 35 images to be captured during the acquisition period. At the end of the acquisition period, each image was automatically analyzed, saved, and a plot of time versus surface or interfacial tension displayed. Repeat measurements (2–4) were conducted on each sample from which equilibrium surface or interfacial tension values were obtained by averaging the values at very long periods, where the surface and interfacial tension values showed little or no change with time. Prior to running tests with the solutions, the instrument was calibrated with water and then checked by measuring the interfacial tension between water and pure hexadecane.

Data processing

The data from the 2–4 repeat measurements of surface and interfacial tension were used to calculate average and standard deviations for each sample, and used in further analysis. Data analysis and plotting was conducted using IgorPro Vesion 5.0.3.0 software (WaveMetrics, Lake Oswego, OR).

RESULTS AND DISCUSSION

Identification of structures of HPESO polysoaps

FTIR

The infrared spectrum of ESO and PESO in Figure 3(A,B) are compared to the spectrum of HPESO, in Figure 3(C). The comparison shows the characteristic oxirane absorption at 823.3 cm^{-1} in ESO is not present in PESO because of the ring-opening polymerization. The IR spectrum of the HPESO in Figure 3(C) was obtained after hydrolysis of PESO by NaOH.

It shows a shift in the ester carbonyl band to 1718.9 cm^{-1} from 1734.5 cm^{-1} when compared with PESO because of strong H-bonding between carboxylic acids forming dimers. Hydrogen bonding weakens C=O bonds, resulting in an absorption shift to a lower frequency.

^1H - and ^{13}C -NMR

Figure 4 shows ^1H -NMR spectra (A) and ^{13}C -NMR spectra (B) of ESO and HPESO. The peak assignments were done using DEPT 135 and COSY 45 NMR experiments. The epoxy protons are observed in the δ 3.0–3.2 ppm region. Methine proton of $-\text{CH}_2-\text{CH}-\text{CH}_2-$ backbone at δ 5.1–5.3 ppm, methylene proton of $-\text{CH}_2-\text{CH}-\text{CH}_2-$ backbone at δ 4.0–4.4 ppm, CH_2 proton adjacent to two epoxy group at δ 2.8–3.0 ppm, $-\text{CH}-$ protons of epoxy ring at δ 3.0–3.2 ppm, $\alpha\text{-CH}_2$ to $>\text{C}=\text{O}$ at δ 2.2–2.4 ppm, $\alpha\text{-CH}_2$ to epoxy group at δ 1.7–1.9 ppm, $\beta\text{-CH}_2$ to $>\text{C}=\text{O}$ at δ 1.55–1.7 ppm, $\beta\text{-CH}_2$ to epoxy group at δ 1.4–1.55 ppm, saturated methylene groups

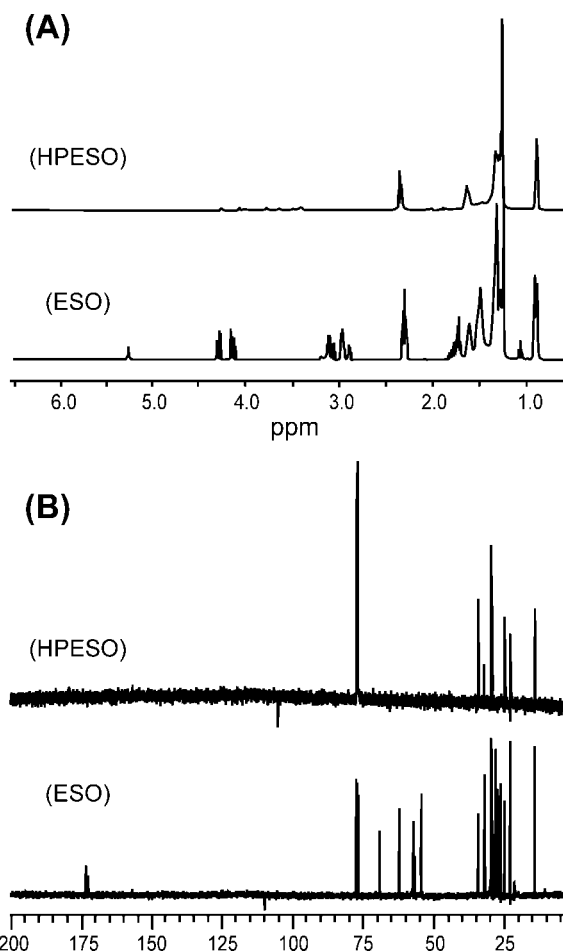


Figure 4 ^1H -NMR (A) and ^{13}C -NMR (B) spectra of ESO and HPESO.

TABLE I
Polysoaps Investigated in this Work

Polysoap	Counterion ^a	M_w (kg/mol)
HPESO-004K	K ⁺	2.615
HPESO-004A	TEA ⁺	2.615
HPESO-003N	Na ⁺	3.219
HPESO-003K	K ⁺	3.219
HPESO-003A	TEA ⁺	3.219

^a TEA⁺, Triethanolammonium.

at δ 1.1–1.4 ppm, and terminal $-\text{CH}_3$ groups at δ 0.8–1.0 ppm region. ¹H-NMR spectrum of HPESO indicates disappearance of proton peaks of epoxy carbon in the range of 3.0–3.2 ppm region.

In ¹³C-NMR spectrum of ESO, peaks at 54–57 ppm are assigned to epoxy carbons. The presence of ¹³C-NMR peak at 173.1 ppm is due to carbonyl carbon of triacylglycerol peaks at 68.9 ppm and 62 ppm, respectively, assigned to CH and CH₂ carbons of the $-\text{CH}_2-\text{CH}-\text{CH}_2-$ glycerol backbone. ¹³C-NMR spectrum of HPESO indicates disappearance of epoxy carbon peaks in the range of 54–57 ppm. Peaks at 68.9 ppm and 62 ppm assigned to CH and CH₂ carbons of $-\text{CH}_2-\text{CH}-\text{CH}_2-$ glycerol backbone also disappeared because of hydrolysis of glycerol. In addition, in solid state ¹³C-NMR spectrum of PESO, a peak at 75 ppm due to the $-\text{CH}_2-\text{CH}-\text{CH}_2-$ glycerol backbone carbons was observed. Also a peak at 175 ppm was observed and assigned to carbonyl carbon of triacylglycerol. The epoxy carbon peaks in the range of 54–57 ppm disappeared because of ring-opening polymerization.

Surface tension of aqueous HPESO polysoaps

The HPESO polysoaps studied in this work are listed in Table I. As can be seen in Table I, the polysoaps varied in their molecular weights and the type of counter ion. The molecular weights were either 2.6 or 3.2 kg/mol. Polysoaps with K⁺, Na⁺, triethanolammonium (TEA⁺) were prepared by varying the chemistry of the base used to neutralize HPESO.

A typical dynamic surface tension data for an aqueous HPESO salt is illustrated in Figure 5. The data in Figure 5 shows triplicate measurements on an aqueous HPESO salt of 3.2 kg/mol molecular weight, TEA⁺ counterion, and 0.186 mM concentration. As can be seen in Figure 5, the surface tension versus time data displays a number of interesting features. The surface tension decreases sharply with time initially, then displays a gradual decrease, and finally levels off to a more or less constant value over a long period of time. The reason for this behavior has to do with the change in the concentration of polysoap molecules at the air–water interface as a function of time. The surface tension of aqueous

HPESO depends on the concentration of HPESO molecules at the air–water interface at a particular time. Initially, the surface concentration is low and, as a result, the surface tension of aqueous HPESO is high, just under that of pure water. With time, HPESO molecules diffuse from inside the drop to the surface. This diffusion causes the concentration of HPESO molecules on the surface to increase and thereby causing the surface tension to decrease with time. The surface tension continues to decrease until the concentration of HPESO molecules on the surface reach its equilibrium value, at which time the surface tension becomes constant and independent of measurement time. The equilibrium surface concentration of HPESO molecule is a function of the concentration of HPESO in the bulk water. Thus, the equilibrium surface tension associated with the equilibrium surface concentration is a function of the concentration of HPESO in water.

The data in Figure 5 shows fairly good reproducibility between the three repetitive measurements. The equilibrium surface tension for the aqueous HPESO solution in Figure 5 is obtained by averaging the last 2–3 values at the end of the measurement period for each of the repeat measurements. The averages and standard deviations from such calculations are used in further analysis.

The effect of HPESO concentration on the surface tension of water is illustrated in Figure 6. In Figure 6, the points are the average equilibrium surface tensions of 2–4 repeat measurements, and the error bars correspond to \pm one standard deviation. The data in Figure 6(A,B) are for the low- and high-molecular weight HPESO polysoaps, respectively. The two HPESO solutions seem to display some similarity and some differences in their surface tension behav-

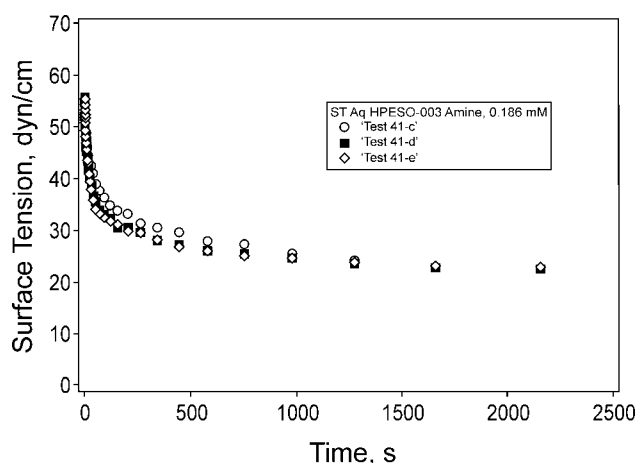


Figure 5 Typical data from repeat measurement of the dynamic surface tension of aqueous polysoap on an automated pendant drop goniometer [polysoap with M_w of 3.219 kg/mol, and TEA⁺ counter ion].

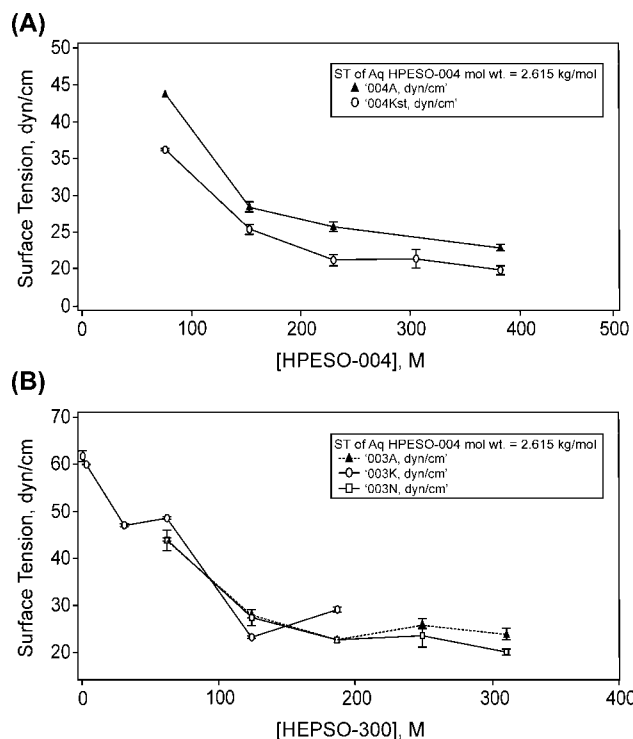


Figure 6 Effect of HPESO concentration on the surface tension of water (A) HPESO $M_w = 2.6$ kg/mol; (B) HPESO $M_w = 3.2$ kg/mol.

iors. As expected, both solutions displayed a decrease in surface tension with increasing concentration of HPESO. In both cases, the surface tension reached a minimum value and more or less remained constant at concentrations above ~ 200 μM . This aqueous HPESO concentration at which the minimum surface tension value was observed corresponds to an equilibrium polysoap concentration at the air–water interface where a complete saturation of the interface occurs. As was observed in Figure 6, further increase in the concentration of HPESO in water will not change the surface concentration of the polysoaps and, hence, the surface tension remains constant. Table II compares the minimum equilibrium surface tension of water because of the polysoaps investigated in this work. As shown in Table II, the minimum equilibrium surface tension values of the various aqueous HPESO polysoaps are in a narrow range of 20–24 dyn/cm, indicating that, the polysoaps have similar surface energies.

A closer look at the data in Figure 6 shows that the two HPESO polysoaps displayed some differences in the effect of counter ions on surface tension. In the case of the low-molecular weight HPESO, the surface tension of the TEA^+ polysoap was consistently slightly higher than that of the K^+ polysoap. However, this was not the case with the higher molecular weight HPESO polysoap, where the surface tensions were mostly independent of the chemistry

TABLE II
Effect of HPESO Polysoaps on the Minimum Equilibrium Surface Tension of Water

Polysoap	M_w (kg/mol)	Surface tension (dyn/cm)
HPESO-004K	2.6	19.9 ± 0.6
HPESO-004A	2.6	22.9 ± 0.4
HPESO-003N	3.2	21.6 ± 0.5
HPESO-003K	3.2	19.9 ± 1.1
HPESO-003A	3.2	23.9 ± 1.4

of the counter ion. The reason for the difference in the response of the two HPESO polysoaps to variations in the counter ion chemistry is not clear. One possible explanation could be the difference in the physical size between the counter ions. TEA^+ , being more bulkier than the other counter ions, will result in fewer counter ion at the interface, which will lead to fewer polysoaps. The result will be lower equilibrium concentration of polysoap at the air–water interface and, hence, higher surface tension. If this is the case, it appears from Figure 6, the effect is more profound on the lower molecular weight HPESO polysoap.

Effect of HPESO polysoaps on the interfacial tension of water-hexadecane

Figure 7 shows the dynamic interfacial tension between water and hexadecane in the presence of the low-molecular weight HPESO polysoap. The data in Figure 7 is for three different concentrations of HPESO in water: 0, 76.5, and 229 μM . The profile of the time versus interfacial tension data is similar to the time versus surface tension data discussed earlier. In the presence of HPESO polysoap in the water, the water-hexadecane interfacial tension shows an initial fast drop, followed by a gradual

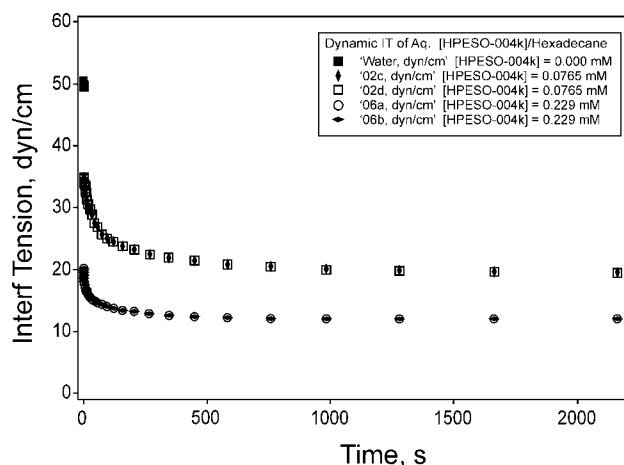


Figure 7 Typical dynamic interfacial tension data of aqueous HPESO/hexadecane [polysoap with M_w of 2.615 kg/mol and K^+ counterion].

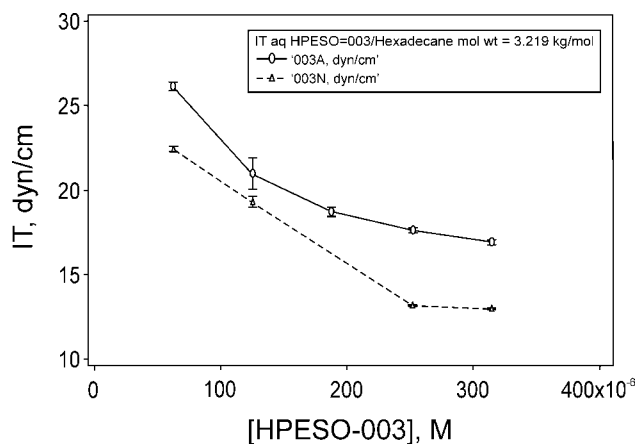


Figure 8 Effect of HPESO concentration on water-hexadecane interfacial tension.

drop and, finally a constant equilibrium value at very long time. It should be noted that the equilibrium interfacial tension value is a function of the concentration of HPESO in the water phase. As demonstrated in Figure 7, the equilibrium interfacial tension decreases with increasing HPESO concentration in the water phase.

The reason for the observed time-interfacial tension profile is the same as that described earlier for the time-surface tension profile. The water-hexadecane interfacial tension is a function of the concentration of the HPESO molecules at the water-hexadecane interface. Initially, the interfacial concentration of HPESO molecules is very low and, as a result, the interfacial tension will be slightly below that of pure water-hexadecane, which is 51 ± 1 dyn/cm.¹⁷ However, as more HPESO polysoap molecules diffuse from the bulk water phase to the water-hexadecane interface and adsorb, the interfacial tension continues to decrease until the concentration of the polysoap molecules at the interface reach its equilibrium value. This will result in the interfacial tension

reaching its equilibrium constant value. The equilibrium interfacial tension and standard deviation for the specific HPESO solution is obtained by averaging the last several values, which show little or no change with time. As can be seen in Figure 7, the measured dynamic interfacial tension for both concentrations showed excellent repeatability.

The effect of HPESO concentration in water on hexadecane-water interfacial tension are compared in Figure 8. The data in Figure 8 is for the high-molecular weight HPESO polysoap. In Figure 8, the points are averages of equilibrium interfacial tension for 2–4 consecutive measurements, and the error bars are \pm one standard deviation. The data in Figure 8 indicate that the equilibrium interfacial tensions are functions of the concentration of HPESO polysoaps. The hexadecane-water interfacial tension decreases with increasing HPESO concentration in water and then levels off to some minimum constant value. This minimum value for the various polysoaps investigated here is in a relatively narrow range of 12–17 dyn/cm (Table III).

The interfacial tension at each concentration corresponds to an equilibrium HPESO concentration at the hexadecane-water interface. The concentration of HPESO polysoap molecules at the hexadecane-water interface increases with increasing HPESO concentration in the water phase until about 250 μ M HPESO in water. At this concentration of HPESO in water, the interface is saturated with HPESO molecules and the interfacial tension and interfacial concentration of HPESO remain constant and independent of HPESO concentration in water.

The data in Figure 8 also compares the effect of Na^+ and TEA^+ counter ions of HPESO polysoap on the water-hexadecane interfacial tension. It appears that the polysoap with TEA^+ is slightly less effective at reducing the hexadecane-water interfacial tension than the Na^+ polysoap. The reason for the difference in the effect of counter ion on interfacial tension is

TABLE III
Calculated Versus Measured Minimum Equilibrium Interfacial Tension Between Aqueous HPESO Polysoaps and Hexadecane

Polysoap	Minimum water-hexadecane equilibrium interfacial tension (dyn/cm)								
	Measured	Calculated ^a						GM-60 ^c	HM-60 ^d
		Ant ^b	GM-80 ^c	HM-80 ^d	GM-70 ^c	HM-70 ^d			
HPESO-004K	11.9 \pm 0.1	7.7	5.6	7.1	8.3	10.4	11.2	14.1	
HPESO-004A	14.2 \pm 0.1	4.6	5.5	6.4	8.4	9.9	11.5	13.8	
HPESO-003N	13.0 \pm 0.04	5.9	5.5	6.7	8.3	10.1	11.3	13.9	
HPESO-003K	12.7 \pm 0.2	7.6	5.6	7.1	8.3	10.4	11.2	14.1	
HPESO-003A	16.9 \pm 0.2	3.6	5.5	6.3	8.5	9.8	11.7	13.7	

^a Using 27.5 dyn/cm for the surface tension of hexadecane.

^b Antonoff method, eq. (2).

^c Geometric mean method, eq. (6), $x_3^d = 0.8, 0.7, 0.6$, respectively.

^d Harmonic mean method, eq. (7), $x_3^d = 0.8, 0.7, 0.6$, respectively.

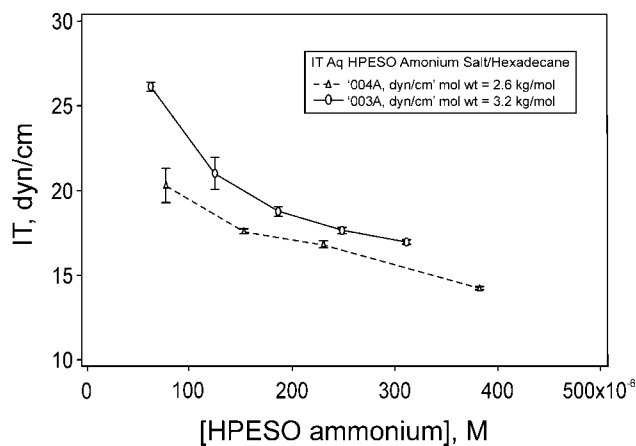


Figure 9 Effect of HPESO molecular weight on hexadecane-water interfacial tension.

not fully understood. One possible explanation could be the effect of counter ions on polysoap adsorption and orientation at the interface. The counter-ions reside in the water side of the interface and can affect the manner in which the polysoap orients and adsorbs at the interface. An orientation that favors closer packing of polysoap molecules at the interface will result in higher equilibrium concentration at the interface, and thereby lead to a lower interfacial tension. Thus, it appears that a favorable orientation is obtained with Na^+ counter ions than that with TEA^+ counter ions. It should be noted that, the surface tension of water for the high-molecular weight polysoap was independent of the polysoap counter ion. The fact that the counter-ion had some effect on water-hexadecane interfacial tension implies a significant alteration of the interface microenvironment properties due to replacement of air by hexadecane.

The effect of HPESO molecular weight on water-hexadecane interfacial tension is compared in Figure 9. The data in Figure 9 is for a solution of TEA^+ polysoaps. As was observed earlier, the interfacial tension decreased with increasing polysoap concentration and leveled off. The interfacial tension appeared to display a slight dependence on polysoap molecular weight. Thus, under identical concentrations, the higher molecular weight polysoap was slightly less effective at reducing the water-hexadecane interfacial tension than the lower molecular weight polysoap. Since the interfacial tension is a function of the concentration of polysoap at the interface, it appears that the presence of hexadecane has favored an increase in the interfacial concentration of the low-molecular weight polysoap over that of the high-molecular weight polysoap. The reason for this difference is not fully understood. One possible explanation is a slightly higher solubility of the high-molecular weight polysoap in the hexadecane

bulk phase than the low-molecular weight polysoap. This will result in a slightly lower equilibrium interfacial concentration for the high-molecular weight polysoap, thereby resulting in higher water-hexadecane interfacial tension.

Estimation of the surface energy of HPESO polysoaps

The surface energy of polysoaps, γ_s , comprises polar (γ_s^p) and dispersive (γ_s^d) components which are related as follows:

$$\gamma_s = \gamma_s^d + \gamma_s^p \quad (1)$$

The interfacial tension of polysoaps with other materials can be predicted from their respective surface energies and surface energy components, using various methods. In this section, predicted interfacial tensions of polysoaps with hexadecane will be compared to the measured values described in the previous section. Such analysis provides insight into the surface energy of polysoaps, since measured surface energy values are used in the various predictive models. In the equations to follow, the subscripts S and H refer to polysoap and hexadecane, respectively.

The simplest method for relating the interfacial tension between two substances with their respective surface energies is the Antonoff method^{18,19} given as follows:

$$\gamma_{SH} = |\gamma_s - \gamma_H| \quad (2)$$

where γ_s , γ_H are the surface energies of the two substances; and γ_{SH} is the interfacial energy.

The simplicity of the Antonoff method is that it does not require knowledge of the polar and dispersive surface energy components of the materials.

The geometric mean (GM) and harmonic mean (HM) methods require knowledge of polar and dispersive components.²⁰ The relationship between interfacial tension and surface tension parameters for HM is as follows:

$$\gamma_{SH} = \gamma_s + \gamma_H - \frac{4\gamma_s^d\gamma_H^d}{\gamma_s^d + \gamma_H^d} - \frac{4\gamma_s^p\gamma_H^p}{\gamma_s^p + \gamma_H^p} \quad (3)$$

The corresponding equation for the GM method is given by:

$$\gamma_{SH} = \gamma_s + \gamma_H - 2(\gamma_H^d\gamma_s^d)^{1/2} - 2(\gamma_H^p\gamma_s^p)^{1/2} \quad (4)$$

Since the surface tension of hexadecane does not comprise a polar component,²¹ γ_H^p in eqs. (3) and (4) is zero. This will eliminate the last term in eqs. (3) and (4). Further simplification of eqs. (3) and (4) is

achieved by replacing γ_H^d by γ_H , and by defining γ_S^d as follows:

$$\gamma_S^d = x_S^d \gamma_S \quad (5)$$

where $x_S^d = \gamma_S^d / \gamma_S$; the fraction of nonpolar components of γ_S and has values between 0 and 1.

The simplified HM and GM equations for the polysoap-hexadecane system are as follows:

$$\gamma_{SH} = \gamma_S + \gamma_H - \frac{4x_S^d \gamma_S \gamma_H}{x_S^d \gamma_S + \gamma_H} \quad (6)$$

$$\gamma_{SH} = \gamma_S + \gamma_H - 2(x_S^d \gamma_S \gamma_H)^{1/2} \quad (7)$$

Equations (2), (6), and (7) were used to predict the hexadecane-water interfacial tension in the presence of HPESO polysoaps. The predicted values were then compared with the measured values at high HPESO concentrations. The interfacial tensions at high concentrations are assumed to be the minimum water-hexadecane interfacial tensions, corresponding to full coverage of the interface by the HPESO polysoap molecules.

The data used in eq. (2) were the surface tensions of hexadecane and those of aqueous HPESO solutions. The reported surface tension of hexadecane is 27.0 dyn/cm,¹⁷ which we were able to verify. For the aqueous HPESO solutions, we used the minimum equilibrium surface tension from the concentration versus surface tension data similar to that shown in Figure 6. This data corresponds to the surface tension of water at full coverage of the air-water interface by the HPESO polysoap molecules, and is summarized in Table II.

For eqs. (6) and (7), in addition to the surface tensions of hexadecane and aqueous HPESO, values for x_S^d are required. In this work, x_S^d was used as a fitting parameter with values between 0 and 1. γ_{SH} values were calculated using HM [eq. (6)] and GM [eq. (7)] methods at various x_S^d values. The corresponding γ_{SH} values were designated as HM-XY or GM-XY, where XY is the fractional value of x_S^d . For example, GM-60 and HM-70 correspond to γ_{SH} values calculated using $x_S^d = 0.6$ by the GM method, and $x_S^d = 0.7$ by the HM method, respectively.

Table III shows a summary of the water-hexadecane interfacial tension calculated using eqs. (2), (6), and (7). Also shown in Table III are the measured interfacial tension values along with the corresponding standard deviations. In addition, Table III shows the x_S^d values that were used in the calculation of the interfacial tensions using the HM and GM methods.

The data in Table III clearly shows that the Antonoff [eq. (2)] method did underestimate the hexadecane-water interfacial tension in the presence of HPESO polysoaps. The Antonoff method has been

found to be a good predictor of interfacial tensions only in a very limited cases, where strict conditions about the surface tensions of the two components must be met.^{20,22} Apparently, this was not the case, hence the method did not do well. On the other hand, the GM and HM methods, specially at x_S^p values of 0.3–0.4 (where $x_S^p = 1 - x_S^d$) seem to predict γ_{SH} values close to the measured values.

SUMMARY/CONCLUSION

A great deal of effort is employed at developing new uses for surplus crops such as soybean. If successful, such effort will lead to a healthy balance between supply and demand so that farmers will get a fair price for their crop.

Polysoaps were obtained from polymerized, epoxidized soybean oil (PESO), by hydrolyzing it with the appropriate base. The resulting HPESO polysoaps were dissolved in purified water and its effect on the surface tension of water and the interfacial tension of hexadecane-water was investigated as a function of concentration, molecular weight, and counter ion chemistry. All of the HPESO polysoaps investigated were very effective at lowering the surface tension of water and the interfacial tension of water-hexadecane. In all cases, the effectiveness of the polysoaps increased with increasing concentration up to about 200–250 μM , above which the surface and interfacial tensions remained constant and independent of concentration. The minimum surface tension of the aqueous polysoaps were in the range 20–24 dyn/cm, and the corresponding values for water-hexadecane interfacial tension were in the range 12–17 dyn/cm.

HPESO polysoaps displayed a slightly higher surface and interfacial tension with TEA^+ than with K^+ or Na^+ counter ions. They also displayed a slight increase of water-hexadecane interfacial tension with increasing molecular weight.

The measured water-hexadecane interfacial tensions were also compared with those calculated using three predictive models. The comparisons showed good agreement with two of the models and poor agreement with the third.

Large quantities of detergents and surfactants are used by consumers and industry for a wide variety of applications. The current worldwide market for detergents and surfactants is in the billions of dollars per year. Also, the current source of raw material for detergents and surfactants is almost exclusively petroleum based. This means that, there is a large opportunity for successful biobased detergents and surfactants to displace petroleum-based products. The work described here demonstrates that soy-based polysoaps are effective at reducing the surface tension of water and the interfacial tension of oil-water.

These are characteristics of immense importance for the various detergent and surfactant applications. Another important characteristic is how products and formulations containing soy-based polysoaps perform in some specific application areas. In the next phase of this research, we will identify large volume application areas and investigate the performance of soy-based polysoaps.

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