

The Effect of the Refining Process on the Interfacial Properties of Palm Oil

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ABSTRACT: The interfacial tension of palm oil against water at 60°C was determined in the presence of monoglycerides with (i) different acyl chain lengths, (ii) the same acyl chain length but with different unsaturation, and (iii) different phospholipids. The interfacial tensions of the oil/water interface were depressed, albeit to different extents, by the presence of these substances, depending on the acyl chain length, unsaturation, and the chemical structure of the species adsorbed. The adsorption of the saturated monoglycerides C12:0, C14:0, C16:0, C18:0 and the unsaturated monoglycerides of C18:1 and C18:3 is consistent with a Langmuir isotherm at the palm oil/water interface. However, fitting of the data for C18:2, L- α -phosphatidylcholine, and lysophosphatidylcholine to the Langmuir isotherm is less satisfactory. The surface areas of the materials adsorbed at the palm oil/water interface are much larger than those of liquid condensed films and closer to those for liquid expanded films. The influence of the nature of the oil (triglycerides), the minor components in the oil, and their interactions with the added lipids at the oil/water interface are briefly discussed. The effect of the refining process on the interfacial properties of palm oil against water was also studied. The efficiency of the refining process in minor oil contaminants' removal and the quality of the oil obtained as reflected by the interfacial properties of the oil is discussed.

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Palm oil, a mixture of triglycerides, is traditionally used in food applications, such as cooking oil, shortening, and margarine. With the advent of the oleochemical industry based on palm and palm kernel oil feedstocks during the last decade, diversification of palm oil usage into nontraditional areas is gaining importance: nonfood areas, notably in cosmetics and personal care products. However, palm oil applications in the pharmaceutical, engineering, and industrial areas have yet to be explored and fully realized. Recently, the use of medium-chain triglycerides in body lotion formulations (1) and of epoxidized palm esters and palm oil as plasticizers (2) has been reported. Inevitably, some of these applications necessi-

tate the use of the oil in an emulsion form, in particular, in salad dressings and pharmaceutical and cosmetics formulations. Thus, to understand and ensure the stability of the emulsions, knowledge of the interfacial properties between the (palm) oil and water is important. While the general relationship between interfacial interactions and stability of emulsions is reasonably well established, reliable predictions of stability of specific vegetable oil emulsions is not always easy. This is because the interfacial region typically contains various surface-active lipid components, which may have originated as impurities in the oil phase or may have been added deliberately during formulation. For example, in a study of palm oil emulsions stabilized by mixtures of Tween 40 and Span 40, it was reported (3) that the inherent nature of the oil and the accompanying natural surface-active materials present in it can influence the prevailing conditions at the oil/water interface and the composition of the interfacial film and its stability.

Crude palm oil before refining contains a number of naturally occurring surface-active materials, such as mono- and diglycerides and phospholipids, albeit in low concentrations. These have been shown to adsorb strongly at the palm oil/water interface during processing of palm fruits in the mill and are responsible for the formation of stable emulsion droplets in the centrifuged sludge that constitutes part of the discharge from the palm oil mill (4,5). Subsequent refining of the oil by various chemical and physical refining methods removes these minor constituents of palm oil to different extents. After refining, commercial refined palm oil still contains trace amounts of these, in particular, mono- and diglycerides, which are known to have an effect on the interfacial properties of an oil/water interface. The lipid compositions of the various partially and fully processed palm oils shown in Table 1 show that chemically refined, neutralized, bleached, and deodorized palm oil (NBDPO) is the purest form of refined palm oil available.

Monoglycerides and their derivatives account for about 75% of the world production of food-grade emulsifiers (6). They are nonionic, but considerably more polar than the triglycerides and exhibit a strong surface activity at the oil/water interface. They are widely used as food emulsifiers, particularly in margarine and tablespread. Phospholipids are the most surface-active of the lipid family. Chemically, phospholipids are mixed esters of fatty acids and phosphoric acid

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TABLE 1
Lipid Composition of Various Partially and Fully Processed Palm Oils

Glyceride composition ^a	Crude palm oil	Degummed and neutralized oil ^b	Degummed and bleached oil ^c	Refined palm oil ^c	Refined palm oil ^b
Free fatty acids	3.25	0.14	2.92	0.04	0.02
Monoglycerides	0.27	0.17	0.17	0.04	0.04
Diglycerides	6.71	5.85	5.41	6.61	3.99
Triglycerides	89.75	93.84	91.50	93.31	95.90
Phosphorus ^d (ppm)	14.60	8.80	2.60	7.00	2.20

^aAll composition in wt%.

^bChemically refined oil.

^cPhysically refined oil.

^dTo convert to phospholipids, multiply by 25.

with glycerol and/or choline. The ionization of the phosphate and alkaline groups makes them strongly amphiphilic. Lecithin, a common phospholipid obtained from the degumming of soybean oil, is a mixture of various phospholipids, with phosphatidylcholine as its main component. Modified phospholipids with different degrees of purity are widely used commercially as emulsifiers, both in food and nonfood industries. Because monoglycerides and phospholipids are highly surface-active, it is worthwhile to investigate whether post-addition of these to purified palm oil causes any change in its interfacial behavior.

This paper examines the influence of the purity of the oil, i.e., after different extents of refining, on the interfacial tension (γ_i) of the oil against water and the effects of post-added monoglycerides and phospholipids on the interfacial properties of the oil (NBDPO). The significance of these findings on the refining and emulsification processes of palm oil is discussed. Relatively little work is reported on the γ_i of vegetable oils generally, and palm oil particularly. Information on such fundamental properties of the triglyceride–water interface is obviously important in understanding the stabilization of food emulsions by emulsifiers.

EXPERIMENTAL PROCEDURES

Materials. NBDPO was used as the standard in all γ_i measurements. The lipid composition of this oil is shown in Table 1, the fatty acid composition in Table 2, and the quality in Table 3. Monoglycerides of 98–99% purity were purchased from Sigma Chemicals (St. Louis, MO) and used as re-

ceived. These are 1-monolauryl (C12:0), 1-monomyristic (C14:0), 1-monopalmitoyl (C16:0), 1-monostearoyl (C18:0), 1-monooleoyl (C18:1, *cis*-9), 1-monolinoleoyl (C18:2, *cis*-9,12), 1-monolinolenoyl (C18:3, *cis*-9,12,15) and are referred to as monoglycerides C12:0, C14:0, C16:0, C18:0, C18:1, C18:2, and C18:3 in the text. Three types of lecithin from Sigma Chemicals were used: (i) type IV-S soybean lecithin (containing *ca.* 40% phosphatidylcholine), (ii) lyso-phosphatidylcholine, and (iii) type XI-E (containing 99% pure L- α -phosphatidylcholine from fresh egg yolk). The molecular weights and purity of these substances are listed in Table 4.

Surface and γ_i measurements. A Krüss digital tensiometer (model K10T; Hamburg, Germany) was used for the measurement of γ_i . Double-distilled water (from an all-glass still) and oil samples were preheated to 60°C in an oven before transferring to the sample container (also maintained at 60°C) in the tensiometer, which was checked daily by measuring the surface tension of twice-distilled water at 60°C. The tensiometer was first tared with the ring completely submerged in the oil phase. This zero adjustment was carried out to compensate for the buoyancy and tension on the shaft of the ring. The ring was then removed, cleaned with methanol and acetone, and flamed. The sample container was half-filled with water (12.5 g), and the cleaned ring was submerged in it. The lighter phase (oil, 12.5 g) was placed carefully on top of the water by delivering it from a pipette. The sample was allowed to equilibrate for 30 min before the ring was pulled through the oil/water interface, and the maximum force to break the film in the oil was taken as the interfacial tension. Preliminary work indicated that the γ_i of NBDPO decreases only slightly with equilibration time against water and attains a

TABLE 2
Fatty Acid Composition of Chemically Refined, Neutralized, Bleached, and Deodorized Palm Oil

Fatty acid	wt%
C12:0	0.2
C14:0	1.0
C16:0	43.9
C18:0	4.0
C18:1	40.6
C18:2	9.6
C18:3	0.3

TABLE 3
Quality of Chemically Refined, Neutralized, Bleached, and Deodorized Palm Oil^a

Peroxide value	2.408 meq/kg
UV ₂₃₃ ^{1%}	1.5509
UV ₂₆₉ ^{1%}	0.3637
Carotene	1 ppm
Anisidine value	1.3121

^aUV, ultraviolet.

TABLE 4
Molecular Weights (MW) and Purity of Monoglycerides and Phospholipids Used in This Work^a

Lipids	MW	Purity (%)
Lysophosphatidylcholine oleoyl (18:1, <i>cis</i> -9)	≈529	≈99
L- α -Phosphatidylcholine	≈760	≈99
Lecithin	≈760	≈40% PC
Monoglyceride		
C12:0	274.5	≈99
C14:0	302.5	≈99
C16:0	330.5	≈99
C18:0	358.6	≈99
C18:1	356.5	≈99
C18:2	354.5	≈99
C18:3	352.5	≈99

^aPC, phosphatidylcholine.

constant value after 30 min. During the preliminary survey, we found that the mean γ_i of NBDPO against water was 20.6 mN m⁻¹ at 60°C, based on the measurements of 10 samples from one batch of oil from one refinery. The measured values ranged from 19.2 to 21.6 mN m⁻¹ with a standard deviation of ± 0.72 mN m⁻¹. The surface tensions of the various processed palm oils were also measured at 60°C using the ring method with the Kruss tensiometer.

RESULTS AND DISCUSSION

Interfacial activity and refining process. The surface tensions of the palm oils at various stages of refining against air are essentially similar in magnitude and fall within a narrow range of 30.6–31.7 mN m⁻¹ (Table 5). However, the γ_i against water show a wide spread of values, with crude palm oil having the lowest mean value of 8.0 mN m⁻¹ and NBDPO the highest at 25.6 mN m⁻¹. The value for NBDPO is similar in magnitude to other commercial vegetable oils reported in the literature (7). Crude palm oil shows the highest interfacial activity against water, as expected, and thus the reason for refining it to remove the undesirable impurities and to render it bland, colorless, and chemically stable. Clearly, as the degree of refining increases, the purity of the oil improves, resulting

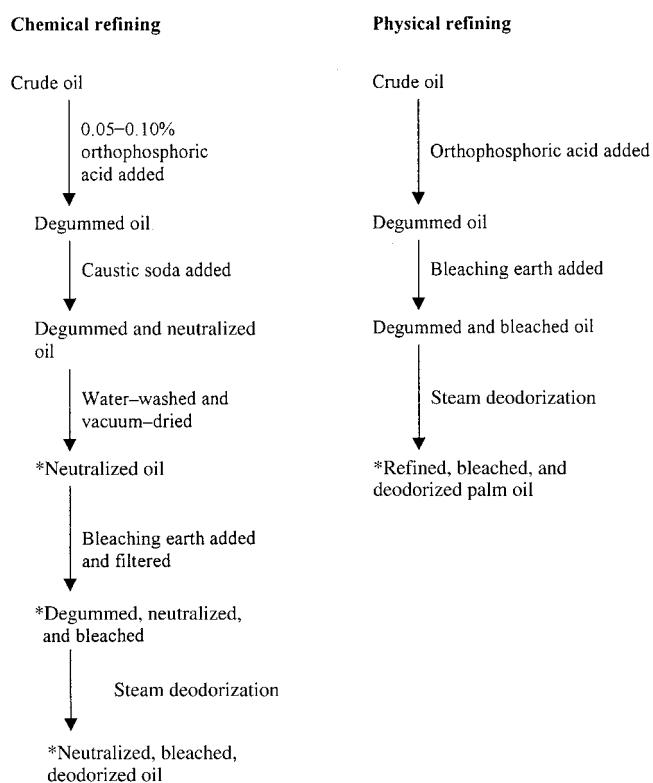


FIG. 1. Flow chart for refining processes for crude palm oil. *Commercially available. Adapted from *Selected Readings on Palm Oil and Its Uses*, Ministry of Primary Industries, Malaysia, 1993, pp. 150–174.

in much higher γ_i (i.e., lower interfacial activities). Chemically refined palm oils exhibit higher γ_i than those refined by the physical method. The difference between the two refining methods is illustrated in Figure 1. Apparently, many surface-active substances, originally present in crude palm oil, still remain after the degumming and bleaching stages of the physical refining process.

To verify this, the various partially processed oils were added to NBDPO, and the γ_i of the mixtures was measured against water, and the results are shown in Figure 2. It shows that the γ_i decreases rapidly with an increase in the amount of

TABLE 5
Surface and Interfacial Tensions of Various Palm Oils Against Water at 60°C

Oil*	Interfacial tension against water (mN m ⁻¹)			Surface tension (mN m ⁻¹)		
	Range	Mean	SD	Range	Mean	SD
Crude palm oil ^a	6.0–9.6	8.0	1.2	30.6–30.9	30.8	0.1
Degummed and bleached palm oil ^b	10.1–15.6	12.7	1.7	30.8–31.0	30.9	0.1
Refined, bleached, and deodorized palm oil ^b	10.6–12.9	11.8	1.1	30.8–31.1	30.0	0.1
Degummed and neutralized palm oil ^c	18.9–24.2	20.8	1.8	31.0–31.7	31.2	0.1
Degummed, neutralized, and bleached ^c	24.7–25.4	25.0	0.3	30.7–31.0	30.9	0.1
Neutralized, bleached, and deodorized palm oil ^c	25.0–26.4	25.6	0.5	30.8–31.1	31.0	0.1

^aBased on 18 samples.

^bBased on 11 samples (physically refined from four refineries).

^cBased on 7 samples (chemically refined from two refineries). *Point of sampling. Refer to Figure 1.

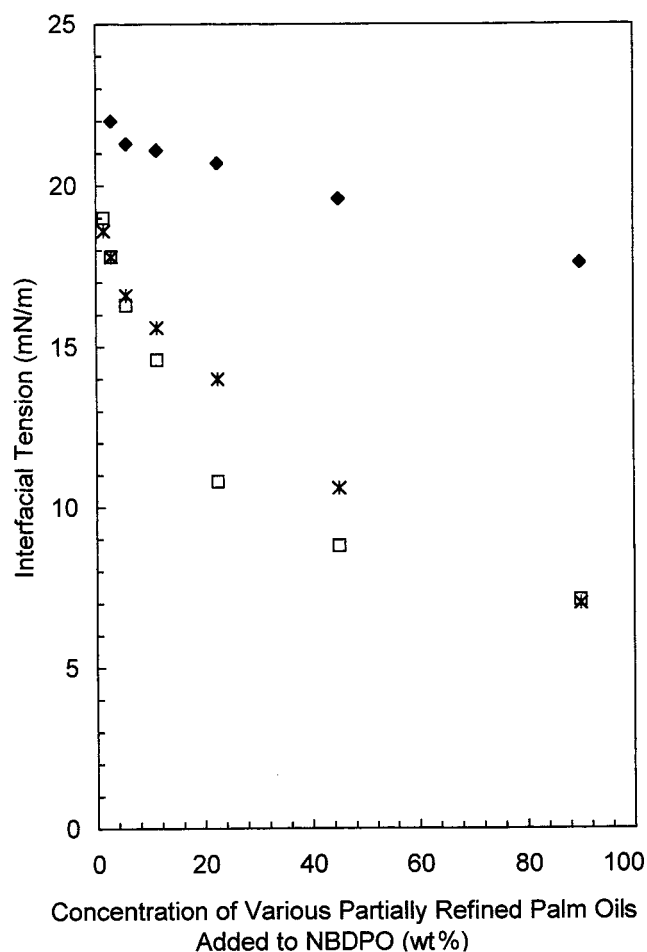


FIG. 2. The effect of various partially refined oils on the interfacial tension of neutralized, bleached, and deodorized palm oil (NBDPO) against water at 60°C. Crude palm oil (□); chemically degummed neutralized oil (◆); physically degummed and bleached (✕).

crude palm oil and physically degummed and bleached oil added separately to NBDPO, whereas the decrease in γ_i with the amount of the chemically degummed and neutralized oil added to NBDPO is much more gradual. The rapid decrease in γ_i with the amount of these impurities added to NBDPO indicates a fast redistribution of these surface-active substances to the oil/water interface and their subsequent transfer to the water phase. This clearly shows that most of the surface-active substances in the oil are removed during chemical neutralization and subsequent washing with water. More surface-active substances are removed with each additional stage of refining as reflected in a decrease in the interfacial activities of the oil/water interface with each stage of refining (Table 5). It also demonstrates that the chemical neutralization refining process is more effective than the physical process in removing surface-active substances from crude palm oil. The surface-active substances removed include monoglycerides, glycolipids, phospholipids, and hydrolysis and oxidation products, such as fatty acids, aldehydes, ketones, hydroperoxides, and peroxides.

The faster rate of deterioration in the quality of physically refined oil, relative to chemically refined oil, could perhaps be attributed to the presence of bigger amounts of these surface-active substances in the former, in particular free fatty acids. Based on the data obtained (from different refineries on different occasions as indicated in Table 5), the wider spread of the γ_i noted for the degummed and neutralized oil, compared to that of the neutralized, degummed and bleached oil, suggests that the efficiency of the surface-active substances' removal is strongly dependent not only on the refining process but also on the type and dosage of bleaching earth used and the duration and temperature of the treatment methods (8).

The γ_i of various vegetable oils (palm oil excluded) against water have been reported (7–11), and big variations in γ_i were observed, which have been attributed to methods of measurements (7), formation of mono- and diglycerides due to hydrolysis of the oil (9), presence of surface-active impurities in the oil (10), and formation of reverse micelles of monoglycerides in the oil phase (11). The decrease of γ_i with time of commercial vegetable oil against water was attributed to the presence of mixtures of monoglycerides (10). The γ_i values of purified vegetable oils were considerably higher than those of lower purity and remained unchanged with time. Our results on the various partially purified palm oils are in general agreement with these conclusions.

Effect of post-added lipids on interfacial properties of palm oil against water. Monoglycerides. The γ_i of NBDPO against water decreased rapidly with an increase in the amount of monoglycerides post-added for all four monoglycerides (Fig. 3). The decrease was almost linear at high concentrations of the monoglycerides. The monoglyceride with the shortest chain, i.e., monolauryl C12:0, was the most surface-active and depressed the γ_i of NBDPO most. The surface activity was in the order C12:0 > C14:0 > C16:0 > C18:0. However, the difference in γ_i among them was small. The trend at low concentrations of monoglycerides added was less clear-cut, with C16:0 being the least surface-active. The effect of unsaturation of the fatty acyl chain is illustrated by the four monoglycerides: C18:0, C18:1, C18:2, and C18:3 (Fig. 4). Generally, an increase in unsaturation of the acyl chain results in an increase in surface activity at the oil/water interface, and the order of increase is C18:2 > C18:3 > C18:1 \approx C18:0. In fact, the values of the γ_i of C18:2 were much lower than those of the rest in the series. Again, the decrease of γ_i with concentration of the added monoglycerides was steep at high concentration, and for C18:2, it was steep and linear over the whole concentration range studied.

Both anionic and polar nonionic emulsifiers were effective in reducing the γ_i of the soybean oil/water system in the presence of milk proteins in the water phase (12). The effect of natural surface-active substances on γ_i of corn and safflower oil/water systems has been reported (13). It was noted that proteins could easily be displaced from the corn oil/water interface by a critical molar ratio of monoglyceride and diglyceride and pH (14). Similarly, monounsaturated monoglyc-

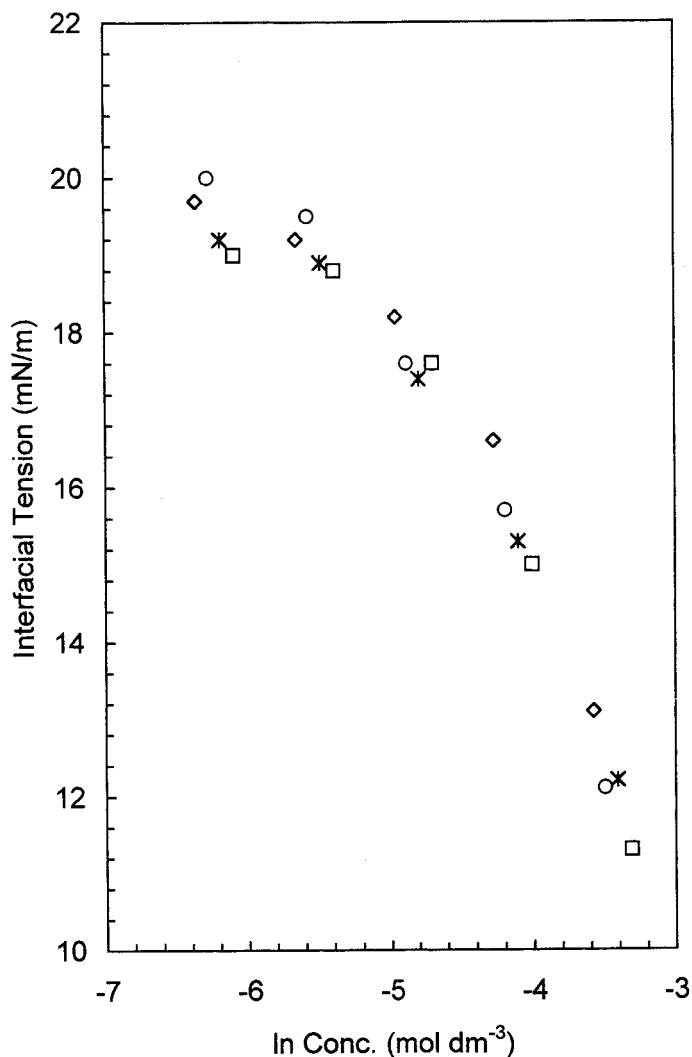


FIG. 3. The influence of acyl chain length of monoglycerides on the interfacial tensions of NBDPO against water at 60°C. C12:0 (□); C14:0 (✱); C16:0 (○); C18:0 (◇). See Figure 2 for abbreviation.

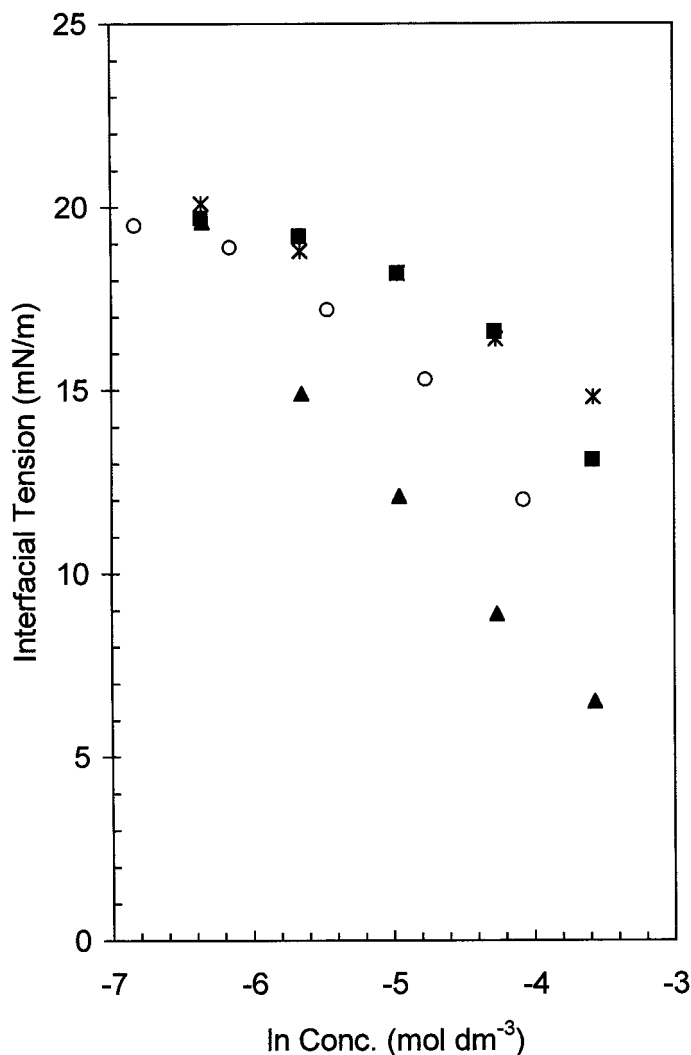


FIG. 4. The effect of unsaturation of the acyl chains of monoglycerides on the interfacial tensions of NBDPO against water at 60°C. C18:0 (■); C18:1 (✱); C18:2 (▲); C18:3 (○). See Figure 2 for abbreviation.

erides were more effective in displacing proteins from fat globules in ice cream mix than the corresponding saturated monoglycerides (15). Thus, the combined effect of unsaturation, mixed adsorbed layer of emulsifiers, and competitive adsorption of the natural surface-active substances at the palm oil/water interface could have given rise to the observed behavior.

The surface area occupied by each molecule at the oil/water interface (A) was calculated from the Gibbs adsorption isotherm:

$$\Gamma = -(RT)^{-1} (d\gamma_i/d \ln C) \quad [1]$$

where Γ is the surface excess concentration, C the concentration of lipid added, R the gas constant, and T the absolute temperature. The $(d\gamma_i/d \ln C)$ values were deduced from the best-fit polynomials of the γ_i vs. \ln (concentration) data. These values increase with increasing concentration and tend toward a

limiting value (slope), Γ_m , at high concentration. At the highest concentration of about $3 \times 10^{-2} \text{ mol dm}^{-3}$ of the mono- and diglycerides studied, the surface area occupied by each monoglyceride molecule was in the order: C16:0 (0.62 nm^2) > C14:0 (0.56 nm^2) \approx C18:0 (0.54 nm^2) > C12:0 (0.44 nm^2). The surface area (A) for each monoglyceride molecule increases with an increase in the acyl chain length, with the exception of C18:0. The γ_i of the monoglycerides at this concentration were within the range of 9.5 to 11.7 mN m^{-1} . For the unsaturated monoglycerides at about the same concentration of $3 \times 10^{-2} \text{ mol dm}^{-3}$, the A values change with the unsaturation of the acyl chain in the order of C18:1 (1.29 nm^2) > C18:2 (1.00 nm^2) > C18:3 (0.54 nm^2) \approx C18:0 (0.54 nm^2). The A value is the largest for C18:1 followed by C18:2. It then decreases to about half of the C18:2 value when the number of double bonds is increased to three as in C18:3. These values are much larger than the value of 0.28 nm^2 reported for the liquid-condensed film produced by 1-mono-

myristin at the air/water interface at 25°C (16). At 60°C and low surface pressure, the short-range forces among the hydrocarbon chains are greatly diminished compared with those found in the liquid condensed state. Structurally, the coplanar ethylenic bond of C18:1 is rigid and electron-rich, and the attached hydrocarbon chain assumes the most favorable position in the horizontal direction at the interface, if sterically permitted. This could result in an expanded film and thus the large A value. However, the incorporation of additional double bonds at the 12th and 15th carbon positions of the acyl chain, as in C18:2 and C18:3, resulted in a drastic reduction in A instead, especially for C18:3. This implies that, unlike C18:1 and C18:2 (whose substantially larger areas indicate that their tailgroups may be adsorbing at the interface along with their polar headgroups), C18:3 tailgroups remain within the oil phase away from the interface. This may be due to coiling of the C18:3 tailgroups in the oil phase prior to adsorption at the interface. The energy required to uncoil the tailgroups before adsorption may be too high to allow significant adsorption of tailgroups relative to their staying coiled in the oil phase. Also, the polar nature of palm oil and its minor components have a profound influence on the ultimate orientation of the polar moieties of the unsaturated monoglycerides at the oil/water interface.

Adsorption of surface-active materials at an interface has often been described by the Langmuir adsorption isotherm:

$$\Gamma = \Gamma_m KC / (1 + KC) \quad [2]$$

where K is the adsorption constant. Equation 1 can be integrated under the boundary conditions $\gamma = \gamma_o$ when $C = 0$:

$$-\int_{\gamma_o}^{\gamma} d\gamma = \int_0^C \Gamma RT d \ln C \quad [3]$$

substituting Γ from Equation 2 and integrating Equation 3 gives

$$\gamma = \gamma_o - \Gamma_m RT \ln (1 + KC) \quad [4]$$

The advantage of using this equation is that there is only one adjustable parameter, K , for data that may span two or three decades of concentration. Using the values of γ_o and Γ_m obtained from the above, good agreement was obtained between Equation 4 and the experimental data (less than 5.0% difference between experimental and calculated values) for the saturated monoglycerides series C12:0, C14:0, C16:0, and C18:0; and the unsaturated monoglycerides C18:1 and C18:3 (see Fig. 5 for examples). This suggests a good representation of the adsorption behavior of these materials by the Langmuir isotherm. Values of K , summarized in Table 6, ranged from 32 to 590. Fisher *et al.* (17) also reported a wide spread of K values for the adsorption of monoglycerides and long-chain fatty acids at the triglyceride/water interface. However, the data for C18:2 did not fit Equation 4 as satisfactorily. The reason is not clear.

The free energy of adsorption, ΔG_{ads} , of these materials at the palm oil–water interface can be derived from K by Equation 5:

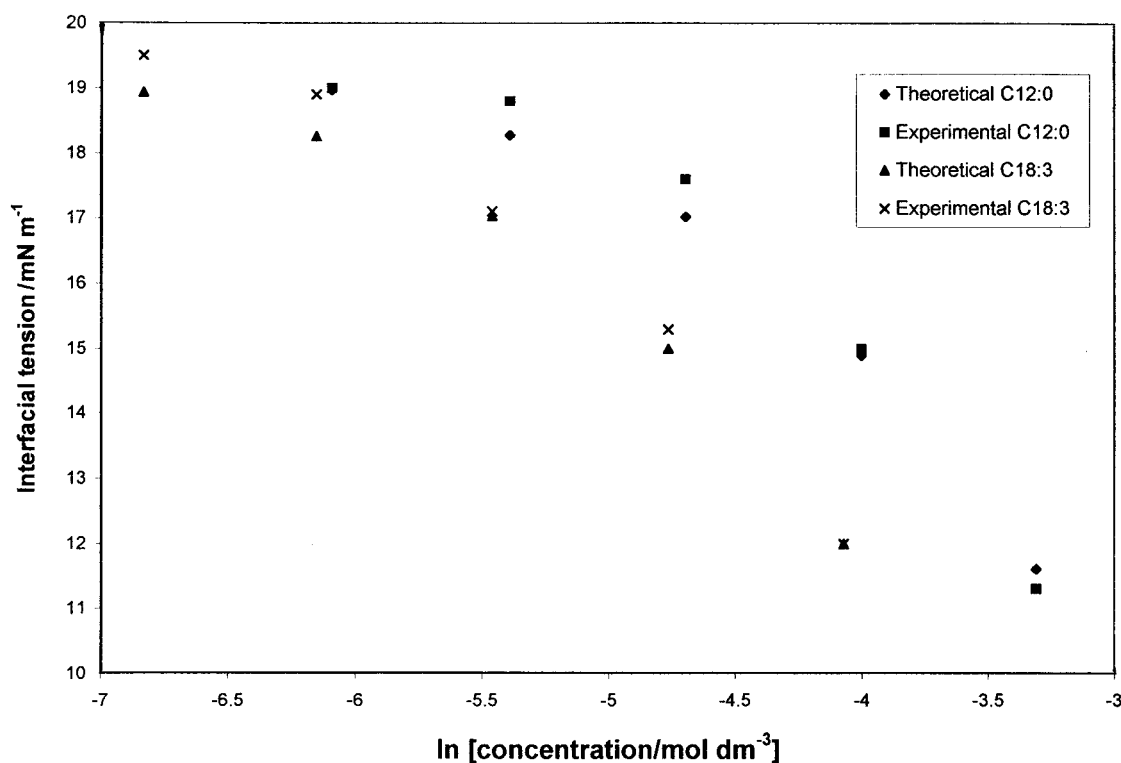


FIG. 5. The interfacial tension as a function of \ln (concentration) of C12:0 and C18:3. The theoretical points are calculated from Equation 4 with $K = 32 \text{ dm}^3 \text{ mol}^{-1}$ for C12:0 and $K = 88 \text{ dm}^3 \text{ mol}^{-1}$ for C18:3.

$$\Delta G_{\text{ads}} = -RT \ln K \quad [5]$$

The values of ΔG_{ads} for the saturated and unsaturated glycerides are listed in Table 6. The general trend is that the value of ΔG_{ads} increases slightly with increasing acyl chain length for the saturated monoglyceride series. The introduction of unsaturation into the acyl chain also increases the ΔG_{ads} values, for example to $-17.7 \text{ kJ mol}^{-1}$ for C18:2. The magnitude of these values is in good agreement with those in the literature for some monoglycerides at the triglyceride/water (17) and the soybean oil/tristearin interfaces (18).

Phospholipids. The surface activity of the three phospholipids at the NBDPO/water interface is shown in Figure 6. The γ_i of the oil/water interface in the presence of phospholipids is much lower than those for the monoglycerides at the same dosage. The decrease of γ_i with concentration is linear for L- α -phosphatidylcholine over the whole concentration range studied, whereas for lysophosphatidylcholine, there is a gradual decrease initially, followed by a steep drop linearly at higher concentration. For lecithin, the decrease is steep initially, followed by a more gradual one. Among the three phospholipids, L- α -phosphatidylcholine is the most surface-active, and lysophosphatidylcholine is the least. The soy lecithin sample, which contains only 40% phosphatidylcholine, is intermediate in surface activity between the two. The presence of two fatty acid chains in L- α -phosphatidylcholine obviously contributed significantly to its enhanced activity, compared to the single-chain lysophosphatidylcholine.

The surface area occupied by lysophosphatidylcholine at the palm oil interface at a concentration of $10^{-3} \text{ mol dm}^{-3}$ at 60°C was about 0.69 nm^2 , whereas that for L- α -phosphatidylcholine was slightly smaller at 0.61 nm^2 at $10^{-5} \text{ mol dm}^{-3}$. The A value of lysophosphatidylcholine decreased rapidly with increase in concentration but does not appear to have reached any limiting value even at $10^{-3} \text{ mol dm}^{-3}$. However, the A value for L- α -phosphatidylcholine does not vary much with concentration and appears to have reached a constant value at low concentrations of the lipid. This could perhaps be attributed to the two-tail structure of the L- α -phosphatidylcholine molecule being bulkier and less compressible than lysophosphatidylcholine. Handa *et al.* (19) reported an A

TABLE 6
The Adsorption Constants (K) and $-\Delta G_{\text{ads}}$ for Various Lipids at the Palm Oil/Water Interface Determined at 60°C and Evaluated from Equation 4^a

Lipids	K values	$-\Delta G_{\text{ads}}/\text{kJ mol}^{-1}$
C12:0	32	9.6
C14:0	40	10.2
C16:0	55	11.1
C18:0	48	10.7
C18:1	117	13.2
C18:2	590	17.7
C18:3	88	12.4
LysoPC	1.08×10^4	25.7
α -PC	6.54×10^5	37.1

^aSee Table 4 for abbreviation.

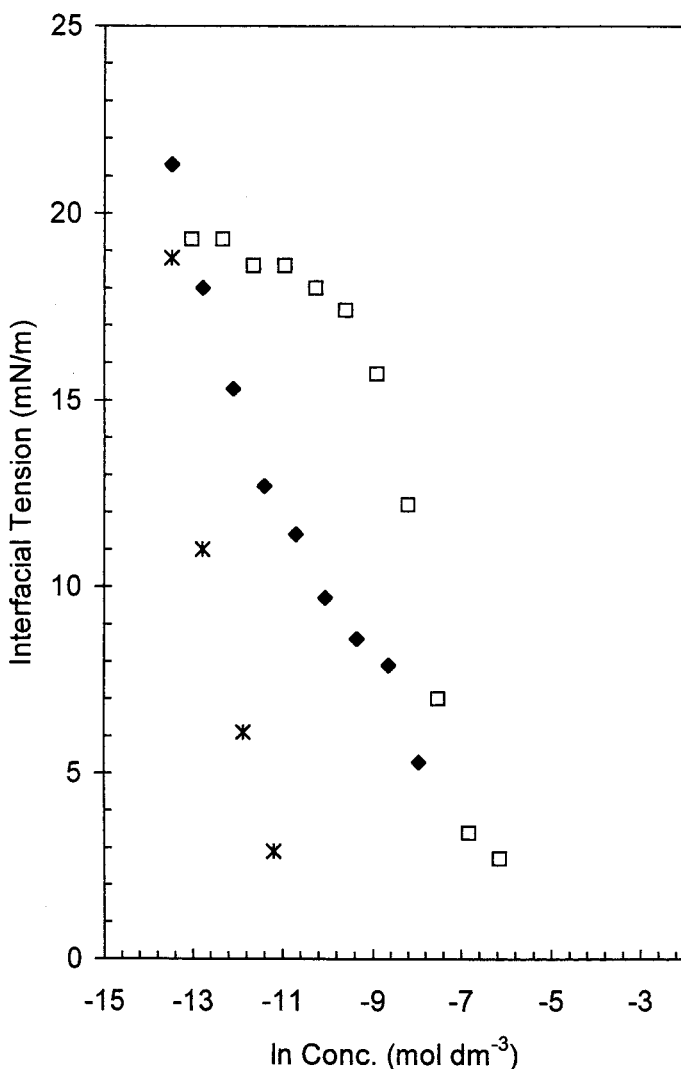


FIG. 6. The effect of phospholipids on interfacial tensions at the NBDPO/water at 60°C . Lysophosphatidylcholine (\square); L- α -phosphatidylcholine (\times); lecithin (\blacklozenge). See Figure 2 for abbreviation.

value of 0.40 nm^2 for phosphatidylcholine from egg yolk at the triolein/water interface. A was reported (20) to be 0.71 nm^2 for egg phosphatidylcholine in lamellar and vesicle surfaces.

At the air/water interface, Van Deenan *et al.* (21) found that closest packing of the distearoyl homologs of various phospholipids gave A values in the range of 0.36 to 0.40 nm^2 . Unsaturation and shortening of the acyl chain length greatly expanded the adsorbed layer of L- α -lecithin, and A increased to 0.60 nm^2 . Jackson *et al.* (22) obtained an A value of 0.60 nm^2 for L- α -dipalmitoylphosphatidylcholine monolayer at 25°C . Other workers (23) have noted that the orientation of the polar group in various phosphatidylcholine monolayers is dependent on the structures of the fatty acid chains in the molecules. This bears directly on the packing of the molecules in the monolayers, giving rise to different surface areas per molecule at the air/water interface for different phosphatidylcholines (23). For example, disruption of the close packing of

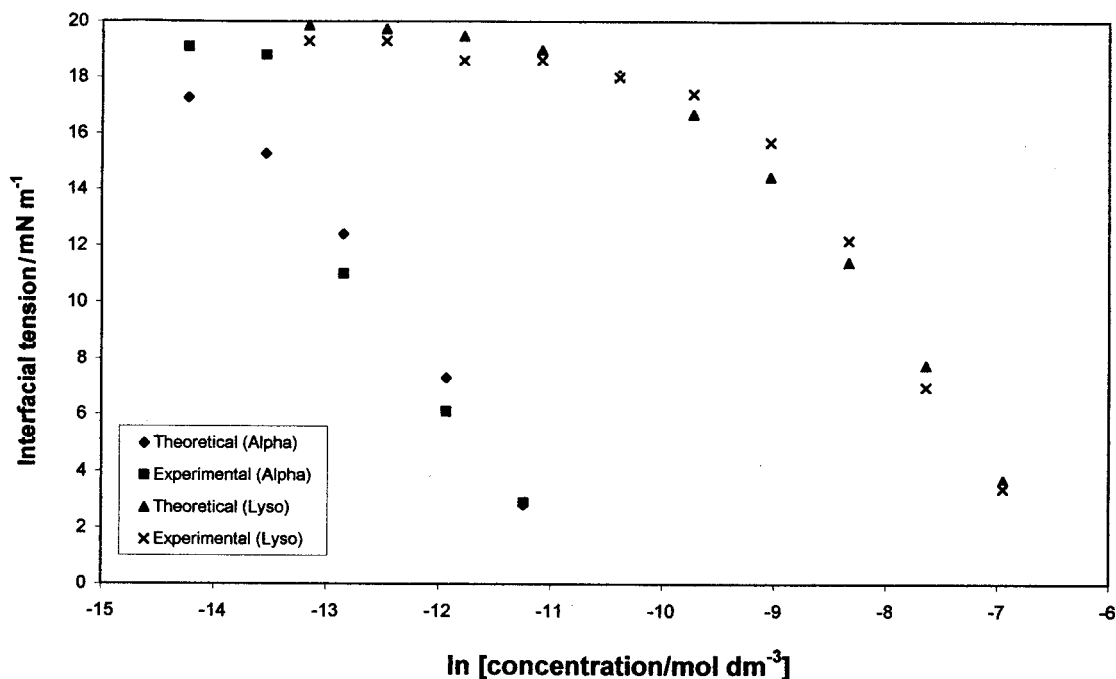


FIG. 7. The interfacial tension as a function of \ln (concentration) of L- α -phosphatidylcholine and lysophosphatidylcholine. The theoretical points are calculated from Equation 4 with $K = 6.54 \times 10^5 \text{ dm}^3 \text{ mol}^{-1}$ for L- α -phosphatidylcholine and $K = 1.08 \times 10^4 \text{ dm}^3 \text{ mol}^{-1}$ for lysophosphatidylcholine.

the acyl chains causes an increase in A for different lecithins. Based on the above and bearing in mind the intrinsic nature of the oil, apparently, our results of A for lyso- and L- α -phosphatidylcholines at the palm oil/water interface are reasonable.

Further, Figure 7 shows that the data for L- α -phosphatidylcholine and lysophosphatidylcholine do not fit the theoretical prediction of Equation 4 as well as the monoglycerides. Between the two, lysophosphatidylcholine seems to give a slightly better fit, indicating the behavior of these molecules adsorbed at the oil/water interface could perhaps be described by the Langmuir model. The ΔG_{ads} value of -26 kJ mol^{-1} for lysophosphatidylcholine, shown in Table 6, is higher than those for the monoglycerides but comparable to values reported for L- α -dipalmitoylphosphatidylcholine at the glass/water interface at 62°C (22).

Lipid monolayers and their adsorption are mostly studied at the air/water interface by the surface balance technique. The orientation of the lipid molecules at the interface depends upon the liquid crystalline phase of the lipid at the prevailing temperature and pressure. Monolayers of fatty acids (24), phosphatides (21), and monoglycerides (16) at the air/water interface have all been reported previously. The behavior of mixed monolayers of different types of phospholipids (15,23) and mixtures of monoglycerides (25), however, depends on the compatibility and solubility of the individual molecules in the mixtures. Considerable differences are expected to arise between adsorption of these substances at the oil/water and air/water interfaces, in addition to differences due to the apolar nature of the oil itself (triglyceride vs. hydrocarbon oils).

For example, the γ_i of the triglyceride/water system usually ranges within $23\text{--}25 \text{ mN m}^{-1}$, whereas that for hydrocarbon/water interface is only about half this value (26). While monoglycerides and fatty acids are strongly adsorbed at the hydrocarbon/water interface, fatty acids are completely soluble in triglycerides. The hydrophobes of hydrocarbons are much more varied compared to the triglycerides, but the latter are affected by minor natural components associated with them. Impurities in the oil are known to cause a decrease of γ_i with equilibration time against water. Thus, complex though the nature of the triglyceride/water interface may be, at least some general conclusions about the adsorption of surface-active substances, both natural and post-added, at the palm oil/water interface can be arrived at. The more expanded nature of the adsorbed layer of these materials at the palm oil/water interface, corresponding to the much larger values of A obtained, is perhaps a direct reflection of the complexity of this interface. The above findings are corroborated by the γ_i results of the NBDPO in the presence of partially refined palm oils, which clearly illustrate the influence of the types of the refining process has on the purity and quality of the final products. It appears that the γ_i of a processed palm oil is a good indicator of the quality as well as the refining process the oil has undergone.

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