

Effect of Premicellar Aggregation on the pK_a of Fatty Acid Soap Solutions

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Associative interactions of the various species found in the premicellar concentration region of aqueous fatty acid solutions have been investigated using acid–base titration. In previous studies, aqueous films of fatty acid salts were investigated at various bulk solution pH values. It was found that there exists a pH where minimum evaporation of water, maximum foamability, maximum foam stability, minimum contact angle on PMMA surface, maximum single-bubble stability, and maximum surface viscosity are observed. It was also found that this optimum pH value is near the measured pK_a of the fatty acid, which in turn depends on the length of the fatty acid chains. Titration of the homologous series of C_8 – C_{12} fatty acids to determine the solution pK_a has shown an increase in apparent pK_a with concentration. The increase in pK_a is maintained at concentrations well below the critical micelle concentration (cmc). Thus, similar to micelle formation, the submicellar aggregates must be responsible for the increase in pK_a as compared to that of soap monomers. Mixing of soap molecules of unequal chain length decreases the pK_a of the solution as compared to that of the two individual components because of disorder produced by the unequal chain length. Results indicate that premicellar surfactant aggregation and molecular association well below the cmc of the soap considerably affects ionization of the polar group. This molecular association results in an increase in the measured pK_a of soap solutions.

Introduction

The manner in which surfactant molecules adsorb to and align at an interface is an important factor in systems involving interfacial films in processes such as foaming, emulsification, and wettability. Among the important properties of a surfactant that dictate the strength, elasticity, and stability of a surface film are chain length compatibility,¹ the average distance between molecules in the monolayer,² and surface activity of the surfactant monomers. The surface activity of a surfactant depends on the chain length as well as the state of ionization of the polar group of surfactant molecules. Strongly ionizable anionic surfactants such as dodecyl sulfate exist predominantly as anions in the aqueous solution, with the undissociated “acid” form present only at very low pH values. Weakly ionizable surfactants such as long-chain fatty acid salts, however, are extremely sensitive to changes in solution pH and exist as different molecular species at various pH values in the aqueous solution^{3–11} as well as in monolayers (Figure 1).^{12–17} At acidic pH

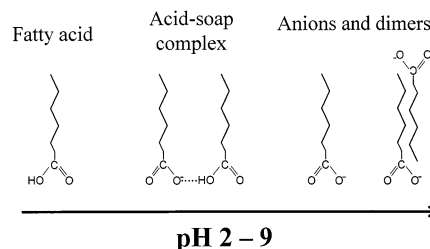


Figure 1. Molecular state of fatty acid below cmc in aqueous solution.

values, the predominant molecule is the undissociated fatty acid (RCOOH). At alkaline pH, mainly carboxylate anions (RCOO⁻) and to a lesser extent ionic dimers ((RCOO)₂²⁻) are present, although the acid soap salt, (RCOO)₂HNa, is also found in extremely alkaline solutions or if sufficient Na⁺ ions are added.¹⁸ At pH 4–8, acids, anions, as well as so-called acid soaps, (RCOO)₂H⁻, all coexist in the aqueous bulk solution.³

Past research conducted in the area of fatty acid surface activity and aggregation behavior has been applied extensively to the mineral flotation industry.¹⁹ Fatty acid salts, especially oleate, are used as selectively adsorbing surfactants (i.e., collectors) in mineral flotation. Collection efficiency of oxide minerals such as hematite with weakly anionic collectors such as oleic acid has been shown to have a distinct maximum at pH around 8.0. Jung was the

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first to develop equilibrium species distribution diagrams for sodium oleate on the basis of available literature data and estimated energy of interactions between molecules.²⁰ These ideas were later developed by Somasundaran and co-workers^{21–23} into thermodynamic models to give a qualitative interpretation of the data on hematite flotation with oleate as well as surface tension data versus oleate concentration and pH.

From this application of equilibrium species distribution diagrams and the knowledge that not all of the possible species are present in significant quantities at any given pH, a hypothesis was developed to explain the reason for maximum flotation of hematite by oleate at pH 8.0 (Figure 44 of ref 24). Oleate anion and dimer activities do not change appreciably when decreasing pH from the alkaline to the neutral region. However, the activities of undissociated acid and acid–soap complexes do increase significantly, leading to increased oleate surface activity and, hence, greater flotation of hematite and lower surface tension at the air/water interface. If pH is further decreased to the acidic region, the activities of the ionic monomers, dimers, and acid–soap complexes decrease while that of the undissociated acid remains the same. This results in a decrease in hematite flotation and an increase in surface tension. Therefore, the maximum in hematite flotation and minimum in surface tension are encountered in the neutral pH range where the greatest number of surface active species exists.²⁵ Further studies have shown that the fluctuations in surface tension at different pH values become more pronounced with increase in oleate concentration in the pre-micellar region.²⁶ This effect was explained by increased pre-micellar aggregation with increased bulk oleate concentration before the critical micelle concentration (cmc) is reached.

For fatty acids and their soaps at high pH, all of the fatty acid molecules become ionized, and repulsion between similarly charged molecules in an adsorbed monolayer of these anions can result in an expansion of the monolayer, which in turn can lead to a weak and unstable film that exhibits poor performance in various interfacial phenomena.^{27,28}

In a previous study,²⁹ the foaming behavior of aqueous sodium laurate solutions below cmc was investigated at various bulk solution pH values. It was found that a maximum in foamability (i.e., foam height) is encountered at a pH value of 7.5. Further studies found that a minimum in evaporative water loss through an adsorbed monolayer, maximum foam stability, minimum contact angle on a PMMA surface, maximum single-bubble stability, and maximum surface viscosity are also observed at sodium laurate/lauric acid solution pH values of 7.5, which is the pK_a of lauric acid when measured by acid–base titration.²⁹

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The change in monolayer characteristics of fatty acids as a function of pH of the bulk solution was first reported by Schulman and Hughes,³⁰ who found that the surface potential (ΔV)–pH relation resembled an acid–base titration curve. For weakly ionized monolayers such as those created by fatty acids, it was proposed that the difference in pH between the surface and the bulk is small.^{31,32} This suggests that one may calculate surface properties, including surface pH, using normal bulk solution values.

Most short-chain carboxylic acids have a pK_a value of approximately 4.8. For example, when acetic acid (CH_3COOH) and propionic acid ($\text{CH}_3\text{CH}_2\text{COOH}$) are dissolved in water, their pK_a values are found to be 4.74 and 4.87, respectively.³³ The pK_a value represents the ionic environment of the solution where 50% of hydrogen atoms are removed from the carboxyl groups by the existing hydroxide ions in the solution. Organic chemists have found that the pK_a can be decreased by attaching an electron-accepting substituent (e.g., chlorine) to stabilize the carboxylate anion.³⁴ The converse effect—that of electron-releasing substituents lowering the acidity and raising the pK_a —exists, although it is less dramatic. However, because electronic effects are transferred through molecular bonds and are not felt beyond two to three carbons, when the chain length of a fatty acid is increased beyond about four carbons, the pK_a becomes constant.³⁵ Therefore, the pK_a value of most carboxylic acids is about 4.8. We have observed, however, that once the chain length of the fatty acid becomes sufficiently long so that the molecules become surface active (i.e., C_8 chain), pK_a values measured by acid–base titration begin to increase.

The present paper shows that fatty acid concentration and chain length compatibility each play an important role in the measured pK_a in the pre-micellar concentration range. The objective of this paper is to determine the molecular mechanisms leading to the unexpectedly high pK_a values of long-chain fatty acids measured by acid–base titration and to consider whether pre-micellar surfactant aggregation can explain this behavior.

Experimental Section

Materials. Sodium caproate (C_6), sodium caprylate (C_8), sodium caprate (i.e., sodium decanoate, C_{10}), and sodium laurate (C_{12}) were supplied by Sigma Chemical Company (St. Louis, MO) and were $\geq 98\%$ purity. Sodium phosphate (monobasic and dibasic), concentrated sodium hydroxide, light mineral oil, and anhydrous calcium chloride were supplied by Fisher Scientific (Fair Lawn, NJ). All solutions were prepared using water that was both deionized and distilled.

Determination of pK_a . The pK_a values of sodium caproate, sodium caprylate, sodium decanoate, and sodium laurate were determined by titration at $25 \pm 1^\circ\text{C}$ with 0.1 M sodium hydroxide using a METROHM 726 Titroprocessor. Because of limited solubilities of the longer-chained soaps, care was taken to ensure that enough molecules were solubilized in water to obtain a well-defined end point. The fatty acid salt solutions were first adjusted to pH ~ 10 by addition of sodium hydroxide and then titrated with hydrochloric acid to obtain the titration curve to the solubility limit of the fatty acid. The pK_a was then calculated as the pH of the solution at half the neutralization volume (i.e., half the

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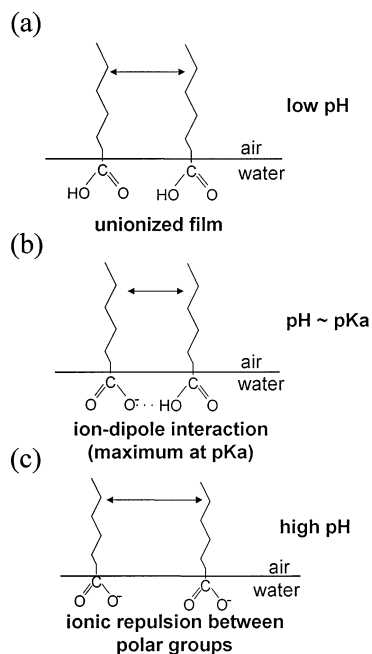


Figure 2. Structure of a fatty acid polar group at different pH values. (a) low pH, (b) pH = pK_a , (c) high pH. A strong ion-dipole interaction among the carboxyl groups near the pK_a value decreases the intermolecular distance and area/molecule at the air/water interface.

volume required to reach the neutralization end point). A fresh fatty acid salt solution was then adjusted to the solubility limit pH by addition of hydrochloric acid and was then titrated with sodium hydroxide to obtain the titration curve and the pK_a . The pK_a values obtained from well-defined end points of the base titration and acid titration were compared for similarity. Five titrations were performed on each solution and mean pK_a values were calculated.

Evaporation Studies. A known amount of anhydrous calcium chloride was measured and placed in a Petri dish. The Petri dish was then covered with vinyl cloth, inverted, and placed 1 mm above the surface of a 0.05 wt % 40-ml fatty acid solution. The rate of evaporation was measured by the increase in weight of the desiccant, anhydrous $CaCl_2$. The percent change in desiccant weight was measured every 15 min over a period of 2 h as a function of solution pH.

Results and Discussion

1. Effect of Chain Length on pK_a . As mentioned above, electronic effects in a fatty acid are not felt beyond two to three carbons in the chain. Therefore, when the chain length is increased beyond about four carbons, the pK_a tends to level off. Increasing the chain length from pentanoic to hexanoic acid, for example, increases the pK_a only slightly from 4.82 to 4.83. Therefore, it is known that *intramolecular* interactions (i.e., the electronic effects on the carboxylic acid moiety by the rest of the molecule) become negligible beyond four carbons in the alkyl chain. However, previous work has shown that the observed pK_a of long-chain fatty acids increases with increase in chain length of the molecule and can be as high as about 9.0 as the chain length increases to C_{16} or greater.²⁹

Figure 2 shows the structure of a fatty acid polar group at different pH values. At low pH (pH \sim 1–2), Figure 2a, un-ionized carboxyl groups are oriented at the interface to face the water. At the pK_a value (where 50% of the molecules are ionized, Figure 2b), there exists a strong ion-dipole interaction between the adjacent carboxyl groups, which causes the molecules to pack more closely. This ion-dipole-stabilized complex is generally referred

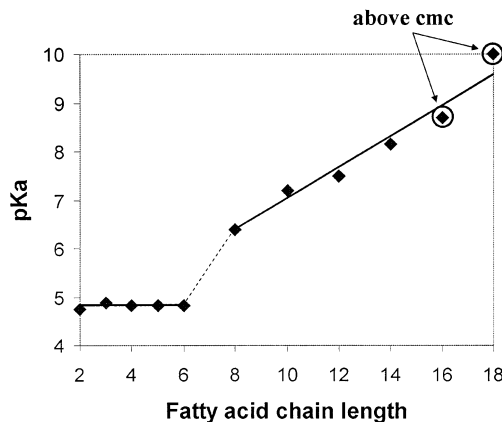


Figure 3. Effect of chain length on the pK_a of fatty acid solutions. (pK_a values are for concentrations below cmc except for C_{16} and C_{18} , which are slightly above cmc.)

to as an acid soap.²⁰ This interaction and subsequent closer molecular packing is consistent with the minimum in evaporation rate of water through a fatty acid monolayer at the pK_a .²⁹ However, at high pH (pH \sim 9–10), where complete ionization of the carboxyl groups causes ionic repulsion between adjacent polar groups and increases the solubility of fatty acid in water (Figure 2c), the intermolecular distance is higher as compared to 2a and 2b.

As mentioned above, most short-chain carboxylic acids have a pK_a value of about 4.8. This value reflects the inclination of the proton located in the fatty acid carboxylic acid group to dissociate to a free hydronium ion in the aqueous solution. Because pK_a depends only upon the electronic effects felt by the acid group, it is not expected to increase by addition of methylene groups to the fatty acid chain. If fatty acid pK_a is measured using acid–base titration, we see that pK_a in fact remains constant for chain length up to C_6 (caproic acid). However, when the fatty acid chain length is increased beyond C_6 , a noticeable increase in pK_a is observed when determined by acid–base titration (Figure 3).

We proposed previously²⁹ that as the surfactant chain length is increased, the molecular packing between surfactant molecules at the interface and in the bulk solution becomes tighter because of van der Waals interactions between the chains. The surface concentration (i.e., moles/cm²) increases and hence the area per molecule at the surface decreases (i.e., intermolecular distance between the surfactant molecules decreases).

As the fatty acid molecules get closer together, the proximity of other charged groups next to any given carboxyl group serves to stabilize the acid proton, making it more difficult to remove it by the free hydroxide ions in the bulk solution. As a result, the measured pK_a of the fatty acid increases. Thus, the above results indicate that *cooperativity* among molecules at interfaces and in the bulk solution induced by van der Waals interactions between chains and the concomitant polar group interactions results in reduced intermolecular distance and an increase in pK_a as measured by acid–base titration.

If one focuses on the adsorbed film alone, it is easy to visualize that as chain length increases, the interaction between chains also increases, and hence intermolecular distance decreases. However, if we focus not only on the adsorbed film, but also on the bulk fatty acid solution in the pre-cmc concentration region, it can be reasoned that as the concentration decreases below cmc, the premicellar aggregates do persist in the solution and reflect the effect of molecular cooperativity in the ionization behavior of

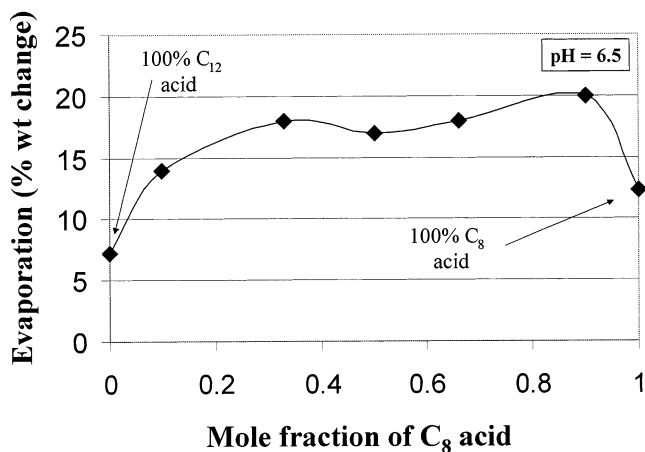


Figure 4. Evaporation of water through an adsorbed film of C_8/C_{12} mixed fatty acid salt solution at pH 6.5. Increased evaporation indicates decreased cohesiveness of the adsorbed film. A similar trend exists for the entire pH range 6.5–9.

the carboxyl groups. Several investigators have shown that there exist premicellar aggregates (e.g., dimers, trimers, oligomers, etc.) in solution.^{36,37} These aggregates are stabilized by interactions in hydrocarbon chains and can be viewed as nothing more than small fragments of micelles existing in the bulk solution. As such, their behaviors are governed by the same interactions discussed previously for the adsorbed film. As long as premicellar aggregates exist in the bulk solution, they will behave similarly to the adsorbed film at the surface (i.e., they will have a high pK_a value). Therefore, if the solution is diluted, and the pK_a does not decrease to 4.8 (i.e., the value for short-chain fatty acids), we can presume that aggregates still exist in the bulk solution.

2. Effect of Chain Length Compatibility on pK_a of Mixed Fatty Acid Solutions. In many systems such as biological membranes, a mixture of fatty acids of different chain lengths often exists in the lipid layer. The way that these molecules interact at an interface must be influenced by the difference in chain lengths. Our group has shown by a series of studies^{1,2,38–41} that compatibility between these molecules of unequal chain length is an important parameter that can affect surface concentration, area per molecule, and intermolecular distance of a monolayer. These studies have shown that the mismatch between two adsorbed chains of unequal length results in a poor molecular packing because of the extra vibrational energy created by the thermal motion of the extra segments of the longer chain.

The resulting increase in intermolecular distance can lead to a greater rate of evaporation from the adsorbed monolayers of mixtures as compared to pure components, as shown in Figure 4 for pH 6.5. As Figure 4 shows, addition of small amounts of the second component (e.g., 10% caprylate to a laurate solution or 10% laurate to a caprylate solution) can strikingly disrupt an adsorbed film to increase the rate of evaporation of water.

Similar results are encountered when measuring the pK_a of mixed fatty acid solutions by pH titration. If a small

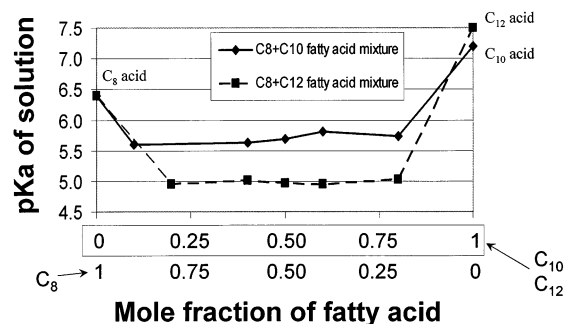


Figure 5. Measured pK_a values of C_8 , C_{10} , and C_{12} mixed fatty acid solutions obtained by acid–base titration at 23 °C.

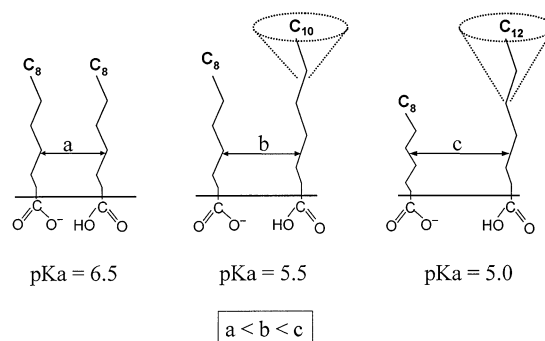


Figure 6. Chain length incompatibility increases intermolecular distance, which may lead to a decrease in apparent pK_a of the solution.

amount of fatty acid of a different chain length is added to a pure fatty acid solution, the apparent pK_a decreases dramatically to values similar to those of short-chain fatty acids. For example, when adding small amounts of sodium caprylate ($pK_a = 6.5$) to an aqueous solution containing only sodium decanoate ($pK_a = 7.2$), the observed pK_a drops down to approximately 5.5, which is one pH unit lower than that of caprylic acid (Figure 5). If the same amount of caprylate is added to a solution of sodium laurate, the pK_a drops lower to a pK_a of 5.0, much lower than pK_a of 6.5 or 7.5 for the pure components. The unequal chain length leads to a disruption in molecular packing and a subsequent decrease in measured solution pK_a (Figure 6).

A similar phenomenon must exist for the premicellar aggregates existing in the bulk solution. A lack of molecular cooperativity between the chains in these aggregates would most likely result in loosely packed molecular aggregates, which according to the above argument would explain the decrease in pK_a with the addition of small amounts of surfactant of different chain length.

3. Effect of Surfactant Concentration on pK_a . All of our previous studies on foamability, foam stability, contact angle, evaporation, and surface viscosity were performed on fatty acid solutions of concentrations below cmc.²⁹ However, each of these interfacial phenomena depends on the behavior of the adsorbed film. The similar associations found between adjacent molecules in the adsorbed film and molecules within a micelle are expected to lead to the same result, namely, an upward shift in pK_a value. Thus, if the fatty acid solution is continuously diluted to concentrations well below cmc, intermolecular associations in the bulk are expected to decrease and, ultimately, a concentration will be reached where this association will not occur, and all of the surfactant molecules will exist as individual monomers. In this case, one would expect the solution pK_a to be 4.8, which is the

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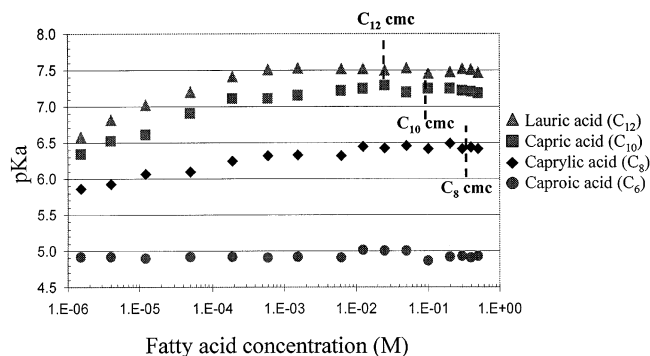


Figure 7. Effect of concentration on apparent pK_a values of fatty acid solutions above and below cmc. Dashed lines indicate cmc.

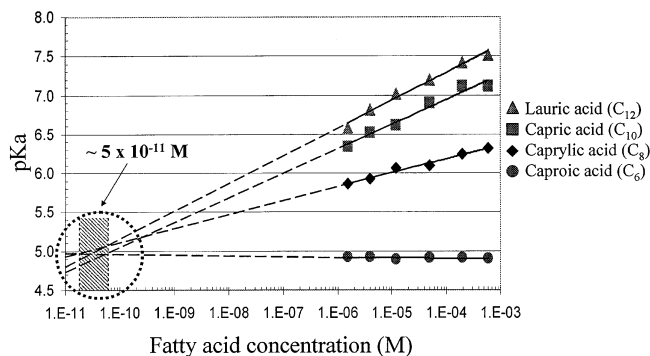


Figure 8. Extrapolated pK_a values of very dilute fatty acid solutions. Values seem to intersect at a pK_a of approximately 5.0.

pK_a of nonassociating short-chain fatty acids. Any deviation from 4.8 would indicate *premicellar association* between molecules in that system.

As can be seen in Figure 7, measured pK_a values of aqueous fatty acid solutions of chain lengths C_8 – C_{12} are indeed found to decrease when these solutions are diluted to concentrations well below cmc. Solutions of caproic acid (C_6), however, maintain a constant measured pK_a of approximately 4.8–5.0, presumably because of its monomeric state. The pK_a values of C_8 – C_{12} long-chain fatty acids remain constant from below the cmc to concentrations as high as 0.5 mol/liter. This indicates that increased concentrations of fatty acid soap or counterions (e.g., Na^+) at these high fatty acid concentrations are in no way changing fatty acid dissociation (i.e., pK_a) in this concentration range. Because pK_a does not depend on fatty acid concentration at or around the cmc, the decrease in pK_a in the 10^{-3} – 10^{-6} M concentration range for C_8 to C_{12} fatty acids can be only interpreted as due to the premicellar association in their solutions.

If pK_a values are extrapolated to increasingly dilute fatty acid concentrations (Figure 8), one can see that the estimated pK_a values of each of the fatty acid solutions would intersect at a value of approximately 5.0 at a concentration of 5×10^{-11} M. It is possible that as the solutions are diluted to this concentration, the population of premicellar aggregates decreases to the point where only monomers are present in solution. Large intermolecular distances at this concentration (10^{-11} moles/liter) would not facilitate molecular association in the form of premicellar aggregates. These monomers would have the same pK_a value as short-chain fatty acids, namely, 4.8–5.0. These results suggest that our commonly accepted view—that above the cmc both micelles and monomers exist in solution while below cmc only monomers are present—is an inaccurate one, and that in fact premicellar aggregates exist well below the cmc, and their behavior is considerably different from that of monomers as far as ionization of the polar group is concerned.

Conclusions

It has been shown that an increase in the chain length of a fatty acid from C_8 to C_{18} increases the apparent pK_a of the solution. However, fatty acids of chain length C_6 and below have a constant pK_a of about 4.8. Upon mixing long-chain fatty acids of unequal chain lengths, pK_a values decrease as compared with those of pure acids. This decrease is due to increased area per molecule caused by thermal motion of the mismatched chains. Retardation of water evaporation from the films of pure versus mixed fatty acids were carried out to show that the greater evaporation occurs in mixed films, indicating poorer molecular packing and hence increased intermolecular distance and greater rate of evaporation.

pK_a values are also found to decrease upon dilution of C_8 – C_{12} fatty acid solutions below cmc. However, they have to be reduced from 10^{-6} to 10^{-11} M to reach the pK_a of short-chain fatty acids by extrapolation. These results indicate that even in micromolar solutions of fatty acids of C_8 – C_{12} , substantial molecular association exists in premicellar aggregates and in an adsorbed film. The behavior of these aggregates is considerably different from that of monomers as far as ionization of the polar group is concerned. The association between the ionized and un-ionized polar groups in such premicellar aggregates will shift the measured pK_a to a higher value.

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