

Cooperativity among Molecules at Interfaces in Relation to Various Technological Processes: Effect of Chain Length on the pK_a of Fatty Acid Salt Solutions[†]

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The orientation of surface-active molecules at interfaces is extremely important in determining the dynamic and equilibrium properties of such systems. Films of fatty acid salts were studied at various pH values of the solutions. 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 pK_a of the fatty acid salts. The experimental results are explained in terms of area per molecule, intermolecular spacing, and cooperativity among soap molecules at the interface. It was further shown that the chain length of the soap molecules can modulate the area per molecule, and hence the intermolecular distance in the film, and thereby influence the ionization behavior of the fatty acid carboxyl group. The pK_a increases from 6.5 to about 9.0 as the chain length of the fatty acid salt increases from C_8 to C_{16} . Cooperativity among surfactant molecules at the interface is controlled by the area per molecule and intermolecular spacing in the adsorbed film. A small change in intermolecular distance of 0.03 Å can significantly influence various technological processes such as foaming, emulsification, wetting, and retardation of evaporation.

Introduction

The manner in which surfactant molecules align at an interface is an important factor in systems involving interfacial films. Among the important properties of a surfactant that dictate the strength, elasticity, and stability of a surface film are chain length compatibility,¹ the distance between molecules in the monolayer,² and surface activity. The presence of a net charge on a surfactant polar group affects its surface activity. Fatty acids, for instance, can become ionized by an increase in the pH of the solution. If all the fatty acid molecules become ionized, repulsion between similarly charged molecules in the monolayer can result in an expansion of the monolayer at high pH,^{3,4} which in turn can lead to a weak and unstable film. The change in monolayer characteristics of fatty acids as a function of pH of the bulk solution was first reported by Schulman and Hughes,⁵ 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 pK_a between the surface and the bulk is small.⁶ This suggests that one may calculate surface properties, including surface pH, using the normal bulk

value of the pK_a . However, the present paper reports that the pK_a of soap depends on the chain length of the soap molecule and can be as high as about 9.0 as the chain length increases to C_{16} .

Most short-chain carboxylic acids have a pK_a value of ca. 4.8. For example, when acetic acid (CH_3COOH) and propionic acid (CH_3CH_2COOH) are dissolved in water, their pK_a values are found to be 4.74 and 4.87, respectively.⁷ The pK_a value represents the ionic environment of the solution where 50% of the hydrogen atoms are removed from the carboxyl group by the existing OH^- ions in the solution. The pK_a can be decreased by attaching an electron-accepting substituent to stabilize the carboxylate anion.⁸ The converse effect—that of electron-releasing substituents lowering the acidity and raising the pK_a —is true, though less dramatic. The pK_a can be raised by increasing the carbon chain length of the carboxylic acid. However, because electronic effects are not felt beyond two to three carbons, 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 from 4.82 to 4.83. Therefore, we know that *intramolecular* interactions (i.e., the effects on the carboxylate anion by the rest of the carbon chain) become negligible beyond four carbons in the alkyl chain. We believe that van der Waals and polar group interactions between fatty acid molecules raise the pK_a from 4.83 for hexanoic acid to approximately 7.5 for lauric acid, and even higher pK_a values for longer-chain carboxylic acids.

The present paper attempts to explain various pK_a -related phenomena and elucidate their technological applications (e.g., foamability, foam stability, retardation

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of water evaporation, contact angle on PMMA, surface viscosity, and single-bubble stability) as a function of the pH of the soap solution.

Experimental Section

Materials. Sodium caprylate (C_8), sodium decanoate (C_{10}), sodium laurate (C_{12}), sodium myristate (C_{14}), and sodium palmitate (C_{16}) were supplied by Sigma Chemical Co. (St. Louis, MO) and were of 99% 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. All experiments were carried out at 23 ± 1 °C unless otherwise stated.

Solution Preparation. Monobasic and dibasic sodium phosphate were used to prepare 0.02 M phosphate buffer solutions.⁹ Phosphate-buffered fatty acid solutions (0.05 wt %) were prepared by dissolving 0.5 g of fatty acid in water and adding phosphate buffer to adjust the solution to a desired starting pH. pH was monitored with an Orion (model 720A) pH meter and adjusted with sodium hydroxide.

Surface Tension and Area/Molecule. Surface tension measurements were obtained from freshly prepared solutions by the Wilhelmy plate method. Before each measurement, the platinum plate was cleaned by heating it to a red/orange color with a Bunsen burner. Area/molecule was calculated using the Gibbs adsorption equation

$$\Gamma = \frac{-1}{2.3RT} \left(\frac{d\gamma}{d \log C} \right) \quad (1)$$

where Γ is the surface concentration, γ is the surface tension, and C is the concentration of surfactant in the solution. The area/molecule at the air/water interface is given by $1/\Gamma$. The slope can be obtained from surface tension measurements plotted against $\log C$.

Surface Viscosity. A deep-channel surface viscometer^{10,11} was used to measure the surface viscosity of 0.025 wt % sodium laurate as a function of pH. Two concentric cylinders form the deep channel of a viscometer. The walls of this channel are stationary, while the floor moves at a constant angular velocity. To measure the centerline velocity of the air/water interface, a small Teflon particle was placed on the surface, and the time for that particle to make one revolution was recorded from visual observation. Using this value, the surface viscosity can be determined by

$$\epsilon = \frac{\eta y_0 \left[\frac{8V_b}{\pi V e^{\pi D}} - 1 \right]}{\pi} \quad (2)$$

where ϵ is the surface viscosity, η the bulk viscosity of the solution, y_0 the channel width, V_b the plate rotational speed, V the centerline velocity of the air/water interface, and D the ratio of depth to width of the liquid channel.

Foamability by Shaking. Foamability measurements on sodium decanoate, sodium laurate, and sodium myristate were carried out at 40 °C. Measurements for sodium palmitate were performed at 50 °C because the soap precipitated out of solution very quickly at temperatures lower than this. Sodium caprylate exhibited little or no foaming at low concentration. Experiments were carried out by vigorously shaking 20 mL of the sample solution for 30 s in a 100-mL graduated cylinder and recording the foamability as the volume of foam produced immediately after shaking. Each solution was tested at least five times as a function of pH.

Foamability by Air Bubbling. A quartz column, 3.5 cm in diameter, was used to measure the foamability of 0.05 wt % sodium laurate by air bubbling. At the base of the cylinder a single capillary, 1 mm in diameter, was used to generate the

bubbles. Fifty milliliters of the sample solution was poured into the column using a long funnel that reached to the bottom to ensure that the walls of the cylinder remained dry and could not act as an additional supply of surfactant molecules, which would increase the foam stability. The air was then turned on at a constant flow rate of 158.2 cm³/min. The foam volume produced after 2 min was recorded. The measurement was repeated at least five times for each pH value tested.

Foam Stability. Foam stability measurements were performed in the same quartz column used in the foamability by air bubbling experiments. Air was blown through 50 mL of 0.05 wt % sodium laurate solution at a rate of 158.2 cm³/min and turned off when the foam reached a desired height (20 cm). The foam half-life (i.e., the time required for the foam to collapse to half of its original height) was measured as a function of pH. The measurement was repeated at least five times for each pH value tested.

Single Bubble Stability. A no. 23 steel needle (nominal 0.64 mm external diameter, nominal 0.33 mm internal diameter) with a flush-cut tip was positioned 2 cm below the surface of a covered 0.05 wt % sodium laurate solution. Air was injected by micrometer rotation through the needle, and a single air bubble was formed and allowed to rise to the surface. The time until collapse of the bubble was recorded. Over 20 measurements at each pH were made and averaged to give a mean bubble lifetime for each pH value tested.

Contact Angle on PMMA. The contact angle between a 0.05 wt % fatty acid salt and air on a clean PMMA surface was observed using the low-power microscope of a contact angle goniometer. Over five measurements were made and averaged to give a mean contact angle for each pH value.

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 3 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 CaCl₂. The percent change in desiccant weight was measured every 15 min over a period of 2 h as a function of solution pH.

Determination of pK_a. The pK_a values of sodium caprylate, sodium decanoate, sodium laurate, sodium myristate, and sodium palmitate were determined by titration at 25 °C with 0.1 M sodium hydroxide using a METROHM 726 titroprocessor. The neutralization end point was first determined. This is the point of inflection on the S-shaped titration curve. Then, the pK_a was calculated as the pH of the solution at half the neutralization volume (i.e., half the volume needed to reach the neutralization end point). Five titrations were performed on each solution, and mean pK_a values for each soap were calculated.

Emulsions. A sodium laurate solution (0.05 wt %) was combined with light mineral oil to create emulsions containing 5 vol % oil at various values of pH. These solutions were first stirred and later sonicated for 30 min to create oil-in-water (O/W) emulsions. A drop of emulsion was placed on a microscopic glass slide, and a cover slip was placed on top. The photographs of emulsions were taken by an optical microscope fitted with a camera.

Results and Discussion

The concentration of sodium laurate used in this study was 0.05 wt % (2.25 mM), which is approximately one-tenth of the critical micelle concentration (cmc) for sodium laurate as reported by Mukerjee.¹² Therefore, the concentration of monomers in solution is high enough that, while micelles are not created, the formation of small aggregates such as dimers, trimers, and tetramers cannot be ruled out.

It is obvious that when dissolving sodium laurate in water in the pH range 6–9, the solution will be made up of different fractions of ionized carboxylate (RCOO⁻), un-ionized fatty acid (RCOOH), and un-ionized fatty acid salt

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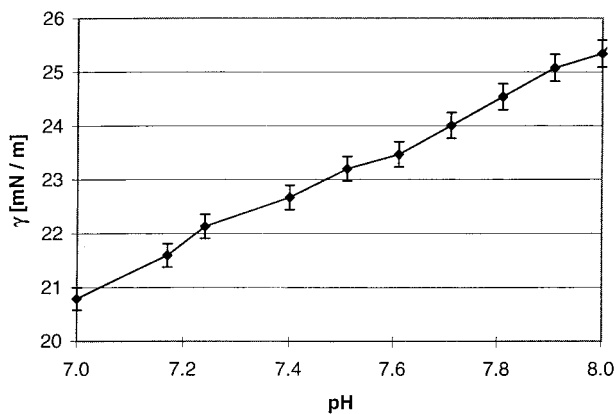


Figure 1. Surface tension (γ) vs pH of 0.05 wt % sodium laurate solution.

(RCOONa). It is known that un-ionized lauric acid is nearly insoluble in water.^{13,14} This makes it the most surface active of the three species in an air/water system. It is also well accepted that long-chain fatty acids undergo an ionization process between pH 4.0 and 10.0.^{15,16} At pH around 8.0 there is an ion molecular complex (RCOOH–RCOO⁻) present in 1:1 proportion.¹⁷ We see in Figure 1 that surface tension of sodium laurate increases with pH. In view of this fact, we propose that the salt form is more water soluble than the (RCOO⁻) and (RCOOH) species found in solution. Therefore, our interpretations of results are mainly in terms of the interactions between (RCOO⁻) and (RCOOH) in the range 6.5–8.5 at the air/water interface.

In the majority of studies on surface activity of a chemical compound, one very frequently begins by examining the change in surface tension with respect to change in a solution property (e.g., concentration, pH, temperature). By using surface tension data exclusively to deduce surface activity, however, one may overlook some interesting effects due to subtle molecular interactions in the adsorbed film. Figure 1 shows a plot of surface tension vs pH of sodium laurate. This figure indicates that surface tension increases monotonically with increasing pH. There seem to be no unusual changes occurring anywhere within the pH range studied (pH 7.0–8.0). The only conclusion that one can draw from this figure, therefore, is that higher pH leads to lower surface activity (i.e., higher surface tension of the solution). However, by depending on the results of a single parameter, one can easily miss very interesting phenomena occurring in such systems. Contrary to the results shown in Figure 1, the remainder of this paper reports very interesting phenomena that occur at or near the pK_a of a fatty acid salt solution.

Figure 2 shows results of the foamability (i.e., foam height) by single-capillary air injection test for sodium laurate. It is clearly evident that the foam height was maximum in the pH range of 7.4–7.6. The foam height at pH 7.5 is three to five times greater than the foam heights near 7.0 and 8.0.

The effect of pH on foam stability is shown in Figure 3. It is interesting that such a dramatic difference in the foam stability—a 30-s half-life near pH 7.1, to a half-life

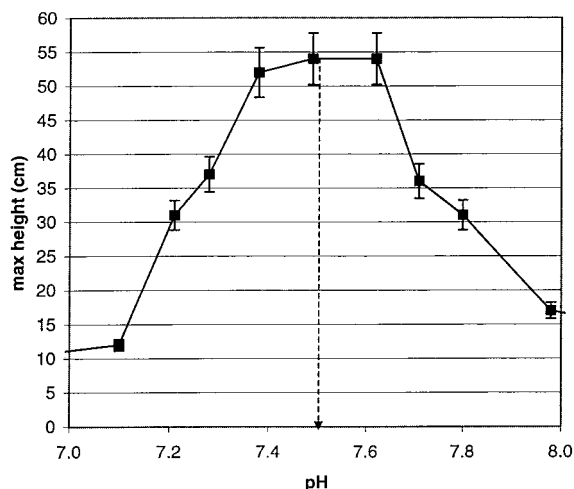


Figure 2. Foam height of 0.05 wt % sodium laurate solution vs pH in foam column prepared by single-capillary injection of air.

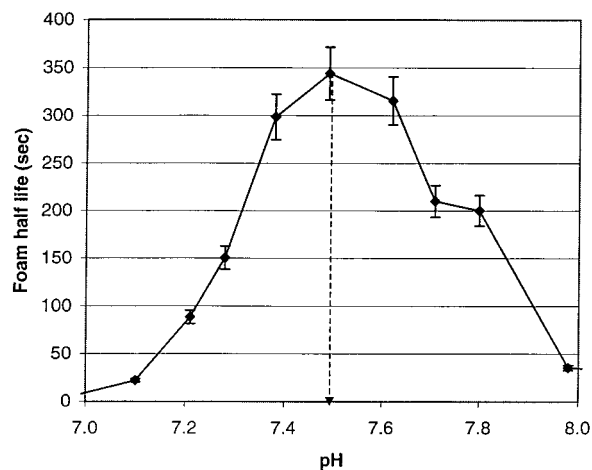


Figure 3. Maximum foam stability of 0.05 wt % sodium laurate solution vs pH in foam column prepared by single-capillary injection of air.

of nearly 350 s at pH 7.5, back to a 40-s half-life at pH near 8.0—can occur within 1 pH unit.

The bulk pK_a value of the 0.05 wt % sodium laurate solution at 25 °C was determined by titration to be 7.48. This suggests that the improved foamability and foam stability observed occur at or very near to the bulk pK_a of sodium laurate.

Foamability and foam stability are not the only interfacial phenomena that show dramatic change near the pK_a value of sodium laurate. As Figure 4 illustrates, contact angle of sodium laurate solution on PMMA and evaporation of water through the adsorbed film show minimum values. Because of the 1:1 ratio of ionized to un-ionized soap molecules at the surface at this pH, an increased intermolecular interaction in the film effectively narrows the pores through which water molecules can evaporate. Also, since more surface-active molecules are packed on the PMMA surface near pK_a , the contact angle is lower.

Figure 4 also shows that surface viscosity and single-bubble stability are maximum near the pK_a . This can also be explained by an increase in intermolecular interaction at the pK_a .

In an emulsification experiment, it was found that an O/W emulsion at pH near the pK_a results in a higher concentration of emulsion droplets compared to other

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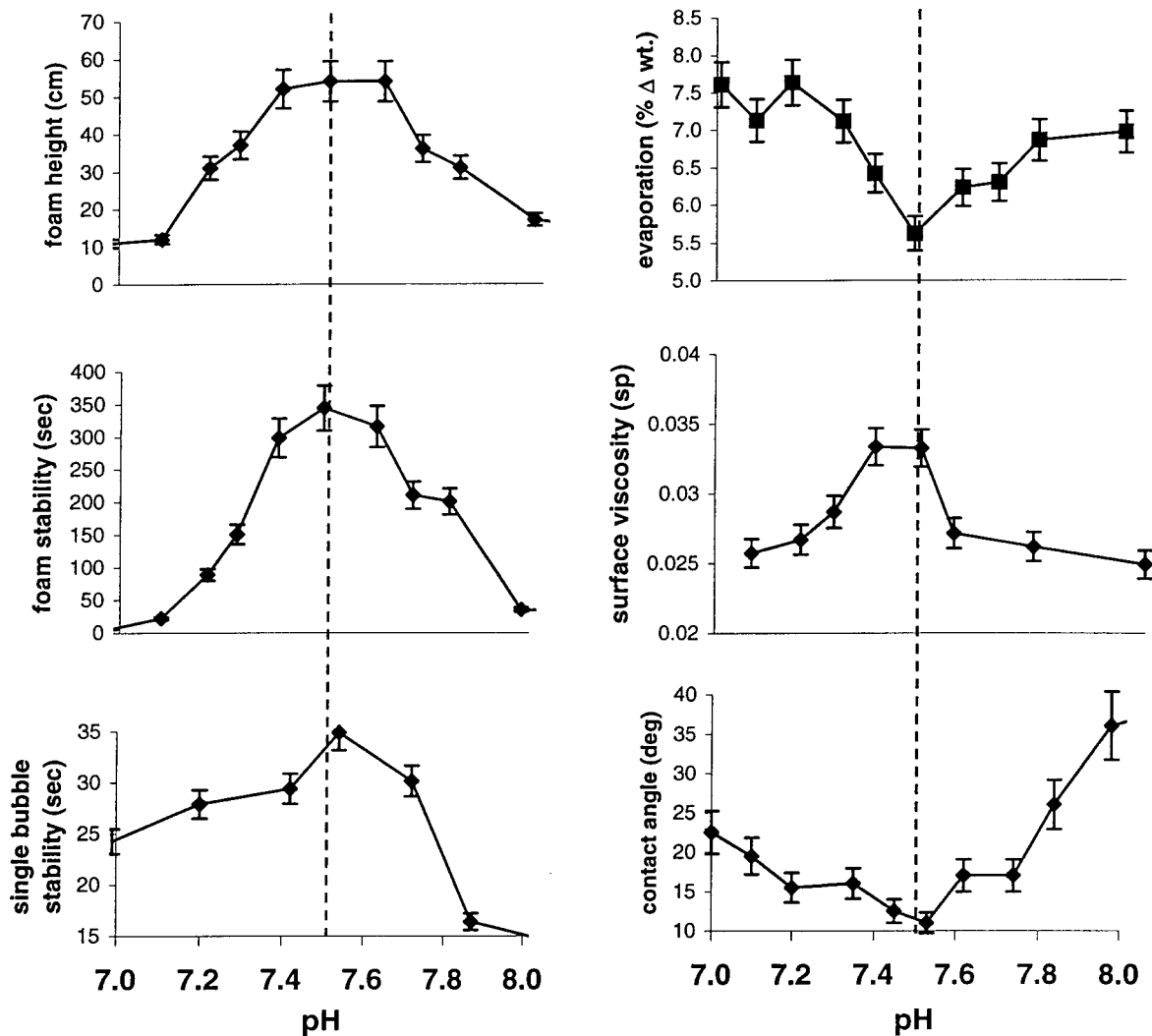


Figure 4. Diagram depicting maxima or minima in various interfacial properties with respect to pH of sodium laurate ($C_{11}H_{23}COO^-Na^+$) solution.

values of pH. This can be seen in Figure 5. Figure 5 also shows that at high pH values, the concentration of emulsion droplets is very small, as the ionized soap becomes more water soluble and less surface-active.

We propose that at pK_a , since 50% of the molecules are in ionized form and 50% in un-ionized form, a strong ion-dipole interaction occurs between these two types of molecules that leads to a dimer formation at this pH. The interaction is much stronger than ordinary hydrogen bonding where no formal charge is present on any atoms. Therefore, this association may be responsible for the effects that are seen in soaps near the pK_a value. At pH values lower than pK_a , the film becomes largely un-ionized and prefers to partition to a lipophilic medium (or to the fatty acid droplets at the surface in the case of an air/water system). At pH values higher than pK_a , the film is almost completely ionized, leading to ionic repulsion between the polar groups and greater solubility in water. Figure 6 schematically shows the ion-dipole interaction between ionized and un-ionized molecules of fatty acid at pH values near the pK_a .

The predicted minimum in area per molecule at pH near pK_a is confirmed by area per molecule experiments for sodium laurate. Table 1 lists parameters of the Gibbs adsorption equation used to determine area per molecule of 0.05 wt % sodium laurate as a function of pH. As can be seen in Table 1 and Figure 7, a minimum in area per

molecule and intermolecular distance is observed at pH ~ 7.5 , which corresponds to the pK_a of sodium laurate.

As the chain length of a fatty acid salt increases, the pK_a value also increases. This is a very interesting phenomenon, since pK_a is governed by ionization in the carboxylic acid moiety of the molecule and not by the electronic distribution in the carbon chain. If one goes from a C_{10} fatty acid chain length to C_{12} , the electronic distribution in the polar group region cannot be significantly altered. It is known^{18,19} that electronic effects do not go beyond three to four carbon atoms. Thus, the effect of the carbon chain length on pK_a must be explained by intermolecular interactions.

We propose that as one increases the chain length of a soap molecule, the surface concentration (i.e., mol/cm²) increases and hence area per molecule must decrease. This will decrease the intermolecular distance between the molecules of soap. Thus, the shift in pK_a as one increases chain length must be due to closer packing of soap molecules at the interface.

Figure 8 shows the foam heights obtained by the shaking method. It was observed that the foam height is maximum at pH values of 6.5, 7.5, 8.8, and 9.15 for C_{10} , C_{12} , C_{14} , and

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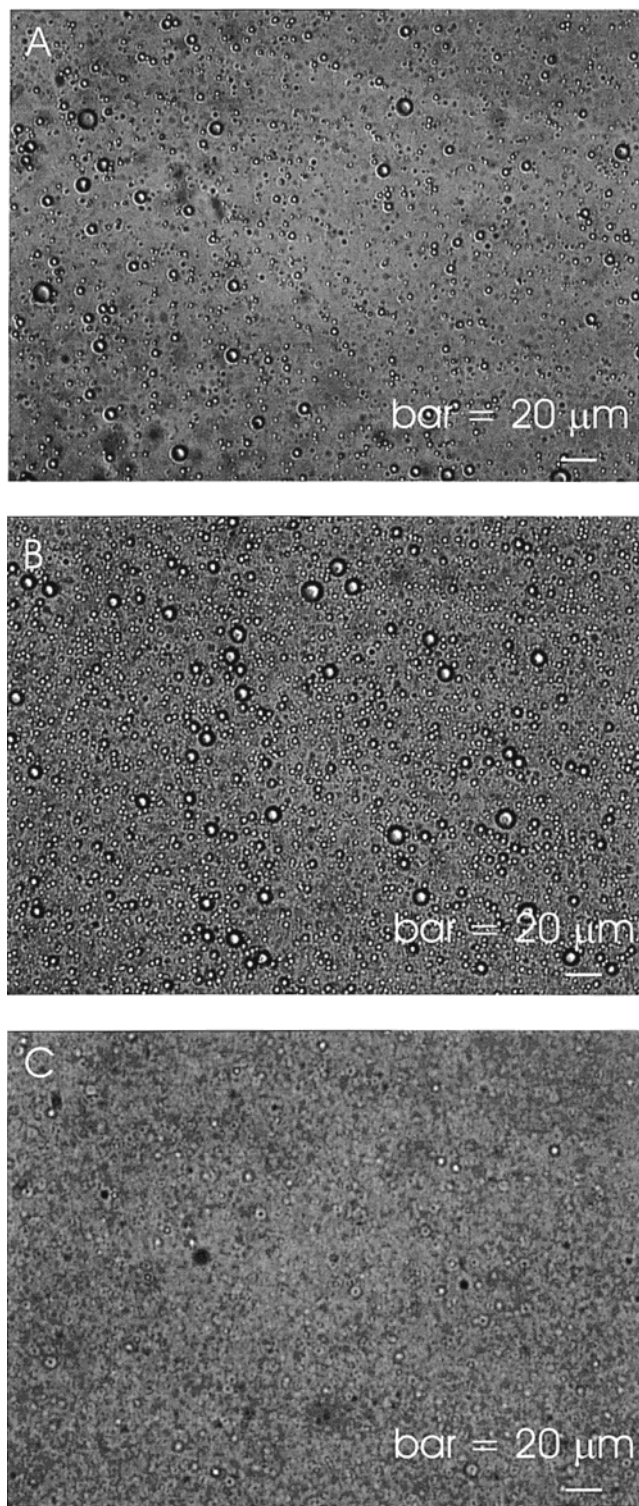


Figure 5. Comparison between O/W emulsions at different values of pH of sodium laurate solution: (A) pH 7.0; (B) pH 7.5; (C) pH 8.0.

C_{16} soap molecules, respectively. The pH value for maximum foam height of C_{16} soap falls between the two pK_a values of C_{16} fatty acid found in the literature. Heikkilä et al.²⁰ reported an apparent pK_a for hexadecanoic acid (i.e., palmitic acid) of 9.7, and Peters²¹ reported a pK_a of 8.5 for the same fatty acid. We found the pK_a of sodium

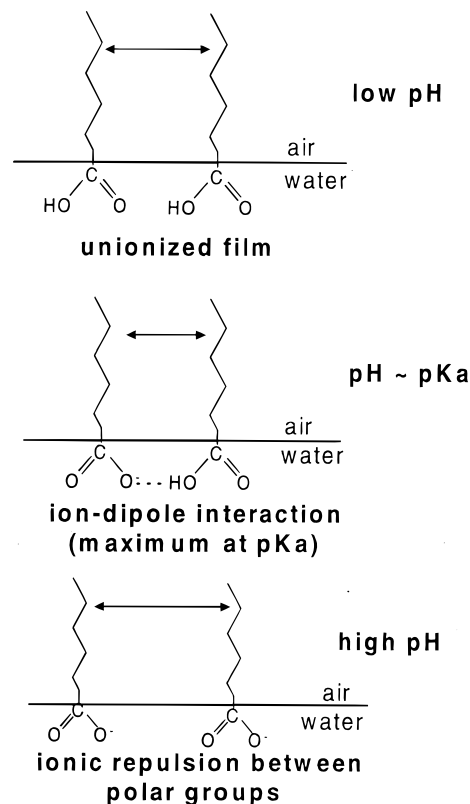


Figure 6. A strong ion–dipole interaction among the carboxyl groups near the pK_a value decreases the intermolecular distance at the air/water interface.

Table 1. Calculated Parameters of Gibbs Adsorption Equation Used in Determination of Area/Molecule of 0.05 wt % Sodium Laurate Solution vs pH^a

pH	$d\gamma/d \log C$	Γ (molecules/Å ²)	$1/\Gamma$ (Å ² /molecule)	intermolecular distance (Å)
7.00	-14.07	0.015	67.2	8.20
7.25	-15.523	0.016	61.0	7.81
7.50	-16.699	0.018	56.7	7.53
7.75	-16.556	0.017	57.2	7.56
8.00	-16.182	0.017	58.5	7.65
8.25	-14.481	0.015	65.3	8.08
8.50	-12.311	0.013	76.9	8.77

^a Temperature = 298 K, sodium laurate formula weight = 222.3 g mol⁻¹, $R = 8.31473 \times 1015$ dyn Å mol⁻¹ K⁻¹.

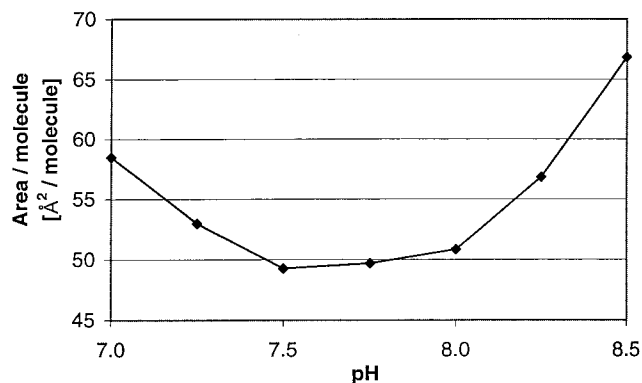


Figure 7. Area/molecule of 0.05 wt % sodium laurate vs pH of solution.

palmitate to be 8.6–8.8 by titration (see Table 2). Christodoulou and Rosano estimated pK_a values of 9.0 for octadecanoic (C_{18}) acid. Our values of pK_a increased with increasing chain length. Table 2 shows a comparison

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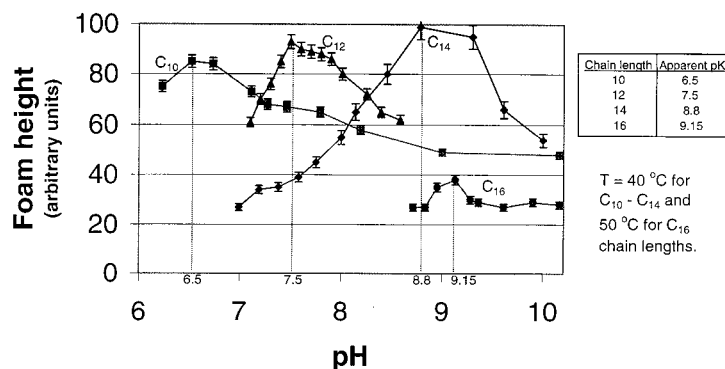


Figure 8. An increase in soap chain length leads to a shift in apparent pK_a , as reflected by foamability during the shaking method.

Table 2. Comparison between Experimentally Determined pK_a Values and Observed Phenomena for Fatty Acid Salts of (C₈–C₁₆) Chain Lengths

soap chain length	measd pK_a	pH of max foam height	pH of min evap rate	pH of min contact angle
8	6.3–6.5	<i>a</i>	6.9	7.0
10	7.1–7.3	6.5	7.1	7.2
12	~7.5	7.5	7.5	7.5
14	8.1–8.2	8.8	8.1–8.3	7.6
16	8.6–8.8	9.15	8.9–9.0	<i>b</i>

^a Negligible foam generated. ^b Insoluble at room temperature.

between experimentally determined pK_a values and observed phenomena near pK_a for fatty acid salts of (C₈–C₁₆) chain lengths. As can be seen in this table, pH values corresponding to minima in contact angle on PMMA and evaporation rate are similar to experimentally determined pK_a values. Again, the shift in pK_a due to increase in chain length seems directly related to increased van der Waals interaction between soap molecules. Thus, the above results indicate that *cooperativity* among molecules at interfaces induced by the van der Waals interactions between chains and the concomitant polar group interactions cause reduced intermolecular distance leading to optimum behavior of various properties exhibited by the soap solution near its pK_a value.

Figure 9 schematically illustrates the proposed mechanism for the effect of increasing chain length on intermolecular distance of fatty acids at their respective pK_a values. It was shown previously by Shiao et al. (1997) that changes in intermolecular distance as small as 0.04 Å induced by mixing surfactants of different chain lengths can significantly influence performance of various technological processes such as foaming, emulsification, lubrication, wetting, and retardation of evaporation by films. We have shown further (Table 1) in the present paper that similar subangstrom changes (0.03 Å) in intermolecular distance can be produced by ionization of

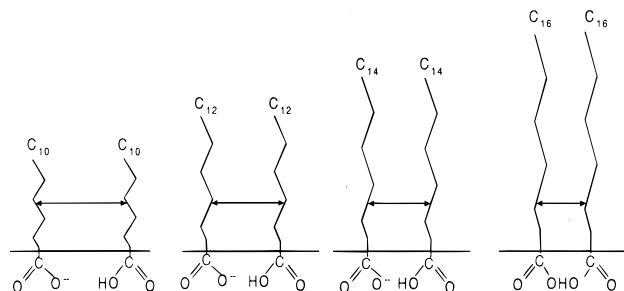


Figure 9. Schematic illustration of the proposed mechanism for the effect of chain length on the intermolecular distance between molecules in the adsorbed film at their respective pK_a values.

the polar headgroups near their respective pK_a values, and this in turn will cause striking changes in the performance of various technological processes.

Conclusions

It has been shown that soap exhibits optimum properties at a pH near its pK_a in various technological processes. Specifically, foam height, foam stability, and bubble lifetime show maximum values, and contact angle on PMMA and water evaporation rate show minimum values at the bulk pK_a of sodium laurate. Further studies indicate that an increase in the chain length of the soap molecule results in a shift in pK_a toward a greater value due to molecular cooperativity induced by van der Waals interactions between hydrophobic chains and greater interactions among polar groups.

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