Solubilization of Selected Free Fatty Acids in Palm Oil by Biodegradable Ethoxylated Surfactants

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The solubilization of three major components, viz., palmitic, oleic, and linoleic acids, in palm oil by ethoxylated surfactants was investigated. The results were analyzed in terms of the molecular properties of surfactants and free fatty acids (FFAs). It was found that the solubilities of these FFAs in various micellar solutions depend not only on their octanol–water partition coefficients (K_{ow}), but also on their physicochemical properties. The study on the solubilization kinetics was conducted by choosing palmitic acid as a model solubilizate and Tergitol 15-S-7 as the model surfactant. A first-order film diffusion model, which accounts for the direct uptake of organic molecules at a solid surface into surfactant micelles, was adopted to analyze the effect of surfactant on dissolution of palmitic acid. It was observed that the presence of surfactant reduced the mass-transfer coefficient. Instead, the overall mass-transfer rate was enhanced because of the much higher driving force from the increased solubilization capacity.

INTRODUCTION

Palm oil is one of the world's most important vegetable oils (*1*). It is used mainly for edible purposes and has become an important raw material for many applications during the past few decades. Increasing interest in the chemistry and biotechnology of palm oil has emerged in recent years, which is mainly attributed to the fact that oleochemicals are derived from renewable sources. The major fatty acids in palm oil are palmitic, oleic, and linoleic acids (*2, 3*) (**Table 1**). In palm oil, each of the saturated palmitic acid and the monounsaturated oleic acid accounts for ca. 40 wt % of the overall free fatty acids (FFAs), depending on harvest conditions and locations of cultivation (*3*).

Palm oil mills produce a large amount of solid and palm oil mill effluent (POME) wastes. The quantity of POME varies with the amount of water used. Typically, the total weight of liquid effluent is estimated at around 0.6 ton per ton of fresh fruit bunches (*4*). The POME wastes are the fiber-free oil components obtained from the clarification zone of oil mills, where the temperature of the POME discharge ranges from 50 to 70 °C. They consist of various suspended components, including a high content of FFAs between 670 and 1800 mg/L, cell walls, organelles, a spectrum of carbohydrates ranging from hemicellulose to simple sugars, a wide range of nitrogenous compounds

Table 1. Fatty Acid Components of Palm Oil[a]

common name	systematic name	percentage of total weight
	Saturated Acids	
lauric	*n*-dodecanoic	<1
myristic	*n*-tetradecanoic	1–6
palmitic	*n*-hexadecanoic	32–47
stearic	*n*-octadecanoic	1–6
arachidic	*n*-eicosanoic	<1
	Monounsaturated Acids	
palmitoleic	*n*-hexadec-9-enoic	<1
oleic	*n*-octadec-9-enoic	40–52
gadoleic	*n*-eicos-9-enoic	<1
	Polyunsaturated Acids	
linoleic	*n*-octadec-9,12-dienoic	5–7

[a] Obtained from the ref *2*.

from proteins to amino acids, and an assembly of minor organic and mineral constituents (*4*). Fortunately, they are nontoxic and biodegradable.

When POME wastes are discharged into a river, they increase the biochemical oxygen demand of water and undoubtedly reduce dissolved oxygen concentration. In addition, the low volatility and aqueous solubility of the free fatty acids in the POME wastes make them persistent. Moreover, a significant amount of FFAs would precipitate from the effluent, in which the temperature of the effluent is cooled to ca. 30 °C in nature. Biological transformation is believed to be a major removal process of FFAs from soil and aquifer systems. Nonetheless, the hydrophobic nature of these contaminants results in their

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Table 2. Selected Properties of FFAs

FFA	molecular formula	MW	log K_{ow}	aqueous solubility (mg/L)
palmitic	$CH_3(CH_2)_{14}COOH$	256.42	7.17[a]	7.74[b]
oleic	$CH_3(CH_2)_7CH=CH(CH_2)_7COOH$	282.45	7.64[a]	230.2[b]
linoleic	$CH_3(CH_2)_4CH=CHCH_2CH=CH(CH_2)_7COOH$	280.44	7.05[a]	180.2[b]

[a] Data obtained from ref *27*. [b] Measured value in this work at 25 °C.

partitioning onto the soil matrix, limiting their bioavailability. It is also likely that settlement of suspended solids would produce objectionable banks of septic sludge in slow reaches of the rivers. Moreover, from an environmental point of view, it is better to eliminate as much FFAs as possible in POME before they are discharged or precipitated to the environment. Consequently, an efficient and economic scheme to enhance the degradation of these FFAs is critical to successfully achieve this goal.

It is generally believed that sorbed hydrophobic pollutants are not directly available to the microbial population. A well-designed bioremediation process should consider methods to mobilize these contaminants from the soil surface and make them available to the microbial population. One common way to achieve the higher bioavailability and biodegradation rate is to increase their aqueous solubilities by adding proper surfactants that do not compete with the solubilizates as a food source to the microbes (*5−7*).

Surfactants are effective in increasing aqueous solubility of a hydrophobic compound. If the concentration of a surfactant exceeds a certain threshold, called the critical micelle concentration (CMC), at a temperature higher than its Krafft temperature, surfactant monomers in aqueous solution will aggregate to form micelles of colloidal size. One of the important properties of a surfactant is that the hydrophobic cores of micelles could offer good affinity for hydrophobic solutes to stay in the micelles and, hence, increase the aqueous solubilities of these practically insoluble solubilizates. Such a process is called solubilization, typically defined as the spontaneous dissolving of an insoluble substance by reversible interaction with the micelles of a surfactant in a solvent to form a thermodynamically stable isotropic solution with reduced thermodynamic activity of the solubilized material (*16*). Under proper conditions, surfactants could solubilize considerable amounts of palm oils and triglycerides in oil-containing micelles, called swollen micelles or microemulsions (*8−10*).

In this study, solubilization of major FFAs in the palm oil by some ethoxylated surfactants is investigated in an attempt to enhance their bioavailability by mobilizing them from precipitates. These oils are mainly the palmitic, oleic, and linoleic acids, listed in **Table 2**. Five ethoxylated surfactants, shown in **Table 3**, having slightly different molecular structures and hydrophile−lipophile balance (HLB) values were chosen in an attempt to differentiate the contribution of their molecular structures to the solubilization processes. Indeed, two of them have been successfully demonstrated in the solubilization and extraction of polycyclic aromatic hydrocarbons (*11, 12*).

MATERIALS AND METHODS

Reagents. Reagent grade palmitic acid, oleic acid, and linoleic acid were purchased from Tokyo Kasei (TCI), Sigma, and Aldrich. At ambient temperature, palmitic acid is a solid, while oleic and linoleic acids are in the liquid state. Selected physical and chemical properties of FFAs are given in **Table 2**.

Table 3. Selected Properties of Surfactants

name	molecular formula	MW	HLB	CMC (mg/L)	micellar size[d] (nm)
T-S-5	$C_{11-15}H_{23-31}O(CH_2CH_2O)_{5.2}H$	415[a]	10.5[a]	30[c]	
T-S-7	$C_{11-15}H_{23-31}O(CH_2CH_2O)_{7.3}H$	515[a]	12.1[a]	39[a]	16.0
N-7	$C_{12-15}H_{25-31}O(CH_2CH_2O)_{7.3}H$	515[a]	12.1[a]	9[a]	18.3
GE-460	$CH_3(CH_2)_{11-13}O(CH_2CH_2O)_{4.5}CH_2COOH$	460	10.4[b]	130[c]	7.6
GE-690	$CH_3(CH_2)_{11-13}O(CH_2CH_2O)_{10}CH_2COOH$	690	13.9[b]	185[c]	4.0

[a] Value given by the manufacturer. [b] Calculated from an equation using HLB = degree of ethoxylation expressed in weight percent divided by 5. [c] Measured value. [d] Measured by dynamic light scattering in 1 wt % surfactant solution at 25 °C; averaged micellar size of T-S-Mix, 17.3 nm.

Tergitol 15-S-5 (T-S-5) and Tergitol 15-S-7 (T-S-7), obtained from Dow, are nonionic secondary ethoxylated alcohols. A mixed nonionic surfactant, T-S-Mix, was made by mixing T-S-7 with T-S-5 in a weight ratio of 3:1, respectively, which gives T-S-Mix an average ethylene oxide (EO) number of 6.7. Another nonionic surfactant, Neodol 25-7 (N-7), a primary ethoxylated alcohol, was obtained from Shell Chemicals. Two anionic ethoxylated surfactants, glycolic acid ethoxylate lauryl ethers with average molecular weights of 460 (GE-460) and 690 (GE-690), were obtained from Aldrich. Relevant properties of these surfactants are given in **Table 3**. T-S-5, T-S-7, and T-S-Mix surfactants have the same hydrophobic hydrocarbon chains, but differ in EO numbers. Likewise, T-S-7 and N-7 surfactants have almost the same molecular weight, HLB number, and carbon number along their hydrophobic hydrocarbon chains, but only differ in molecular configurations. Namely, the ethoxylated alcohol group is located in the end position of the N-7 surfactant molecule, whereas T-S-7 has a secondary one. More importantly, these surfactants are readily biodegradable. All chemicals and surfactants were used as received. Deionized water with resistivity greater than 18.2 MΩ·cm was used in sample preparations.

Apparatus. A Krüss DSA-10 tensiometer was used to determine the CMCs of the surfactants. The CMC was estimated by plotting the surface tension data against the surfactant concentration as the abscissa. The concentrations of fatty acids were measured by using a gas chromatograph (Perkin-Elmer Autosystem XD), equipped with a flame-ionization detector and an HP-Innowax column (30 m × 0.25 mm × 0.25 μm). Helium was used as the carrier gas with a flow rate of 40 sccm (standard cubic centimeters per minute) and a split ratio set at 50:1. The detector and injection temperatures were set at 300 and 250 °C, respectively. All the concentrations of free fatty acids given in this study were the average from at least quadruplicate measurements on each sample in, at least, three different batches of experiments under the same conditions. The error for each reading was ensured within 5% from the mean values.

Equilibrium Solubilization. The equilibrium solubilities of palmitic, oleic, and linoleic acids in aqueous solutions of T-S-Mix, T-S-7, N-7, GE-460, and GE-690 were determined using screw-capped glass culture vials of 15 mL. Surfactant solutions above CMCs, from 0.5 to 4.0 wt %, were prepared. For the solubilization of palmitic acid, each vial was filled with granular palmitic acid in excess and then with 10 mL of these surfactant solutions at different concentrations. The vials were then put on a rotary mixer for 5 days to reach equilibrium in a temperature-controlled room (ca. 23 °C), since equilibrium solubilization could be achieved after 5 days of mixing as indicated from preliminary experiments.

For equilibrium solubilization studies of oleic and linoleic acids, excess amounts of liquid acids were filled into screw-capped glass vials containing 10 mL of surfactant solutions. All the solubilization experiments were performed with a minimum mixing period of 7 days in a temperature-controlled room. All sample vials were inverted for 2 days to achieve complete separation of the unsolubilized oil phase from the aqueous phase. Samples from the aqueous phase below the oil phase were withdrawn to determine the concentrations of oleic and linoleic acids by gas chromatography (GC).

Dissolution Kinetics for Palmitic Acid. Solid palmitic acid was chosen as the contaminant used in the dissolution study to quantify the impact of Tergitol 15-S-7 surfactant on its dissolution rate. To
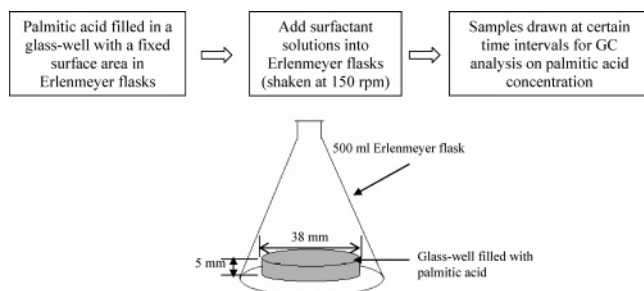
Figure 1. Flow diagram and a schematic figure showing the modified Erlenmeyer flask used for experiments in dissolution kinetics.
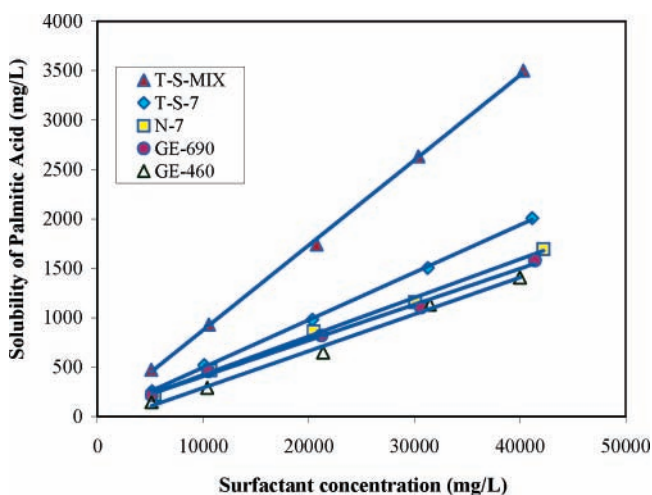

Figure 2. Solubilization of palmitic acid by ethoxylated surfactants (WSR).

Figure 3. Solubilization of oleic acid by ethoxylated surfactants (WSR).

Figure 4. Solubilization of linoleic acid by ethoxylated surfactants (WSR).

quantify the mass-transfer coefficient of palmitic acid from its solid surface into water or micellar solutions, an experimental system similar to that described by Grimberg et al. (*13*, *14*) was developed. A 500 mL Erlenmeyer flask, schematically shown in **Figure 1**, was modified by welding a short cylindrical glass well (38 mm internal diameter and 5 mm height) onto its bottom. Approximately 2 g of palmitic acid (melting point 64 °C) was melted in a water bath at 70 °C, then pipetted into the well, and allowed to cool at room temperature. After the melt solidified, the flask was rinsed with methanol and water to remove condensed palmitic acid from the glass wall and to simultaneously smooth the surface of the palmitic acid. Tergitol 15-S-7 micellar solution of 200 mL was added into a flask placed on an orbital shaker at 150 rpm at ca. 23 °C. Palmitic acid concentration in the bulk liquid was monitored over time by withdrawing 1 mL of the micellar solution. The specific surface area for each sampling interval was determined by dividing the surface area by the corrected liquid volume, i.e., initial minus sample volume taken.

RESULTS AND DISCUSSION

Solubilization of Free Fatty Acids by Nonionic Surfactants. The equilibrium solubilization curves for palmitic, oleic, and linoleic acids in the micellar solutions of T-S-Mix, T-S-7, N-7, GE-460, and GE-690 at ambient temperature (ca. 23 °C) are shown in **Figures 2**−**4**. It is evident that the relationship between the apparent solubilities of these FFAs and the surfactant concentrations above the CMC is linear. These linear enhancements in solubility above the CMC are consistent with the solubilization data reported for other hydrophobic organic compounds of environmental concern (*11*, *15*).

There are a few common expressions to quantify the solubilization capacity of the surfactant, one of which is the micelle−water partition coefficient K_{m} that indicates the distribution of organic molecules between the micellar pseudophase a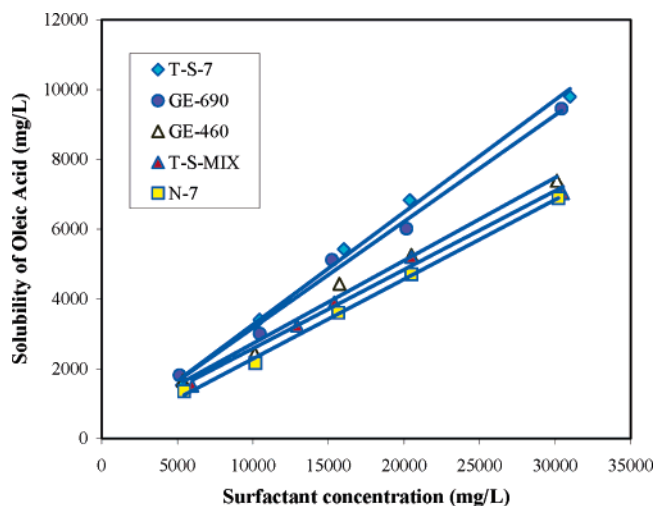nd the aqueous phase. Two others are the mass solubilization ratio (WSR) and the molar solubilization ratio (MSR). The WSR is defined as the weight of the FFA solubilized by a unit mass of surfactant above its CMC. Similarly, the MSR is described as the number of moles of FFA solubilized by each mole of surfactant above its CMC.
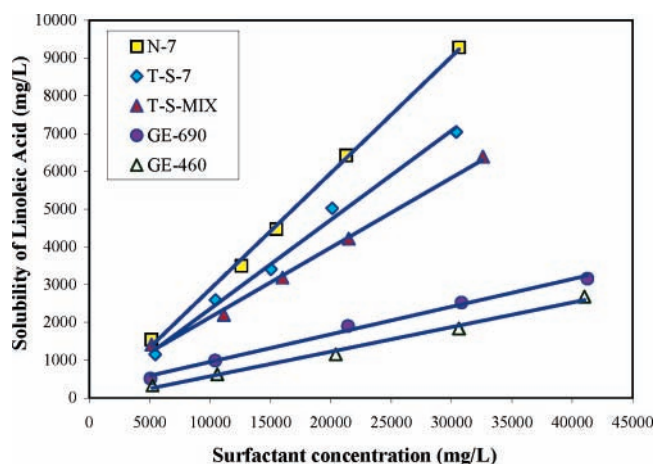
The micelle−water partition coefficient K_{m} can be expressed as follows:

$$K_{\mathrm{m}} = X_{\mathrm{m}}/X_{\mathrm{a}} \qquad (1)$$

where X_{m} and X_{a} are the mole fractions of FFA in the micellar pseudophase and in the micelle-free aqueous phase, respectively. Moreover, X_{m} can be calculated in terms of MSR (*15*):

$$X_{\mathrm{m}} = \mathrm{MSR}/(1 + \mathrm{MSR}) \qquad (2)$$

In addition, X_{a} is often approximated in dilute solutions by

$$X_{\mathrm{a}} = C^{*}_{\mathrm{a}} V_{\mathrm{w,mol}} \qquad (3)$$

where C^{*}_{a} is the aqueous solubility of solute and $V_{\mathrm{w,mol}}$ is the molar volume of water at the experimental temperature.

Explicitly, the MSR could be written as follows (*15*):

$$\mathrm{MSR} = \frac{C_{\mathrm{FFA}} - C_{\mathrm{FFA,CMC}}}{C_{\mathrm{surf}} - \mathrm{CMC}} \qquad (4)$$

where C_{FFA} and $C_{\mathrm{FFA,CMC}}$ (M) are the apparent solubilities of FFA in molarity in the micellar solutions having a surfactant
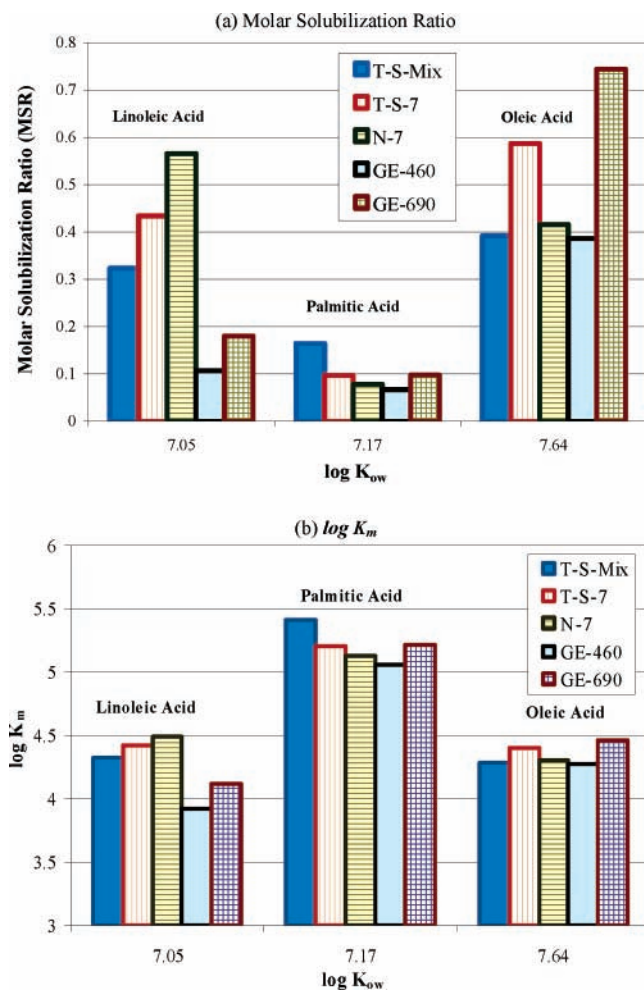
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Figure 5. MSR and log K_m as a function of log K_{ow}: (**a**) MSR; (**b**) log K_m.

concentration equal to C_{surf} (M) and the CMC of the surfactant. The MSR and WSR can be obtained from the slope of the solubilization curve in proper units. Here, the term "apprarent solubility" is used since the solubilities of FFAs contain both the contribution directly from molecular solubilization and that made by micelles.

Interestingly, the maximum MSRs for each FFA among these surfactants differ. For example, **Figure 5** gives the solubilization capacity in terms of MSR and log K_m, and indicates that the MSR of palmitic acid decreases as the HLB of nonionic surfactants increases. For example, T-S-Mix has the lowest HLB number among nonionic surfactants used in this work and, thus, is regarded as the most hydrophobic surfactant among them. T-S-Mix can solubilize palmitic acid ca. 50–100% more than T-S-7 and N-7. This could be attributable to the fact that the nonpolar saturated palmitic acid is preferentially solubilized in the hydrophobic cores of the nonionic micelles. Moreover, values of log K_m for palmitic acid decrease slightly in surfactants with larger HLB numbers (**Figure 5**).

For two anionic surfactants, GE-460 and GE-690, used in the study, consistent results were obtained for the three fatty acids. GE-690 has a higher solubilization capacity, in terms of MSR or log K_m, than GE-460, though they share similar molecular structures. They have the same hydrophobic hydrocarbon chains and one carboxylic group in the end position, but only differ in the units of ethylene oxides (EOs). Their hydrocarbon chains may give them the same degree in the van der Waals attraction between the hydrocarbon chains of sur-

factants and FFAs. Meanwhile, the carboxyl groups on FFAs will favorably interact with the carboxyl groups of surfactant molecules. However, more EO units give GE-690 more polar nature and, consequently, more van der Waals attraction with FFAs.

However, for oleic and linoleic acid, the maximum solubilization was achieved when GE-690 and N-7 were used, respectively. Solubilization is a partition process of organic substances between an aqueous and a micellar phase. This process can be affected by many factors, including the molecular properties of surfactants and solubilizates, such as the loci of solubilizates in micelles and the bending elasticity of surfactant films in micelles, and some environmental factors (*16*). In general, the most important characteristics of a surfactant in terms of solubilization power are its HLB number and molecular structure (*15, 17, 18*).

Micelles of surfactants having lower HLB values from the same homologous series can provide a more hydrophobic environment preferentially for hydrophobic solubilizates. In addition, surfactants with a lower HLB number tend to have greater micellar core volumes compared with surfactants of the homologue, but with a higher HLB value (*16, 19*). This idea has been used to explain the greater solubilization capacity of dodecyl alcohol ethoxylates for nonpolar hydrophobic organic compounds including dodecane, decane, hexane, and cyclohexane (*18*). Mackay (*20*) also reported that a decrease of solubilization capacity is generally expected with a decrease in micellar size. Tanford (*21*) has come up with a good empirical equation to estimate the hydrophobic core volume of a micelle from its aggregation number and number of carbon atoms of the surfactant lipophile. In general, surfactants having lower HLB numbers favor solubilization of nonpolar hydrocarbons. However, with a decreasing HLB number, aqueous solubility of the surfactant also diminishes and it may form other aggregates, such as liquid crystalline phases, instead of micelles, in water.

As aforementioned, the molecular structure of a surfactant also plays a vital role in the solubilization capacity. Pennell et al. (*22*) reported that Witconol 2722 (Tween 80) could solubilize dodecane and PCE (tetrachloroethylene) 2 or 3 times as much as Tergitol NP-15 and Witconol SN-120, even though these surfactants have similar HLB values and aggregation numbers, except that Witconol 2722 micelles have the largest core volume.

Figure 5b exhibits the logarithmic values of the micelle–water partition coefficient K_m of these three FFAs by different surfactants. It shows that the effect of surfactant on log K_m values for each FFA is not as significant as that on MSR. However, among FFAs, for a certain surfactant, palmitic acid has a greater log K_m than the other two acids. This arises from the more hydrophobic and less polar nature of palmitic acid, as shown in its low aqueous solubility among these three FFAs. For a hydrophobic compound, the hydrophobic affinity between the compound and the hydrophobic micellar core is the primary driving force for solubilization (*11, 15*). Therefore, the solubilization behavior of these compounds is more predictable than that of the polar ones.

Valsaraj and Thibodeaux (*23*) obtained theoretically and empirically a linear relationship between log K_m and logarithmic values of the octanol–water partition coefficient, log K_{ow}, for 11 organic compounds solubilized by sodium dodecyl sulfate. Subsequently, Edwards et al. (*15*) also reported a linear relationship between log K_m and log K_{ow} for the solubilization of several polycyclic aromatic hydrocarbons (PAHs) by a few

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nonionic surfactants. Diallo et al. (*18*) studied the solubilization of several alkanes and aromatic hydrocarbons by dodecyl alcohol ethoxylates and had a similar observation. A linear relationship between log K_m and log K_{ow} was also reported for PAHs when perfluorinated surfactants and linear alcohol ethoxylates were used (*11*, *24*). Instead, owing to the higher polarity of oleic and linoleic acids, the linear relationship between log K_m and log K_{ow} does not hold in this work (**Figure 5**).

In addition, Jafvert et al. (*25*) have proposed the following approximate equation to relate K_{ow} to K_m:

$$K_m = K_{ow}(aN_c - bN_h) \tag{5}$$

where a and b are fitted parameters, N_c is the number of carbons in the hydrophobic group of the surfactant, and N_h is the number of hydrophilic groups of the surfactant. As a result, eq 5 fails to describe the solubilization behavior of the FFAs by nonionic surfactants used in this work.

For polar compounds, unlike nonpolar ones, solubilization preferably occurs at the shallow palisade of micelles, or even at the polar micelle−water interface. That is, more space in the same micelle is available to solubilize the polar substances. For example, slightly polar solubilizates, benzene for example, that partition both in the interior of micelles and at the micelle−water interface have been reported (*26*). This may explain why higher solubilization capacity measured by MSR could be achieved in some surfactants for oleic and linoleic acid than palmitic acid.

However, interesting results were found for solubilization of oleic and linoleic acids in nonionic micellar solutions (**Figure 5** and **Table 2**). Oleic acid (log K_{ow} = 7.64) (*27*) is slightly more hydrophobic than linoleic acid (log K_{ow} = 7.05) (*27*). A larger portion of oleic acid would tend to reside in the micelles. Consequently, the K_m of oleic acid is thought to be larger than that of linoleic acid. Instead, the solubility of oleic acid in aqua or micellar solutions is larger than that of linoleic acid. Though oleic acid is more hydrophobic than linoleic acid, it is more polar, which may attribute to the uncommon findings in their solubilities. For example, the dielectric constant (*28*) and dipole moment (*29*) of oleic acid are 2.336 at 293.2 K and 4.8033 × 10^{-30} C·m, compared to 2.754 at 293.2 K and 4.0628 × 10^{-30} C·m for linoleic acid.

If only considering the factor of hydrophobicity, oleic acid has to be solubilized in the core of the micelles or in the deeper palisade, compared to linoleic acid. However, higher polarity makes oleic acid favorable to be solubilized in the shallow palisade of the micelles as well. Hence, the space for solubilization of oleic acid in a micelle is enlarged and the solubility is increased, accordingly. A similar result was also reported by Pennell et al. (*22*). In their system, tetrachloroethylene (log K_{ow} = 2.88) and 1,2-dichlorobenzene (log K_{ow} = 3.38) were solubilized in micellar solutions of Witconol 2722 (Tween 80), Witconol SN-120, and Tergitol NP-15. Though 1,2-dichlorobenzene is more hydrophobic, it still can be solubilized more efficiently in terms of MSR.

Solubilization of oils by micellar solution is quite complicated. Even the governing mechanism could be either by diffusion or interfacially (*30*, *31*). Among surfactants used in this study, N-7 has the largest micellar volume. Nonetheless, it does not always give the highest solubilization capacity for different oils. Chen et al. (*30*, *31*) have shown that preferential or synergistic solubilization in the mixtures of triolein and FFAs or long-chain hydrocarbons by micellar solutions would occur. They have shown that the bigger solubilizates, such as triolein, could be solubilized faster by more flexible micelles, even though those

solubilizates have smaller saturation concentrations in those micellar solutions. For instance, micelles of T-S-7, more elastic than those of N-7 in their system (*30*, *31*), can solubilize triolein more quickly. Evidence is also seen in the lower cloud-point temperature of T-S-7 (37 °C) than N-7 (50 °C) at 1 wt %, which implies more elastic T-S-7 micelles require lower energy for the uptake of the solubilizate (*30*, *31*).

Cosurfactants, usually very polar or amphiphilic, are often formulated with surfactants to weaken the interbilayer forces of surfactant aggregates to form stable microemulsion phases, which could have significant solubilization capacity of hydrophobic compounds, such as FFAs, oils, and lipids (*19*). The common cosurfactants include short-chain alcohols, e.g., 1-pentanol, 1-hexanol, and even 1-decanol. In addition to including cosurfactants, an alternative to form a microemulsion phase is to use the double-chain surfactants, for example, T-S-Mix and T-S-7 in this work, other than straight-chain surfactants, e.g., N-7 (*19*, *31*).

Furthermore, the concept of "optimum curvature" of a surfactant monolayer has been frequently adopted to quantify the solubilization capacity of surfactants through the Helfrich curvature free energy (*19*). Near the solubilization limit of oil, the oil-containing swollen micelles and the microemulsion droplets would have a radius equivalent to the optimum curvature, also called "spontaneous curvature", of surfactant monolayers (*32*). For example, if the reciprocal of the radius of the hydrocarbon core of an oil-in-water (O/W) microemulsion droplet, assumed to be covered with a surfactant monolayer, is much less than spontaneous curvature, a significant portion of oil must be expelled from the microemulsion droplet to the bulk phase to decrease the curvature free energy (*19*).

Dissolution Kinetics of Palmitic Acid in the Micellar Solutions of Nonionic Surfactants. A dissolution process includes direct molecular dissolution of solute into the bulk phase, and mass transfer of the same solubilizate from the interface of the solubilizate−surfactant solution to the bulk solution through a stagnant boundary layer by micelles. In a well-mixing system, the concentration gradient exists solely in this thin film. For a constant interfacial area, a first-order mass-transfer model applies for the dissolution process (*13*, *14*):

$$r = \frac{dC}{dt} = ka(C^* - C) \tag{6}$$

where C denotes the total solute concentration at time t, mg/L, C^* stands for the solubility of solute in micellar solution or water, mg/L, a is the specific interfacial area, m^{-1}, and k represents the observed mass-transfer coefficient, which is a combined function of the aqueous-phase mass-transfer coefficient k_a and the mass-transfer coefficient in the micellar phase k_{mic}, cm/min. In this work, solid palmitic acid is used as the model solubilizate. Moreover, the observed mass-transfer coefficient could be regarded as a contribution from two parts as mentioned above:

$$k = \alpha k_a + (1 - \alpha)k_{mic} \tag{7}$$

where α denotes the contribution from molecular mass transfer. Its value should fall between 0 and 1. If no surfactant is added, α is equal to unity, since no mass transport by micelles could possibly happen. In concentrated-enough micellar solutions α will approach zero, meaning that the solubilizate−solution interface is almost covered by surfactants. Noticeably, at higher
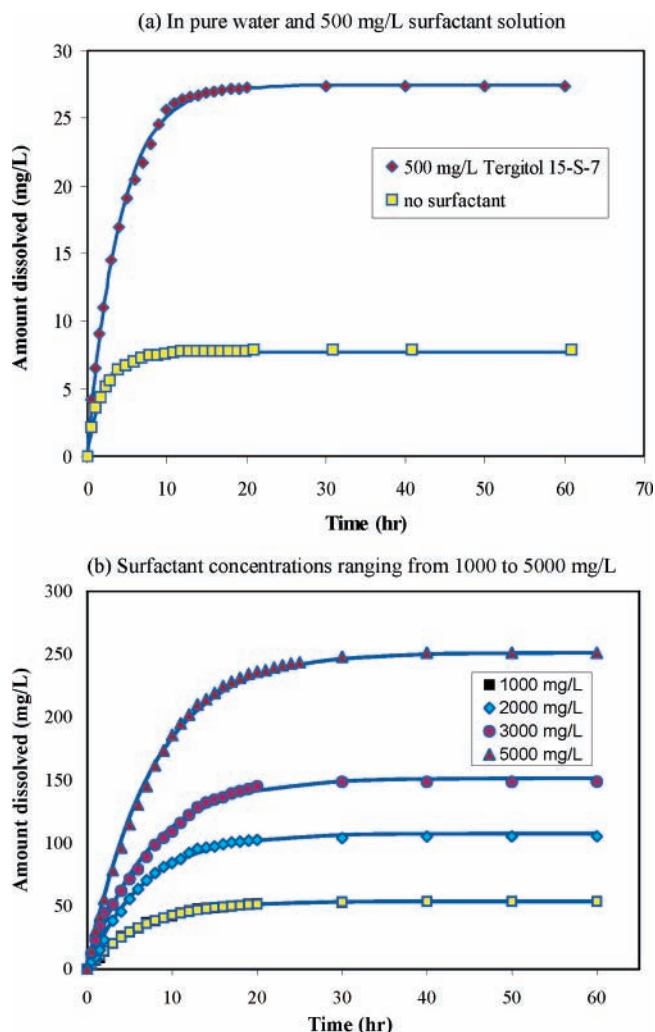
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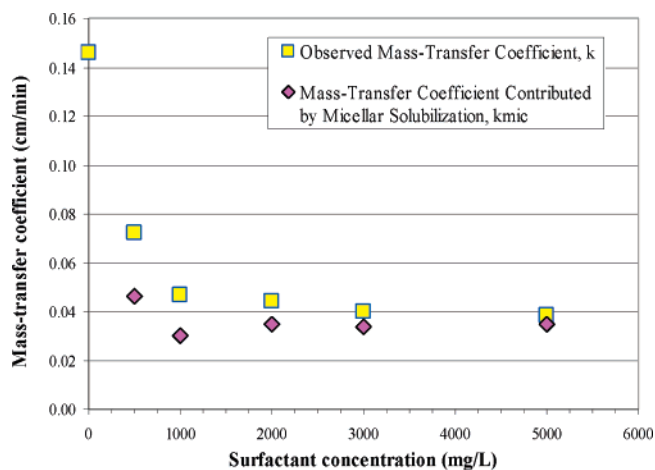**Figure 6.** Dissolution of palmitic acid as a function of time.

Figure 7. Observed mass-transfer coefficient for palmitic acid dissolution as a function of surfactant concentration for Tergitol 15-S-7.
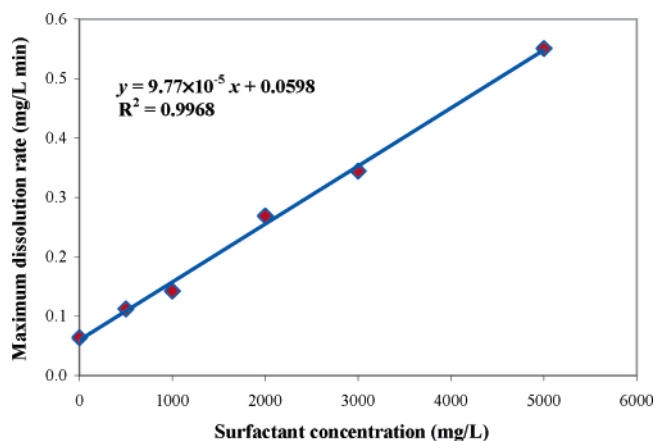

Figure 8. Maximum dissolution rate of palmitic acid as a function of surfactant concentration.

surfactant concentrations, the rate-limiting step in our model is the diffusion of solute-saturated micelles across the boundary layer (*33*).

Figure 6 shows the dissolution of palmitic acid in micelle-free water and micellar solutions with various surfactant concentrations. All observed mass-transfer coefficients and apparent saturation concentrations of palmitic acid were obtained by using the nonlinear regression with eq 6. The observed mass-transfer coefficient is shown in **Figure 7** as a function of T-S-7 concentration.

The aqueous mass-transfer coefficient of palmitic acid in pure water is around 0.146 cm/min. The observed mass-transfer coefficient decreases significantly with addition of surfactant and then approaches asymptotically a constant value with a further increase in surfactant concentration. Similar results have been reported in the literature as well (*13, 14, 34*). Interestingly, the overall mass-transfer rate actually increases due to the enhanced solubility of solute C^*, viz., the larger concentration differences ($C^* - C$).

Furthermore, the observed mass-transfer coefficient k can be expressed as a combination of k_a and k_{mic} in the following form: [13,14]

$$k = \frac{k_a + \dfrac{\text{WSR}}{C^*_a}(C_{surf} - \text{CMC})k_{mic}}{1 + \dfrac{\text{WSR}}{C^*_a}(C_{surf} - \text{CMC})} \qquad (8)$$

where C^*_a is the saturation concentration of solute in the aqueous phase, viz., its aqueous solubility. Parameters including k_a, WSR, C^*_a, and CMC can be determined independently. Thus, the only unknown parameter is k_{mic}. The aqueous solubility of palmitic acid at the experimental temperature (25 °C) is 7.74 mg/L, which is close to the value of 7.2 mg/L (*28*) at 20 °C. WSR obtained from the solubilization curve in **Figure 2** is equal to 0.048, and k_a equals 0.148 cm/min. Using eq 8, the values of k_{mic} for palmitic acid were calculated and are given in **Figure 7**, which indicates that the values of k_{mic} are almost the same.

The values of α in eq 7 at different surfactant concentrations could be easily converted from **Figure 7**. Initially, α drops steeply at first and then smoothly with increasing surfactant concentration. Thus, the dissolution model, which accounts for direct dissolution of bulk organic molecules into micelles, could adequately describe the observed effect of nonionic surfactant T-S-7 on the observed mass-transfer coefficient of palmitic acid.

On the basis of the values of k obtained, the maximum dissolution rate of palmitic acid, $r = kaC^*$, i.e., $C = 0$ in eq 6, was calculated at different surfactant concentrations (**Figure 8**). The maximum dissolution rates increase linearly with the surfactant concentration. Moreover, the aqueous solubility of solubilizate in the aqueous phase, C^*, is known to be linearly proportional to the surfactant concentration in micellar solutions (*11, 12, 18, 22−25*). At much higher surfactant concentrations, the mass-transfer coefficient k will be attributable

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to k_{mic} only, which approaches a constant value (**Figure 7**). Consequently, the linear relationship between the maximum dissolution rate r and surfactant concentration, exhibited in **Figure 8**, could be extended to a higher surfactant concentration, until it reaches the upper limit of the surfactant micellar phase.

Though it has been mentioned previously, it is worth pointing out that the dissolution rate is indeed attributed to two competing factors: enhanced solubility and decreased mass-transfer coefficient. Increasing surfactant concentration decreases to some extent the mass-transfer coefficient, but increases the solubility of the solute. Consequently, the dissolution rate becomes larger at higher surfactant concentrations, although the overall mass-transfer coefficient k is reduced in the presence of surfactant. For example, for a Tergitol 15-S-7 concentration of 3000 mg/L, the apparent saturated concentration of palmitic acid is increased by about 20-fold compared to that of palmitic acid in the absence of surfactant (see **Figure 2**). In the meantime, the mass-transfer coefficient k is only reduced by a factor of 3.65.

Conclusions. The solubilities of the free fatty acids, viz., palmitic, oleic, and linoleic acids, are linear functions of surfactant concentrations above CMC. For palmitic acid, due to its higher hydrophobicity, the hydrophobic affinity of its molecules to the micelle core governs its solubilization. In contrast, for the other two acids, because of their higher polarity, solubilization both within the micellar core and at the micelle−water interface may occur. A first-order dissolution model, which accounts for the direct uptake of palmitic molecules into the surfactant micelles at the solid−water interface, describes well the dissolution of palmitic acid. Due to the slower diffusion of surfactant micelles, the presence of surfactant reduces the observed mass-transfer coefficient. However, the overall mass-transfer rate was enhanced because of the much larger driving force contributed by solubilization.

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