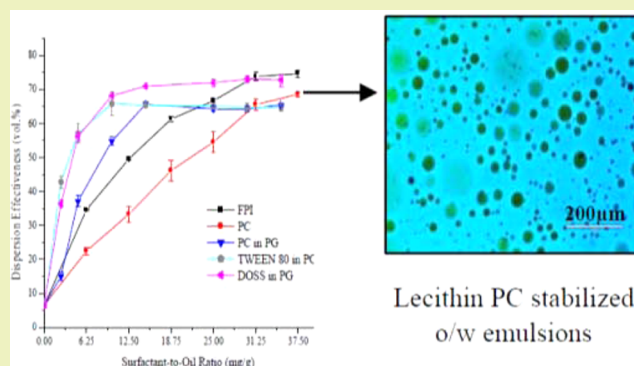


Soybean Lecithin as a Dispersant for Crude Oil Spills

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ABSTRACT: The toxicity of oil spill dispersants to marine organisms has necessitated the search for alternative dispersant formulations that are environmentally benign. Soybean lecithin, a well-known surface active agent in the food industry, is effective at stabilizing oil-in-water emulsions. In addition to its excellent emulsification properties, it is biodegradable, less toxic than the traditional chemical dispersants, and ecologically acceptable. In this study, soybean lecithin was used to formulate dispersants for crude oil spill application. Soybean lecithin was fractionated into phosphatidylinositol (PI) and phosphatidylcholine (PC) enriched fractions using ethanol. The fractionated PI was deoiled and characterized with Fourier transform infrared spectroscopy (FT-IR). The crude soybean lecithin (CL) and the fractionated PI and PC were solubilized in water and their dispersion effectiveness determined using the U.S. EPA's baffled flask test. The dispersion effectiveness of these solubilized dispersants was compared with that of solid crude lecithin (SL). The dispersion effectiveness of PC was found to be higher than those of SL, CL, and PI at all the surfactant-to-oil ratios (SORs) tested. However, when the fractionated PI was modified or "functionalized" (FPI) with additional hydroxyl groups to alter the hydrophilic–lipophilic balance (HLB), its dispersion effectiveness improved remarkably and was higher than that of PC. At higher SORs (>28 mg/g), the dispersion effectiveness of FPI was slightly higher than that of solubilized DOSS and Tween 80 in propylene glycol. The dispersion effectiveness of PC and FPI on Texas (TC) and light crude (LC) oil samples were almost the same. PC and FPI performed better at the higher salinity of 3.5 wt % than the lower salinities of 0.8 and 1.5 wt %. The findings from this study suggest that dispersants formulated from fractionated PI and PC have the potential to replace traditional dispersant formulations.

KEYWORDS: Lecithin, Phosphatidylcholine, Phosphatidylinositol, Oil spills, Chemical dispersants



INTRODUCTION

The accidental release of natural crude oil and its refined products into marine waters is a major problem for the coast guards of most countries worldwide. An oil spill is defined as a discrete event in which oil is discharged through neglect, by accident, or with intent over a relatively short time.¹ Different response measures such as the application of chemical dispersants, burning of oil in situ, shoreline cleanup, and the use of mechanical containment and collection are adopted whenever oil spills occur. Among these oil spill response methods, chemical dispersant application is one of the few response measures that, when adopted under the right circumstances and with judicious use of dispersants, leads to reduced environmental and economic impact of the oil spill.² Dispersants are one of the only feasible response options for large-scale oil spills.

A chemical dispersant is a mixture of surfactants (anionic and/or nonionic) and a hydrocarbon solvent.³ When chemical dispersants are applied to an oil spill and sufficient energy is exerted to the dispersant–oil mixture, the slick is broken down into smaller droplets due to the reduction of the oil–water interfacial tension.⁴ The oil droplets diffuse both vertically and

horizontally by the action of the sea waves and remain in the water column because they possess very little rising velocity.⁵ The increased surface area that arises from the smaller oil droplet size helps to accelerate biodegradation of the oil by bacteria action and hence reduces the environmental impact of the spilled oil.^{2,6}

The use of chemical dispersants as a means of combating oil spills is being accepted worldwide due to improvement in dispersant formulations and the use of Net Environmental Benefit Analysis (NEBA) in deciding whether or not dispersants should be used. With over 3 decades of research, it is now clear that the use of chemical dispersants to counter the effects of oil spills has led to a reduction in toxicity and the environmental problems that first-generation chemical dispersants caused.⁷

However, indiscriminate application of chemical dispersants during oil spills has increased concerns about the environmental impact of using chemical dispersants.⁸ For example, an

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estimated 2.1 million gallons of dispersants were applied to the Gulf of Mexico during the Deepwater Horizon oil spill of 2010 to disperse approximately 205 million gallons of crude oil.³ Environmental and human toxicity issues arose when such a voluminous amount of chemical dispersant was applied. The chemical dispersant used for the Gulf of Mexico oil spill, Corexit 9500A was moderately toxic to cleanup workers and Gulf of Mexico aquatic species.⁹ Four thousand gallons of Corexit 9580 were also applied to disperse part of the 11 million gallons of crude oil spilled during the Exxon Valdez oil spill, which occurred on Prince Williams Sound, Alaska. Though Corexit 9580 helped disperse some of the spilled oil, its use was discontinued because scientific data on its toxicity was incomplete. Corexit 9580 contains 2-butoxyethanol, which was known to be carcinogenic.¹⁰ The dispersant formulations used during the 1967 Torrey Canyon and 1996 Sea Empress oil spills were devastating to aquatic species.^{8,11} The chemical surfactants and the solvents used in formulating these dispersants are responsible for their toxicity. Some of the chemical surfactants (e.g., dioctyl sodium sulfosuccinate (DOSS)) used in their formulation are synthesized chemically, are of petroleum origin, are toxic to aquatic species, are not easily biodegradable, and the byproducts of their manufacturing processes can be environmentally hazardous.¹²

The popular perception that natural products are always better for the environment has led to the suggestion that petrochemical surfactants should be replaced with surfactants based on renewable oil seeds or animal-fat-derived materials because the change would minimize the environmental impact of surfactant containing products.¹³ Although this popular perception is not always correct, the natural surfactants are indeed better for the environment. Soybean lecithin is a well-known natural surfactant in the food, cosmetics, and paints industries. Its use in these industries stemmed from its availability and excellent emulsifying behavior.¹⁴ Soybean lecithin has been used to form food emulsions such as milk, butter, margarine, cheese, chocolate, and ice cream.¹⁵ The emulsification properties of soybean lecithin can be associated with its phospholipid constituents, which are well-known emulsifiers, wetting, and dispersing agents. The most common types of phospholipids are phosphatidylcholine (PC), phosphatidylinositol (PI), phosphatidylethanolamine (PE), and phosphatidylserine (PS). Ethanol can be used to fractionate PI and PC from the lecithin, each of which has different solubilities in this solvent.^{14,16} From the American Oil Chemists' Society (AOCS), fractionating crude lecithin with ethanol results in an ethanol soluble PC-enriched fraction and ethanol insoluble PI-enriched fraction. The neutral lipids can be removed from the PI-enriched fraction through deoiling with acetone since neutral lipids are soluble in acetone but insoluble in ethanol. Research has shown that PI and PC have different emulsification properties and can be used to form either water-in-oil (w/o) emulsions or oil-in-water (o/w) emulsions.¹⁷

Increased environmental awareness and strict legislation has made environmental compatibility of dispersants an important factor in their applications.^{12,18} To reduce the toxicity and environmental impact of dispersants, there is a need to look into the way dispersants are formulated. To this end, this study aims at formulating a more environmentally friendly dispersant for crude oil spill applications. Recent studies have shown that a blend of 60 wt % lecithin and 40 wt % Tween 80 is an effective emulsifier.¹⁹ This study proposes the use of a natural surfactant, soybean lecithin dissolved in water, as a dispersant for crude oil

spill applications. Such a dispersant formulation is expected to be environmentally benign because soybean lecithin is biodegradable, less toxic, and ecologically acceptable. Lecithin has been used to increase the biodegradation rate of dispersed oil because it contains phosphorus and nitrogen, which are known to accelerate bacteria activity.^{12,20} Therefore, such a dispersant formulation will not only disperse the spilled oil, but it will also aid in the biodegradation of the dispersed oil. The use of water as the delivery medium will eliminate the use of hydrocarbon solvents and result in a less toxic dispersant formulation. In this study, PI and PC were fractionated from crude soybean lecithin using ethanol. PI and PC were solubilized in water and their dispersion effectiveness compared with those of solubilized crude soybean lecithin in water (CL), powdered soybean lecithin (SL), solubilized Tween 80, and dioctyl sodium sulfosuccinate (DOSS) in propylene glycol. Various factors such as ethanol fractionation of crude soybean lecithin into PC and PI, structural modification of PI, salinity, crude oil type (Texas crude, TC and light crude, LC), and PI-to-PC ratio in the formulated dispersant were examined for influences on the dispersion effectiveness.

■ EXPERIMENTAL SECTION

Materials. Soybean lecithin was purchased from Stakich Inc. (Bloomfield Hills, MI) and Koptec ethanol 200 proof was obtained from VWR. The following chemicals were obtained from Sigma-Aldrich: dioctyl sodium sulfosuccinate salt (DOSS) and Tween 80. Sodium thiosulfate (0.1 N) and propylene glycol were obtained from Macron Chemicals and Spectrum Chemicals, respectively. Hanus (iodine monobromide) solution and chloroform were purchased from RICCA and EMD Chemical Company, respectively. Potassium iodide (10 w/v %) and starch indicator were obtained from BDA Chemicals. Instant Ocean salt was obtained from Instant Ocean (Blacksburg, VA). The heavy crude oil (Texas crude (TC)) was obtained from Texas Raw Crude International (Midland, TX) whereas the light crude (LC) was obtained from Ohmsett (Atlantic Highlands, NJ). The major compounds present in the crude oil samples, the properties of the crude oil as well as the composition of the Instant Ocean salt have been reported by Nyankson et al.²¹

Experimental Procedure. Fractionation of Crude Soybean Lecithin with Ethanol. The method used to fractionate the soybean lecithin is similar to the one described by Wu et al.¹⁴ Approximately 3 g of crude lecithin was weighed into a centrifuge tube, then 9 g of ethanol (95%) was added. The tube was closed and heated in a water bath at 60 °C for 60 min, stirring every 15 min during heating to enhance the dissolution of the PC in ethanol. After heating for 60 min, the mixture was centrifuged for 5 min. The ethanol phase was poured off into a glass vial and the ethanol evaporated at 70 °C. Because the ethanol soluble fraction is made up of PC,²² evaporating the ethanol resulted in a "solid residue" that was made up of PC. The "solid residue" that remained after evaporation was labeled as PC (PC-enriched fraction). The solid residue that remained in the centrifuge tube after centrifugation was then deoiled with acetone according to the AOCS official method Ja 4-46²³ and was labeled as PI (PI-enriched fraction). The PI was characterized by Fourier transform infrared spectroscopy (FT-IR).

To evaluate the effect of structural modification of PI on its dispersion effectiveness, some of the PI samples were stored in vials over a period of 10 weeks before they were solubilized to form dispersants. Changes that occurred in the PI structure during storage were examined by FT-IR and iodine value (IV) determination. The dispersants formulated from the freshly fractionated PI was designated as PI whereas those formulated from the modified or "functionalized" PI was designated as FPI.

Solubilized Dispersant Formulations. The PC and PI obtained from fractionating crude lecithin with ethanol have different solubility properties. Although PC could be dissolved in water and propylene

glycol, PI could only be dissolved in water. In view of this, different dispersant formulations were made in water and in propylene glycol. Different concentrations of solubilized DOSS, Tween 80, and PC (0.05, 0.1, 0.2, and 0.3 mg/ μL) were prepared by dissolving an appropriate amount of DOSS, Tween 80, or PC in an appropriate volume of propylene glycol. The soybean lecithin dispersants were formulated by dissolving PC, PI, FPI, and the crude soybean lecithin in water (CL). That is a solubilized dispersants of 0.1 mg/ μL concentration were prepared by dissolving appropriate amounts of each sample in an appropriate volume of water.

Soybean lecithin dispersants were also formulated by varying the FPI-to-PC ratios but keeping the concentration of FPI and PC in the water as 0.1 mg/ μL .

Product Characterization. Fourier Transform Infrared (FT-IR) Spectroscopy. A Nicolet IR100 FT-IR spectrometer with infrared spectra 400–4000 cm^{-1} was used for the analysis. The equipment used a TGS/PE detector and a silicon beam splitter with 1 cm^{-1} resolution. Approximately 100 mg of KBr was mixed with 1 mg of the sample to prepare the sample discs. The KBr background spectrum was subtracted from the spectrum of each individual sample.

Iodine Value Determination. To investigate whether or not the number of C=C double bonds were reduced after storage, the PI samples were tested for their iodine value (IV) just after fractionation (PI) and also after it has been stored for 10 weeks (FPI). Two hundred and fifty milligrams (250 mg) of the samples were weighed and dissolved with 10 mL of chloroform in a 500 mL stopper flask. Twenty-five milliliters (25 mL) of Hanus solution was added to the flask and cocked immediately. The mixture was then swirled to ensure good mixing and was immediately placed in the dark for 60 min. The blank solution was simultaneously prepared by adding 10 mL of chloroform to 25 mL of Hanus solution in another 500 mL flask. After the 60 min, 20 mL of 10% potassium iodide solution was added together with 100 mL of deionized water. The resulting solution was titrated with 0.1 N sodium thiosulfate using 3 mL of starch solution as an indicator. The buret reading was taken at the end of the titration.

Synthetic Sea Water Preparation. Different concentrations, that is 35, 15, and 8 g/L (representing 3.5, 1.5, and 0.8 wt %), of synthetic seawater were prepared by dissolving appropriate amounts of Instant Ocean sea salt in 1 L of distilled water and leaving it on a magnetic stirrer for 48 h to dissolve all the salt

Baffled Flask Test. The baffled flask test, which is a revised protocol,⁴ is used to evaluate dispersion effectiveness of chemical dispersants and is being considered by the U.S. EPA to replace the swirling flask test. To analyze the dispersion effectiveness of the solubilized PC, DOSS, and Tween 80 in propylene glycol, 100 μL of crude oil was added to 120 mL of synthetic seawater in a baffled flask. Four microliters (4 μL) of the solubilized dispersant was added directly on top of the oil and the baffled flask placed on a shaker (VWR advanced digital shaker, Model 3500) set at 200 rpm for 10 min. A settling time of 10 min was allowed after which 30 mL of the aqueous media with dispersed oil was drawn and then the dispersed oil was extracted with DCM and quantified with UV–vis at an absorbance difference of 300–400 nm.

The baffled flask procedure for determining the dispersion effectiveness of the solubilized PI, FPI, PC, and CL in water was the same as described above, but instead of using 4 μL of the solubilized dispersant for the analysis, different volumes were used (5, 10, 15, 20, 25, and 30 μL).

The baffled flask test procedure for determining the dispersion effectiveness of the powdered crude lecithin (SL) was the same as described above, but instead of taking a specific volume of the solubilized samples, an appropriate amount of the solid crude lecithin particles was weighed and used for the analysis.

Optical Microscopy of Emulsions. The emulsions were prepared as described in the baffled flask test procedure and the optical microscopy images were taken with an EVOS FL autoimaging system just after the 10 min settling time.

All experiments were conducted in at least triplicate.

RESULTS AND DISCUSSION

Dispersion Effectiveness of Solubilized PI, FPI, PC, CL, and Solid Crude Lecithin (SL). Lecithin is a widely used commercial term for a complex mixture of phosphatides produced from a vegetable source such as soybeans or an animal source such as eggs.^{15b} Soybeans are the major source of lecithin owing to its unique functionality and availability.¹⁴ The major components in soybean lecithin are phosphatidylcholine (PC), phosphatidylethanolamine (PE), and phosphatidylinositol (PI). These phospholipids are responsible for the emulsification properties exhibited by lecithin.

Generally, the dispersion effectiveness of SL, CL, PI, FPI, and PC increased with increasing surfactant-to-oil ratio (SOR), as can be seen in Figure 1. The increase in dispersion effectiveness

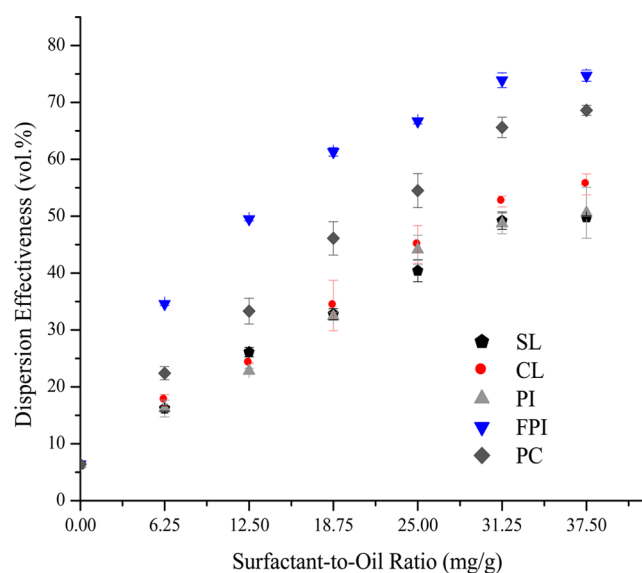


Figure 1. Dispersion effectiveness of PI, FPI, PC, CL, and SL.

with increasing SOR can be attributed to the production of more stable emulsions due the generation of emulsions with smaller droplets and lower rising velocity. A decrease in droplet diameter with increasing SOR is well established in the literature, and can be attributed to a number of factors such as faster adsorption of surface active agents at the oil–water interface and its subsequent reduction in interfacial tension, thereby facilitating droplet breakup.²⁴ In addition to this, more surfactant is available to completely cover the oil droplets and this results in a more stable emulsion.²⁵ A significant phase separation was observed at low SORs, and this was attributed to the instability of the emulsions formed at low SORs, which resulted in coalescence and creaming of the emulsion droplets. Oiling-out was pronounced for CL, SL, and PI at low SORs. However, negligible oiling-out was observed at high SORs, especially for PC and FPI.

The possibility of solid dispersant particles being used for oil spill remediation has already being reported. Henceforth, the dispersion effectiveness of crude powdered soybean lecithin (SL) was examined using TC as the crude oil sample, and the result is reported in Figure 1. By varying the surfactant-to-oil ratio (SOR), it can be seen that the dispersion effectiveness of SL increased from 6.4 vol % at SOR of 0 mg/g to 49.8 vol % at SOR of 37.5 mg/g. However, a slightly higher dispersion effectiveness value of 55.6 vol % was obtained at SOR of 37.5 mg/g when the crude powdered soybean lecithin was

solubilized in water (CL) at 0.1 mg/uL concentration. This trend was expected since for dispersion to occur, the phospholipids should be able to diffuse to the oil–water interface. With liquid state diffusion being faster than solid state diffusion, more phospholipid molecules are likely to settle at the oil–water interface and hence this resulted in the relatively higher dispersion effectiveness values obtained with CL at higher SORs. The lower dispersion effectiveness obtained for SL and CL compared to the fractionated PC is not surprising because current studies suggest that SL solubilized in ethanol is not an excellent emulsifier.¹⁹

To improve on the dispersion effectiveness values recorded by SL and CL, the crude soybean lecithin was fractionated into PC- and PI-enriched fractions. The crude lecithin purchased from Stakich Inc. (Bloomfield Hills, MI) was made up of phosphatidylcholine, phosphatidylinositol, and neutral lipids (triglycerides and tocopherols). Fractionating with ethanol resulted in 34 wt % ethanol soluble PC and 66 wt % ethanol insoluble PI. From the AOCS, the ethanol soluble fraction is mainly made up of concentrated PC and only a small fraction of PI whereas the ethanol insoluble fraction is made up of concentrated PI, a small fraction of PC, and the neutral lipids.^{15b,22} Further deoiling of the PI-enriched phase with saturated acetone removed the acetone soluble neutral lipids, leaving the oil-free PI. From mass balance calculations, the ethanol insoluble PI fraction was made up of 85 wt % oil-free PI-enriched fraction and 15 wt % acetone soluble neutral lipids. Fractionating the crude lecithin purchased from Stakich Inc. therefore resulted in 34 wt % ethanol soluble PC, 56 wt % oil-free ethanol insoluble PI, and 10 wt % acetone soluble neutral lipids. The chemical structures of the PI and PC are shown in Figure 2.

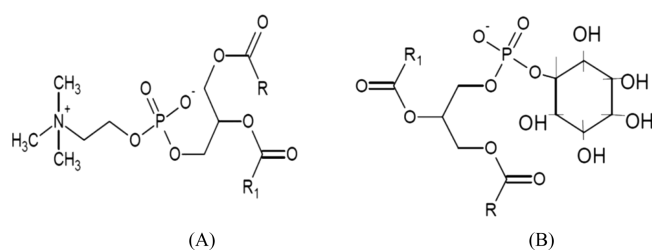


Figure 2. (A) Chemical structure of PC and (B) chemical structure of PI.

Figure 2 shows that phosphatide molecules contain two long-chain fatty acids esterified to glycerol and a phospho-diester bonding a choline or inositol. The hydrophilic portion of the molecules is the phospho-diester portion whereas the hydrophobic portion is the fatty acid end,^{15b} which are R and R₁. The phospholipids appear to be made up of fatty acids of the C16 and C18 series. Some of the fatty acids present in phospholipids are palmitic acids, linoleic acids, and oleic acids.^{15b,26} PC is known to contain approximately 58 and 20 wt % linoleic and palmitic acids, respectively whereas PI is made up of 25 and 44 wt % linoleic and palmitic acids, respectively.⁷ These values suggest that both PI and PC contain a higher amount of unsaturated fatty acids.

The amphiphilic nature of these molecules is responsible for their emulsification property. PC and PI were solubilized in water and their dispersion effectiveness determined by the baffled flask test. Three different observations were made with these dispersant formulations.

First, the dispersion effectiveness of the solubilized PC in water (PC) was higher than that of SL and CL at all the SORs tested. For example, at SOR of 37.5 mg/g, the dispersion effectiveness values of PC, CL, and SL were 68.6, 55.6, and 49.8 vol %, respectively. The hydrophilic–lipophilic balance (HLB) of crude soybean lecithin has been reported to be about 4.²⁷ Crude lecithin is more lipophilic, and therefore based on the Bancroft rule, which states that a surfactant that preferentially partitions into water favors the formation of oil-in-water (o/w) emulsions and that a surfactant that preferentially partitions into oil favors the formation of water-in-oil (w/o) emulsions;²⁸ crude lecithin is expected to favor the formation of w/o emulsions, which would explain the comparatively lower dispersion effectiveness values observed for CL and SL. The use of lecithin to form o/w emulsions requires modification of the lecithin to increase its hydrophilicity, and this was achieved through solvent fractionation. The results showed that the PC-enriched fraction has a better o/w emulsification property. Fractionation of the crude lecithin into PI- and PC-enriched fractions resulted in the distribution of the components present in the crude lecithin between the various fractions. This distribution resulted in PI and PC having different physical and chemical properties from the crude lecithin. A change in the relative concentrations of its constituent molecules will result in a change in its HLB. The HLB of purified PC has been reported to be around 7;²⁷ that is, the HLB of the fractionated PC is close to the range that favors the formation of o/w emulsion.²⁹ This observation is in agreement with other results in the literature that suggest that PC is an excellent o/w emulsifier.^{17b}

Second, the dispersion effectiveness of the PC dispersant formulation was higher than that of the PI formulation. It has been stated that although the ethanol soluble fraction (PC-enriched) supports the formation of o/w emulsion, the ethanol insoluble fraction (PI-enriched) supports the formation of w/o emulsion.²⁷ Because the dispersion effectiveness of the freshly fractionated PI is almost the same as those of SL and CL (Figure 1), the HLB of deoiled PI is expected to be lower than 4, and therefore, freshly fractionated PI is expected to favor the formation of w/o emulsion. Fractionating the crude lecithin resulted in the formation of anionic PI and zwitterionic PC. Because PC is zwitterionic, it forms a monomolecular interfacial film that binds water molecules at the surface and serves as a physical barrier against coalescence.

An interesting observation was made when the PI was stored for a period of 10 weeks before it was used to formulate the dispersant. Because polar lipids are insoluble in acetone, whereas neutral lipids are not, deoiling of the PI with acetone removed the neutral lipids, which consisted of triglycerides and tocopherols from PI. Tocopherols are antioxidants present in lecithin; hence its removal resulted in a PI that is less oxidatively stable.¹⁰ Acetone may be considered to be the solvent of crystallization because the deoiled PI has a higher degree of crystallinity, and hence the deoiled PI was crystalline, granular, powdery, and had high surface/volume ratio, which also contributed to its reduced stability.¹⁵ The C=C double bonds in the unsaturated fatty acids present in PI are known reactive sites for hydroxylation. With these unique properties of the deoiled PI and the fact that the deoiled PI is slightly hygroscopic, it was prudent to store them in air over a period of time to examine whether or not it was possible to alter the hydrophilicity of the deoiled PI through natural oxidative process without using any chemical treatment. That is, the

hydrophilicity of PI can be modified by the introduction of additional hydroxyl groups onto the PI structure and this can be achieved by either hydroxylation or by hydrolysis. The storage of the PI over such a period was to examine how natural oxidation (hydroxylation) of the PI affected its emulsification properties. As can be seen in Figure 1, the dispersion effectiveness values of the dispersant formulated from PI, which has been modified by storing for 10 weeks (FPI), were higher than those of the PC, SL, CL, and PI. At the SOR of 37.5 mg/g, the dispersion effectiveness values of FPI, PI, PC, SL, and CL were 74.7, 50.6, 68.6, 49.8, and 55.6 vol %, respectively. From Figure 2, it can be seen that PI contains a bonded hydroxyl group in its chemical structure. Hydroxylation of PI will result in the introduction of additional hydroxyl groups into its structure. To investigate this, equal amounts of PI that have been stored for 2 days (PI-2days), 3 weeks (PI-3weeks), and 10 weeks (PI-10weeks) in the same environmental conditions (temperature of 298 K and an average relative humidity of 65%) were analyzed with FT-IR. The area under the bonded hydroxyl peak represents the concentration of the hydroxyl group in the compound. The FT-IR spectra are shown in Figure 3.

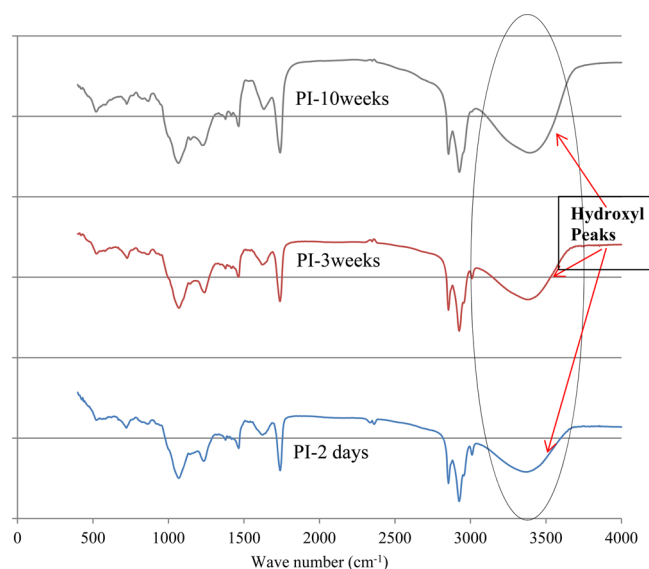
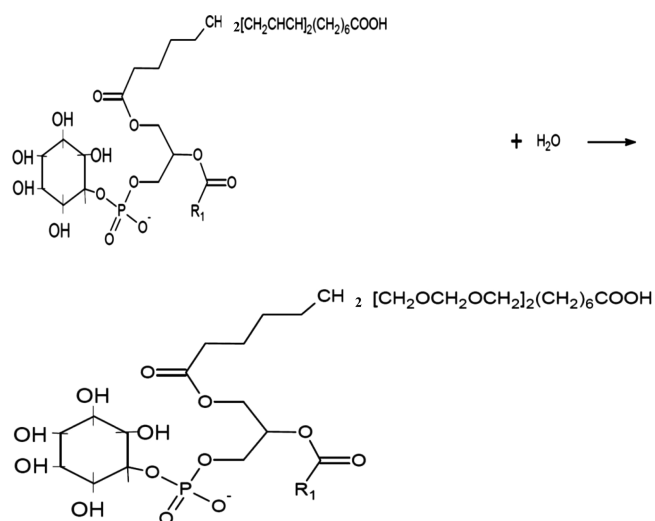


Figure 3. FT-IR spectra for PI-2days, PI-3weeks, and PI-10weeks.

The peak between wavenumbers 3200 and 3600 cm^{-1} represents the bonded hydroxyl group in the PI structure. As can be seen in Figure 3, the area under the bonded hydroxyl group increased with storage time. That is, the concentration of the bonded hydroxyl group is greater in PI-10weeks and least in PI-2days. Therefore, more hydroxyl groups were introduced into the PI structure during storage. Both hydrolysis and hydroxylation reactions will introduce additional hydroxyl groups into the PI structure. However, hydrolysis reaction is not likely to occur during storage since this reaction is known to occur in lecithins in the presence of strong acids or bases.^{7,8} The possible reaction occurring during storage may be a hydroxylation reaction. In hydroxylation reaction, water molecule reacts at the double bonds of the unsaturated fatty acids in the phospholipid structure. It should be noted that the average relative humidity over the storage period was 65%. Assuming that R_1 and R_2 are palmitic and linoleic acids in the PI structure in Figure 2, the following reaction may occur:



The above reaction will result in the reduction of the number of $\text{C}=\text{C}$ double bonds, thus the degree of unsaturation will be reduced. To examine if the reaction that occurred resulted in the reduction of $\text{C}=\text{C}$ double bonds, the iodine values (IV) of PI-2days and PI-10weeks were determined. The IV for PI-2days was determined to be 96 and was within the range stated in the literature,²⁷ whereas that of the PI-10weeks was 72. The significant reduction in the IV after storage depicts a reduction in the degree of unsaturation of PI-10weeks compared to PI-2days. There was therefore approximately 25% reduction in IV after storing the PI for 10 weeks.

It can be deduced from the area under the hydroxyl peak in the FT-IR spectra that this reaction is very slow because the bonded hydroxyl group concentration for the PI stored for 3 weeks (PI-3weeks) was almost the same as that of PI-2days. Therefore, enough storage time should be allowed for the reaction to take place. Preliminary studies not reported in this paper showed that 10 weeks was enough to allow this reaction to take place because the iodine value reduction for samples stored for 10 to 18 weeks were similar and were between 25 to 27%, which is within the 25 to 30% recorded in the literature.¹⁵ As a result, the storage time used in the study was enough to introduce an adequate amount of hydroxyl groups into the PI structure. Instead of allowing the hydroxylation reaction to occur naturally, this reaction can be induced by reacting the PI with hydrogen peroxide and water in the presence of lactic acid as a catalyst.⁸ The 25–27% reduction in IV recorded in this study, which fell within the range of IVs obtained by chemical treatment of crude lecithin proves that the emulsification behavior of PI can be improved by storing it in air over a long period of time. Hydroxylation reactions introduce additional hydroxyl groups into the PI structure and, as a result, hydrophilicity is increased. An increase in hydrophilicity subsequently shifted the HLB of PI toward the range (8–18)¹⁶ that favors the formation of an o/w emulsion, and this shift is responsible for the increase in the dispersion effectiveness observed with FPI. A typical HLB of chemically hydroxylated lecithin has been reported to be around 8,¹⁶ which is more hydrophilic than that of the freshly fractionated PI.

The introduction of additional hydroxyl groups onto the PI structure affected the structural arrangement of PI at the oil–water interface. The additional hydroxyl groups make it possible for the PI to attain the “loop worm” structure at the oil–water interface, which improved the emulsion stability.³⁰ The additional hydroxyl groups help increase the interaction at

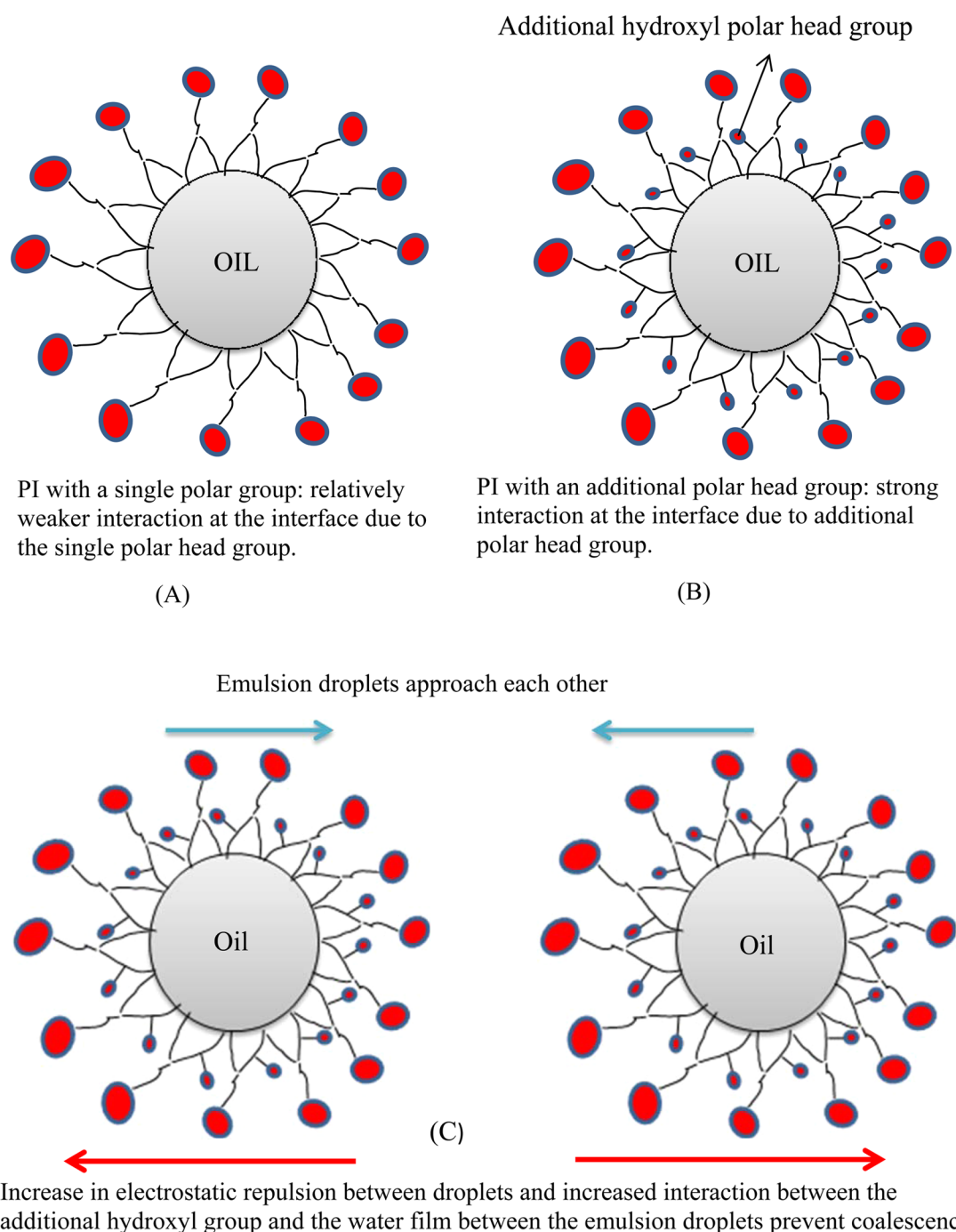


Figure 4. Mechanism for emulsion stabilization: (A) structural arrangement of freshly fractionated PI molecules at the oil–water interface, (B) structural arrangement of fractionated PI that has additional hydroxyl groups (FPI) at the oil–water interface, and (C) contribution of the additional hydroxyl group in stabilizing emulsion droplets.

the oil–water interface and hence reduced the tendency of the emulsion droplets to coalesce (Figure 4). The reduction in the tendency of the emulsion droplets to coalesce will enhance the emulsion stability and hence increase the dispersion effectiveness. In addition to the improvement in the interaction between the hydroxyl groups and the liquid film at the oil–water interface, the additional hydroxyl groups are likely to increase the surface potential at the oil–water interface since emulsion formed by FPI, which is anionic surfactant, will be stabilized by the negative charge formed by the polar head group at the oil–water interface. The increment in the surface

potential due to the presence of additional hydroxyl groups will increase electrostatic repulsion between the emulsion droplets, protecting the emulsion from processes such as creaming and coalescence.^{31,32,32b} In addition, the crowding of the anionic head group will introduce electrostatic repulsion among the charged head groups and this will affect the characteristics of the monolayer at the oil–water interface. The introduced hydroxyl groups which are less hydrophilic than the anionic head will moderate the electrostatic interactions among the anionic head groups. The net result will be a densely packed interfacial layer that will make it possible to attain high

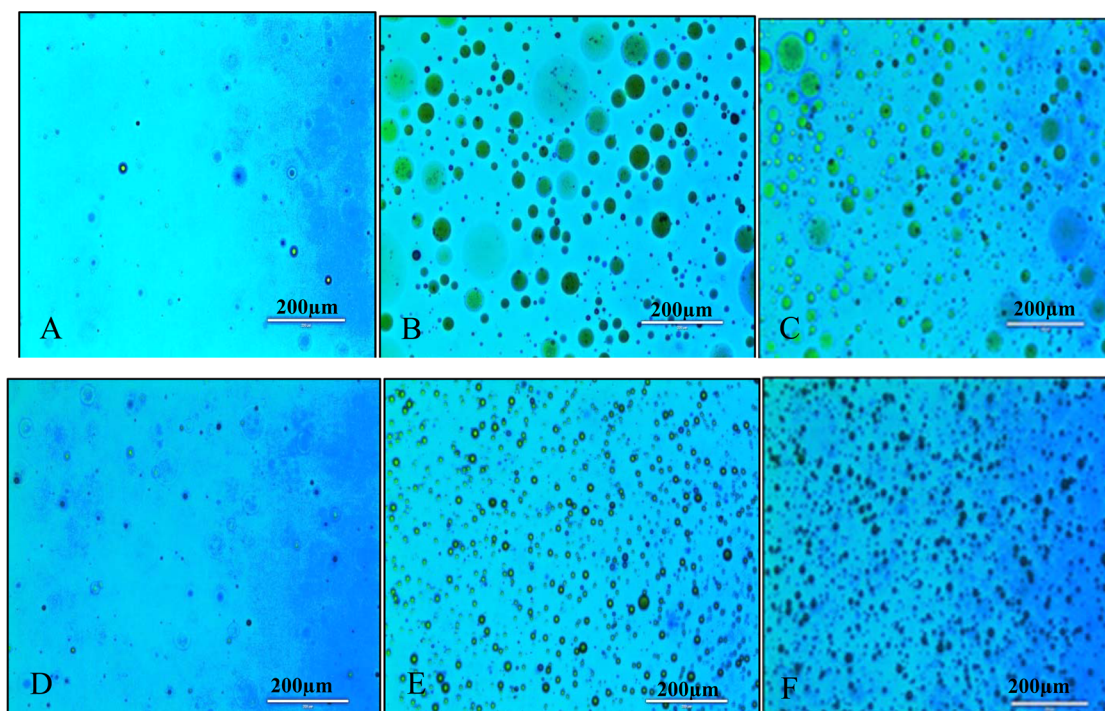


Figure 5. Optical microscopy of TC oil-in-water emulsions: (A) PC at 6.25 mg/g SOR, (B) PC at 18.75 mg/g SOR, (C) PC at 37.5 mg/g SOR, (D) FPI at 6.25 mg/g SOR, (E) FPI at 18.75 mg/g SOR, and (F) FPI at 37.5 mg/g SOR.

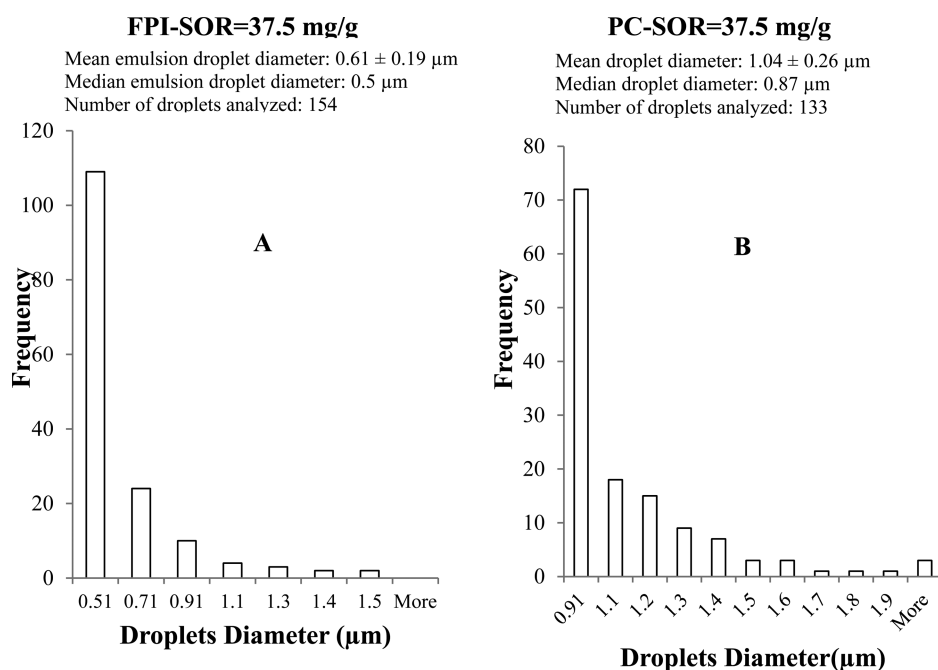


Figure 6. Histogram for emulsion droplets diameter (with TC) for (A) emulsions obtained from PI at SOR = 37.5 mg/g, and (B) emulsions obtained from PC at SOR = 37.5 mg/g.

dispersion effectiveness. This is responsible for the high dispersion effectiveness values observed for FPI.

Optical microscopy images of the emulsions formed with FPI are shown in Figure 5D–F. It can be seen that as the SOR increases, the emulsion droplet density increases. It was also observed that, an increase in emulsion droplet density was accompanied by flocculation of the droplets. The droplet sizes of the FPI emulsion were relatively smaller than that of the PC as can be seen from the histogram represented in Figure 6. The

histogram was obtained by taking optical microscopy images of the emulsion droplets after the 10 min settling time in the baffled flask test and analyzing the images for droplet size using the ImageJ software. The smaller droplet sizes and the higher droplet density further substantiate why the emulsion formed with FPI was more stable and hence resulted in a higher dispersion effectiveness than PC.

The emulsification property of the PC, however, remained constant over the same storage time, depicting that the

hydroxylation reaction did not naturally occur in PC. This can be attributed to the nature of the fractionated PC compared to that of the PI. Although the PI-enriched fraction was hygroscopic, granular, and flowable, that of the PC was tacky. As a result, there was more surface area available for the hydroxylation reaction to occur in PI than in PC. The optical microscopy images of the emulsions formed with PC are shown in Figure 5A–C, and it can be seen that the emulsion droplet density increases with increasing SOR but the droplet densities were lower than that of FPI. It was also observed that at SORs of 18.75 and 37.5 mg/g, some of emulsion droplets flocculated.

The effect of the HLB on dispersion effectiveness was observed as stated earlier and has been summarized in Figure 7.

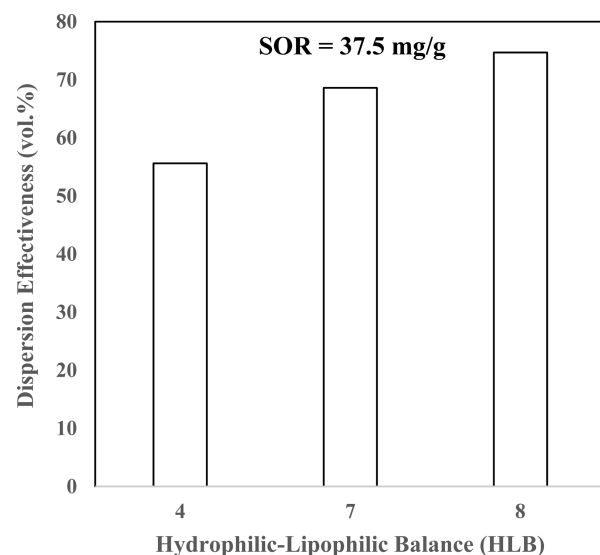


Figure 7. Effect of HLB on dispersion effectiveness.

The HLB of the crude soybean lecithin, PC, and hydroxylated lecithin (FPI) have been reported to be about 4, 7, and 8, respectively. At the SOR of 37.5 mg/g, the dispersion effectiveness of the formulated dispersants with HLB values of 4, 7, and 8 were 55.6, 68.6, and 74.7 vol %, respectively, as can be seen in Figure 7. The highest dispersion effectiveness was observed with the most hydrophilic surfactant, whereas the lowest dispersion was observed with the hydrophobic surfactant.

According to the Bancroft rule, the surfactant with the HLB value of 4 will support the formation of w/o emulsions whereas the surfactants with HLB values of 7 and 8 will support the formation of o/w emulsions. It is therefore not surprising that the surfactants with the relatively high HLB values recorded the highest dispersion effectiveness.

For a dispersant formulation to be listed on the National Contingency Plan (NCP) Product Schedule, it should be able to disperse at least 50 ± 5 vol % of the oil used in the laboratory test. As can be seen in Figure 1, PC and FPI at SOR of 25 mg/g meet this criterion; therefore, our dispersant formulations can be used to combat oil spills, should they occur.

Comparing the Dispersion Effectiveness of Solubilized FPI and PC with Solubilized DOSS and Tween 80. The dispersion effectiveness of the natural surfactants (FPI and PC) was compared with that of synthetic chemical surfactants (DOSS and Tween 80), and the results are shown in Figure 8.

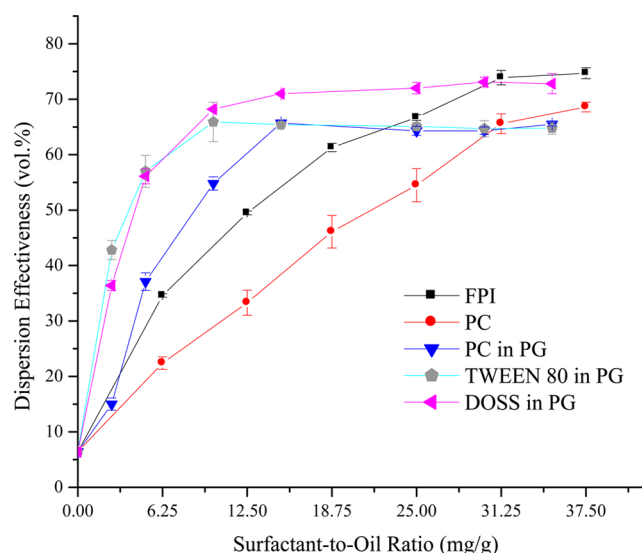


Figure 8. Comparison of the dispersion effectiveness of solubilized FPI and PC with solubilized DOSS and Tween 80.

From Figure 8, it can be seen that the dispersion effectiveness values of Tween 80 and DOSS were higher at lower SORs compared to those of PC and FPI. However, at higher SORs, the dispersion effectiveness of FPI was slightly higher than those of Tween 80 and DOSS, the dispersion effectiveness of PC solubilized in propylene glycol was almost the same as that of DOSS, and the dispersion effectiveness of PC solubilized in water was slightly higher than that of DOSS.

These observations can be explained in terms of the efficiency of the surfactants used in the formulation of the dispersants in forming emulsions and the structural arrangement of the surfactants molecules at the oil–water interface.

Below a SOR of 12.5 mg/g, the dispersion effectiveness values of DOSS and Tween 80 were significantly higher than those of FPI and PC. This trend can be attributed to the excellent efficiency of the surfactants DOSS and Tween 80 in forming emulsions. The surfactant efficiency is defined as the bulk phase concentration necessary to reduce the interfacial tension by a predetermined amount.¹³ A smaller amount of DOSS and Tween (lower SOR) is enough to create a more stable o/w emulsion than when using the same amount of FPI and PC. This can be attributed to the significant reduction in interfacial tension by Tween 80 and DOSS at lower SORs. Nevertheless, solubilized PC in PG recorded much a higher dispersion effectiveness than PC in water at lower SORs. This can be related to the effect that solvents used in formulating dispersants have on dispersion effectiveness. In previous studies, we concluded that dispersants formulated in propylene glycol usually give higher dispersion effectiveness and this can be related to solvent viscosity, density and its solubility in water.²¹ The propylene glycol may also serve as a cosurfactant by adsorbing at the oil–water interface and further reducing the interfacial tension. From Figure 8, it can be seen that the shape of the dispersion effectiveness versus SOR plot was the same for the dispersants formulated in PG; that is, the dispersion effectiveness was higher at lower SORs but leveled off at higher SORs. On the other hand, the dispersion effectiveness of PC and FPI in water kept on rising steadily from lower SORs to higher SORs, further proving the impact of the choice of solvents on interfacial tension reduction.

The leveling off of the dispersion effectiveness of DOSS and Tween 80 at higher SORs can be explained in terms of their critical micelle concentration (CMC). At concentrations lower than the CMC, the oil–water interfacial tension reduces significantly with increasing surfactant concentration. However, at surfactant concentrations above the CMC, the oil–water interfacial tension remains relatively constant. The dispersion effectiveness will therefore increase with increasing surfactant concentration below the CMC but it will level off at surfactant concentrations higher than the CMC. The CMCs of Tween 80 and DOSS are 13 mg/L and 0.125% (w/v), respectively.³³ These values are expected to be much lower in the synthetic seawater due to the effect of neutral ions on CMC.^{33b} As an example, at SORs of 25, 31.25, and 37.5 mg/g, the concentration of Tween 80 in the synthetic seawater during the baffled flask test were 16.7, 20.8, and 25 mg/L, respectively. These surfactant (Tween 80) concentrations were above the CMC of Tween 80. It is therefore not surprising that the dispersion effectiveness values of Tween 80 leveled off at these concentrations, as can be seen in Figure 8. The CMC of lecithin is dependent on the fatty acid chain length and has been reported to be around 120 mg/L.³⁴ The maximum concentration of lecithin PC and FPI (25 mg/L) used in the baffled flask test was below the CMC of lecithin. This is responsible for the gradual increase in the dispersion effectiveness of the PC and FPI formulated dispersants. In addition to this, high concentration of nonadsorbed surfactants may influence emulsion stability.³⁵

Though the dispersion effectiveness for DOSS and Tween 80 leveled off at higher SORs, it can be seen that, the dispersion effectiveness of DOSS is lower than that of Tween 80. With DOSS being an anionic surfactant, a possible repulsion between the polar head group while adsorbing at the oil–water interface may have accounted for the reduction in the dispersion effectiveness. Studies have shown that DOSS easily desorbs into salt water after emulsion formation,³⁶ and this desorption results in the coalescence of smaller emulsion droplets into larger ones. Visual observations made during the baffled flask test attest to this fact because there was oiling-out and creaming of the emulsions formed with solubilized DOSS. The formation of larger emulsion droplets increases their rising velocity and as a result, these oil droplets fell out of the sampling zone during the analysis done with the baffled flask test. The oxyethylene “hairs” in Tween 80 are important for providing steric stabilization to the oil droplets and preventing their coalescence.³⁶ The rate of desorption of Tween 80 from the oil–water interface has therefore been reported to be much slower than that of DOSS,³⁷ and this is responsible for the much higher dispersion effectiveness recorded for Tween 80 at higher SOR.

From the above paragraphs, it can be concluded that a larger amount of lecithin (FPI and PC) will be required to attain higher dispersion effectiveness. Usually, it is better to use a lower amount of dispersant (lower SOR) because it reduces cost and toxicity. However, soybean lecithin is less toxic and is not expected to have any negative impact on aquatic species and cleanup workers. In addition to this, the cost of DOSS and Tween 80 per gram is respectively 36 and 12 times that of lecithin.³⁸ The solvent (water) used for solubilizing PC and FPI is also less costly than propylene glycol, which was used to solubilize Tween 80 and DOSS. These suggest that dispersants formulated with lecithin PI and PC will be less costly when compared to those formulated with DOSS and Tween 80. It

should be noted that water is also more environmentally benign than propylene glycol, which is hydrocarbon based.

Effect of FPI/PC Ratio on Dispersion Effectiveness.

With the fractionated PC and FPI recording much higher dispersion effectiveness values than the crude lecithin, it was worth examining how the dispersion effectiveness will change by varying weight percent or ratios of FPI and PC. Varying the FPI-to-PC ratios resulted in dispersion effectiveness values that were almost the same as those recorded for 100 wt % PC (Figure 9). The HLB of FPI and PC are probably similar, hence

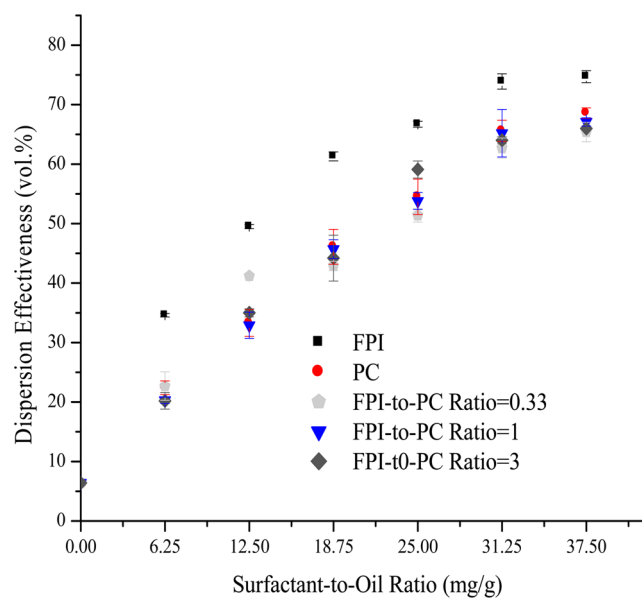


Figure 9. Effect of FPI-to-PC ratio on dispersion effectiveness.

combining them in different ratios did not have a dramatic impact on the combined HLB and the dispersion effectiveness. Though lecithin is known to be zwitterionic, fractionating lecithin resulted in the formation of an anionic PI and zwitterionic PC. With PC having both positive and negative charge head groups, these groups are likely to interact with the negative charge head groups of the PI. These interactions which may be attractive or repulsive will affect the structural arrangement of the surfactants at the oil–water interface. This arrangement will result in the formation of an “expanded” monomolecular film at the oil–water interface,¹³ which subsequently has a negative impact on the dispersion effectiveness.

Effect of Texas Crude (TC) and Light Crude (LC) Oil Samples on Dispersion Effectiveness.

The effect of crude oil type on the dispersion effectiveness was investigated with solubilized PC and FPI in water. Previous studies with these oil types showed that particulate dispersants formulated with DOSS disperse the LC much better than the TC, and thus it was worth examining how phospholipids (PC and PI) would disperse these crude oil types.

The asphaltene content, API gravity, and chemical composition of these oil types were determined in a previous study.²¹ The TC was much heavier with lower API gravity than the LC, and the asphaltene contents of the TC and LC were 6 and 4.1 wt %, respectively. With these values, one would expect the dispersion effectiveness for the LC to be higher than that of the TC but, as can be seen in Figure 10, the dispersion effectiveness on LC and TC were almost the same for both PC

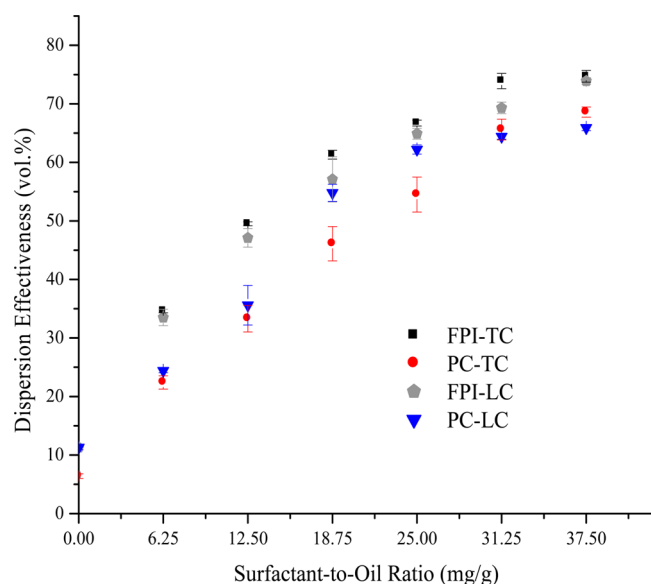


Figure 10. Effect of Texas crude and Light crude on dispersion effectiveness.

and FPI. As the composition of oil varies, it is reasonable that a particular dispersant formulation could be more effective with one oil type than another, but as can be seen PC and FPI dispersed both the LC and TC almost equally. That is, FPI and PC can produce stable emulsions, irrespective of the asphaltene content, API gravity, and chemical composition of LC and TC. PC and FPI were therefore less sensitive to the composition of the crude oils used in this study. This observation gives FPI and PC a significant advantage over other synthetic surfactants such as DOSS, which in our previous studies, dispersed LC better than TC.

Effect of Salinity on Dispersion Effectiveness. The stability of emulsions formed by anionic surfactants can be influenced by the presence of salt ions because the concentration of the salt ions can influence the droplet size of the emulsion.³⁹ Because different surfactant systems respond differently to the presence of salt ions, the dispersion effectiveness of the dispersant formulations were tested in different salinity environments using Texas crude (TC) oil.

From Figure 11, it can be seen that the dispersion effectiveness of PC and FPI in TC increased with increasing salinity.

PI and PC are anionic and zwitterionic surfactants, respectively, and therefore, the polar head groups of these surfactants are likely to interact or bind with the salt ions. However, binding of these salt ions is competitively inhibited by water and at a 4:1 molar ratio of water to the phospholipid, ion binding is inhibited completely.^{15b} The molar ratio of water to FPI or PC used in the baffled flask test was more than 4 because the amounts of phospholipids were varied from 0.5 to 3 mg, which corresponds to SORs of 6.25 and 37.5 mg/g, respectively. It is therefore unlikely that the change in dispersion effectiveness observed with salinity is due to the binding of the ions to polar head groups. Binding of the ions to the polar head group will affect the hydrophilicity and the arrangement of FPI and PC molecules at the oil–water interface. This is because the bound neutral ions will reduce the electrostatic repulsion among the charged head groups. The presence of the neutral electrolyte will also affect micelle formation since the critical micelle concentration will change.

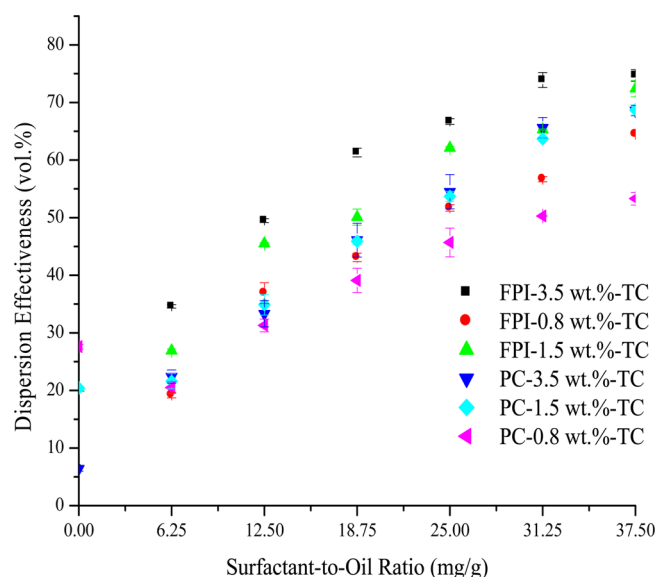


Figure 11. Effect of salinity on dispersion effectiveness of PC and FPI in TC.

Therefore, it is likely that the salt ions present screened the polar head groups and hence resulted in the reduction in electrostatic repulsion that existed between them. A reduction in the repulsion between the polar head group will allow a condensed or close packed arrangement of surfactant molecules at the oil–water interface. As a result, the stability of the emulsions was improved and higher dispersion effectiveness observed at higher salinity. Though there is the tendency for droplet aggregation to occur at higher salinity,⁴⁰ as can be seen in Figure 5, at SORs of 18.75 and 37.5 mg/g, this did not result in a reduction in dispersion effectiveness. A visual observation of the emulsions formed at salinity environments of 0.8 and 1.5 wt % indicated that there was oiling-out due to the coalescence of oil droplets depicting the instability of the emulsions formed at these salinities.

CONCLUSIONS

The results from this study show the potential of dispersants formulated with lecithin (FPI and PC) to replace the traditional liquid chemical dispersant formulations. This study showed that PC and PI obtained by fractionating crude soybean lecithin with ethanol disperse crude oil to different extents. The dispersion effectiveness of freshly fractionated PC was higher than that of the crude soybean lecithin (CL) and freshly fractionated PI. However, after structural modification of PI (FPI), its dispersion effectiveness improved remarkably and was higher than that of PC. This was attributed to the introduction of additional hydroxyl groups into the PI structure, which increased its hydrophilicity and resulted in improved dispersion effectiveness. The dispersion effectiveness of the FPI was lower than that of solubilized DOSS and Tween 80 in propylene glycol at lower SORs, whereas at higher SORs, the dispersion effectiveness of FPI was higher than that of solubilized DOSS and Tween 80 in propylene glycol. Dispersants formulated by varying the ratio of FPI and PC resulted in a dispersion effectiveness that was almost the same as that of PC. The dispersion effectiveness values of FPI and PC in both LC and TC oil samples were similar, despite differences in the composition of these oil samples. Varying the salinity environment during the analysis resulted in higher dispersion

effectiveness at a salinity of 3.5 wt % and a lower dispersion effectiveness at 0.8 wt %.

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Notes

The authors declare no competing financial interest.

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