Hydrophilicity of Nonanoic Acid and Its Conjugate Base at the Air/Water Interface

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ABSTRACT: A general adsorption model based on partial dissociation was developed for carboxylic acids. The model was applied to the adsorption of nonanoic acid at the air/water interface. Two cases were selected for experimental verification: acid-only and acid with a constant Na⁺OH⁻ concentration. The model was applied simultaneously at both conditions, and the hydrophilicity of the ionic states was quantified by the adsorption constants, \( K_A \) and \( K_{A^+} \). It was found that the adsorption constant for the acidic group is significantly higher than that for the carboxylate group, \( K_{A^+}/K_A \sim 272 \). The model lays important groundwork for modeling and predicting carboxylic/carboxylate adsorption.

INTRODUCTION

The adsorption of anionic surfactants at the air/water interface has been a key phenomenon for the soap and detergent industry. In the history of chemistry, the anionic surfactant is probably the first synthesized chemical on records, with natural soap having been produced since ancient times in Mesopotamia. An example of the recorded recipe is shown in Figure 1. The action of soaps is still experienced in industrial and household activities with modern detergents. However, despite a long history of applications, the nature of these surfactants at the air/water interface remains inadequately described.

In the literature, thermodynamic analysis is often applied to quantify the adsorbed concentration of surfactant

\[
dy = -nRTd(ln(C_b))
\]

where \( R \) is the ideal gas constant, \( T \) is the temperature, \( \gamma \) is the surface tension, \( C_b \) is the bulk concentration, \( \Gamma \) is the surface excess concentration, and \( n \) is the prefactor. The prefactor \( n \) depends on the ionic nature of the surfactant, with values of 1 and 2 for nonionic and ionic surfactants, respectively.

Carboxylic acids, with a partial ionization, exist in an equilibrium between associated (carboxylic) and dissociated (carboxylate) forms. Hence, eq 1 with a constant prefactor, either 1 or 2, is not appropriate. Because the equilibrium is concentration-dependent, the degree of ionization is different from the bulk to the surface. Due to the increase of concentration at the surface, the associated fraction should be higher at the surface than in the bulk. This has been validated with amino acids: the carboxylic acid group is ionized at a significantly higher pH at the surface than in the bulk. As a result, the adsorption model of a binary mixture, which excludes the conversion between the two surfactants, is not suitable either.

The lack of a theoretical model prevents an effective validation of the hydrophilicity of carboxylic and carboxylate groups. It is well accepted that surfactant adsorption is governed by a balance between the hydrophobic tail and the hydrophilic head. Hydrophobicity is directly correlated with hydrocarbon length, whereas hydrophilicity is largely unquantified. The hydrophilicity is qualitatively related to the solvation/solubility of head groups. As a result, an ionized state, with a higher solubility, would have a higher hydrophilicity than the nonionized state. The most significant result for hydrophilicity was obtained a few decades ago with alkyl phenols (\( \text{C}_x\text{H}_{2x+1}\text{C}_6\text{H}_4\text{OH} \)) and alkyl phenolates (\( \text{C}_x\text{H}_{2x+1}\text{C}_6\text{H}_4\text{O}^- \)). The dissociated state, phenolate, requires at least four carbons (\( x > 4 \)) to become surface active. On the other hand, the associated state is surface active with \( x = 0 \) (phenol) or 1 (p-cresol). Hence, four carbons in the hydrophobic tail are required to balance the increased “hydrophilicity” from phenol to phenolate.

The ionization degree and adsorption are coupled to the equilibrium of the system to quantify the adsorption of these weak electrolytes. As far as we are aware, there is only one quantification method in the literature, which is based on a thermodynamic model. However, the method requires the surface tension of pure surfactant. Consequently, the method is applicable for liquid acids only, with up to four carbons for monocarboxylic and five carbons for dicarboxylic acids, respectively. There are no quantitative methods to model the
relative adsorption of longer-chain carboxylic acids, which exist in the solid form at room temperature.

In summary, there is no theoretical prediction of the adsorption or hydrophilicity of long-chain carboxylic acids and their conjugate bases. This study focuses on the adsorption of nonanoic acid. The acid was selected for several reasons. First, it is partially dissociated under normal conditions. Hence, both ionized and nonionized species exist, at significant percentages, in the bulk. Second, the dissociation constant can be determined by pH measurements. Finally, the carboxylic acid remains an important and economical surfactant for commercial soaps and detergents. A proper understanding of the relative adsorption at the air/water interface can lead to important applications of soap at both the oil/water and solid/water interfaces.

Because these ionic states exist in equilibrium, separate quantification at the interface is impossible. Hence, a new model is needed to simultaneously account for both interfacial adsorption and reaction equilibria. A successful model can provide important information on the relative adsorption between different ionic states of the surfactant head.

### THEORETICAL MODELING

In this analysis, the ionization reaction, \( \text{AH} + \text{H}_2\text{O} \leftrightarrow \text{A}^- + \text{H}_3\text{O}^+ \), is incorporated into the adsorption process. The equilibria in the bulk and within the interfacial zone (Figure 1) are governed by the reaction constant

\[
k_a = \frac{C_A C_{\text{H}_2\text{O}}}{C_{\text{AH}}}
\]

where \( k_a \) is the reaction constant (M) and \( C_i \) (i = A, H\(_3\)O\(^+\), and AH) are the bulk concentrations of their respective species.

Although water is also involved in the reaction, the concentration of water as a solvent is too large (~55 M) to be affected by acid ionization. Accordingly, water is not included in the reaction equilibrium. The value of \( k_a \) can be obtained by routine pH measurements and used to compute the exact composition between \( C_A \) and \( C_{\text{AH}} \) in the bulk. The thermodynamic analysis, eq 1, is applied to the system of all species

\[
d\gamma = -RT \sum_i \Gamma_i \text{d(ln(C_i))}
\]

Hence, all species (ionized acid, neutralized acid, and ions) have to be included in the model. In this study, the partial ionic binding is applied. The interfacial zone can be divided into two layers (Figure 2): (i) the outer layer, which contains surfactant tails and the water surface, and (ii) the inner layer, which contains the surfactant heads and other ions. Both layers

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**Figure 1.** Mesopotamian clay tablet (ca. 3rd millennium BC) showing recipes for a natural soap. Courtesy of Penn Museum, image number 150014.

**Figure 2.** Adsorption of carboxylic acid at the air/water interface.
are part of the interfacial zone and thus included in eq 3. The surface adsorption of each species is governed by an equilibrium between the number of vacant sites on the surface and the species concentration. In this case, the adsorption is based on hydrophobic tails. Hence, the equilibria are given by

\[ K_A = \frac{\Gamma_A}{\Gamma_v C_A} \]  
\[ K_{AH} = \frac{\Gamma_{AH}}{\Gamma_v C_{AH}} \]  
where \( \Gamma_v \) is the number of vacant sites (mol/m\(^2\)) and \( K_A \) and \( K_{AH} \) are adsorption constants (M\(^{-1}\)).

Total available sites on the surface, \( \Gamma_{max} \), is given by

\[ \Gamma_{max} = \Gamma_v + \Gamma_A + \Gamma_{AH} \]  
combining with the above equations

\[ \Gamma_v = \frac{\Gamma_{max}}{1 + K_A C_A + K_{AH} C_{AH}} \]  
consequently, the adsorbed concentrations of two species are given by

\[ \Gamma_A = \Gamma_{max} \frac{K_A C_A}{1 + K_A C_A + K_{AH} C_{AH}} \]  
\[ \Gamma_{AH} = \Gamma_{max} \frac{K_{AH} C_{AH}}{1 + K_A C_A + K_{AH} C_{AH}} \]  
The above two equations follow the Langmuir isotherm for binary mixtures.

The adsorption system has three adsorption parameters: \( K_A \), \( K_{AH} \) and \( \Gamma_{max} \). If only the salt-free solution is used, one would get a single set of data and the fitting of the theoretical model would be unreliable. Consequently, the study employs another set of conditions: an excessive and hence essentially constant \( C_{Na} \), and the constant Na\(^+\) concentration can significantly simplify the governing equations. In both cases, eq 3 can be further simplified and used to calculate the adsorption. The model can be applied simultaneously to both conditions to obtain the adsorption constants for both species.

**Acid-Only Solution.** The salt-free solution contains only three species: A\(^-\), AH\(^+\), and H\(_2\)O\(^+\). Neutrality requires \( \Gamma_A = \Gamma_{H_2O} \) and \( C_A = C_{H_2O} \). Because \( k_a \) is constant, \( d \ln(C_{AH}) = 2d \ln(C_A) \). Substitution of these terms into eq 3 results in

\[ \frac{1}{2RT} \frac{d\gamma}{d \ln(C_A)} = \Gamma_A + \Gamma_{AH} \]  
The concentration of ionized acid, \( C_A \), can also be calculated from the total acid concentration, \( C_b \) (\( C_b = C_A + C_{AH} \)), and eq 2

\[ \frac{C_A^2}{k_a} + C_A = C_b \]  
The positive root of the above equation is

\[ C_{H_2O} = C_A = \sqrt{C_b k_a + \frac{k_a^2}{4} - \frac{1}{2} k_a} \]  
Hence, the total adsorption, \( \Gamma_{total} = \Gamma_A + \Gamma_{AH} \), can be obtained as a function of \( C_A \) from eqs 8–10, and 12.

**Acid with a Constant Concentration of Na\(^+\).** Four species are presented in the system with high NaOH concentrations: A\(^-\), AH\(^+\), Na\(^+\), and OH\(^-\). All hydronium ions are presumed to be neutralized by the excessive OH\(^-\). If the bulk concentrations of all four species are variable, eq 3 would result in a complicated form. However, if Na\(^+\) is maintained constant in the bulk, \( d \ln(C_{Na}) = 0 \), then Na\(^+\) is no longer involved in eq 3. The conditions of constant \( C_{Na} \) and variable \( C_b \) can be experimentally obtained and consequently were selected for this study. Therefore, eq 3 reduces to

\[ \frac{d\gamma}{d \ln(C_A)} = -RT (\Gamma_A d \ln(C_A) + \Gamma_{AH} d \ln(C_{AH}) + \Gamma_{OH} d \ln(C_{OH})) \]  
Under an alkali condition, eq 2 reduces to

\[ k_A = \frac{C_A}{C_{AH}} = \frac{C_A}{C_{AH}} \frac{k_w}{C_{OH}} \]  
where \( k_w \) is hydrolysis constant of water (\( k_w = 10^{-14} \)). The balance of charges gives

\[ C_{OH} + C_A = C_{Na} \]  
Substituting \( C_{AH} = C_A - C_{Na} \) and \( C_{OH} \) from eq 15 into eq 14

\[ k_w = \frac{C_A}{C_{Na} - C_A} + C_A = C_b \]  
Equation 16 can be used to calculate the corresponding \( C_A \) at any given value of \( C_b \) and \( C_{Na} \). Differentiating the logarithmic term of eq 14 gives

\[ d \ln(C_{OH}) = d \ln(C_A) - d \ln(C_{AH}) \]  
Equation 13 is simplified as

\[ \frac{d\gamma}{d \ln(C_A)} = -RT [(\Gamma_A + \Gamma_{OH}) d \ln(C_A) + (\Gamma_{AH} + \Gamma_{OH}) d \ln(C_{AH})] \]  
Neutrality in the interfacial layer also requires

\[ \Gamma_A + \Gamma_{OH} = \Gamma_{Na} \]  
Hence, eq 18 reduces to

\[ \frac{d\gamma}{d \ln(C_A)} = -RT [(\Gamma_{Na}) d \ln(C_A) + (\Gamma_{AH} + \Gamma_{Na}) d \ln(C_{AH})] \]  
Because Na\(^+\) ions are located further inside the bulk, one can relate \( \Gamma_{Na} \) to the bulk concentration. Consequently

\[ \Gamma_{Na} = \lambda \gamma C_{Na} \]  
where \( \lambda \) is the effective thickness of the interfacial layer. The value of \( \lambda \) is corroborated later with experimental results.

**Fitting Procedure.** A fitting procedure is applied to both experimental data simultaneously. Because the experimental data only presents the \( \gamma \)-versus-\( C_b \) relationship, further conversion is required from surface tension. The overall fitting procedure consists of the following steps

1. In case of acid-only, the corresponding \( C_A \) is calculated by eq 12. Consequently, the surface tension data are obtained as a function of \( C_A \) (i.e., \( \gamma \) vs \( C_A \))
2. In case of constant Na\(^+\), \( C_A \) and \( C_{AH} \) are obtained from \( C_b \) and \( C_{Na} \) using the bisection method. Consequently, the correlations between \( d \ln(C_A) \) versus \( d \ln(C_b) \) and \( d \ln(C_{AH}) \) versus \( d \ln(C_b) \) are obtained.
both $d \ln(C_A)$ versus $d \ln(C_b)$ and $d \ln(C_{AH})$ versus $d \ln(C_b)$ are linear and easy to obtain.

3. The surface tensions under both conditions are fitted to experimental data via eqs 10 and 20, respectively. The adsorption was then fitted to find $\Gamma_{\text{max}}, \Gamma_{Na}, K_A$, and $K_{AH}$.

## EXPERIMENTAL SECTION

**Materials.** Nonanoic acid and sodium hydroxide solution were obtained from Sigma-Aldrich. Acid purity was specified as $\geq 98.0\%$, and the sample was used without further purification. Water was purified by an Ibis ultrapure system (conductivity $> 17.5$ MΩ cm).

**Methods.** The main focus of this study was on obtaining the surface tension below the critical micelle concentration (CMC) under both unadjusted and high concentrations of NaOH. Due to different solubilities, the following two experimental methods were employed to measure the surface tension: the Wilhelmy plate method and the pendant bubble method. Both methods have been described in detail in the literature.

As discussed in Introduction, nonanoic acid is difficult to dissolve at room temperature. To dissolve acid into water, the acid/water mixture was first sonicated and heated to 60 °C. The solution was then allowed to cool to room temperature (25 °C). At high concentrations, $>2$ mM, some residue was

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Figure 3. Experimental setup for the pendant bubble method.

Figure 4. Surface tension as a function of bulk concentration.
observed on water surface. With decreasing concentration, the residue was gradually reduced to a point at which it was no longer observable. This critical concentration was around $\sim 2$ mM. Hence, a specific setup and procedure were used (Figure 3) to overcome the uncertainties around this critical limit. The method is based on the pendant shape of an air bubble formed after cooling. The apparatus consisted of a video camera, an optical rail for proper alignment, a light source, syringe, needle, plastic cuvette, pH meter (Aqua-pH from TPS Instruments Ltd.), and an electrode.

The starting concentration was 2 mM. After cooling, an air bubble was formed at the end of a needle submerged in the solution. Further dilution was obtained by adding a controlled quantity of water to the initial solution and stirring. After stirring, a new pendant bubble was formed in the solution. In this procedure, any excessive and nonsoluble acid will stay on the water surface, not on the surface of the newly formed bubble. A stainless steel needle with a nominal outer diameter of 1.8 mm, which was attached to a syringe, was used, and a pH sensor was also submerged inside the solution. Several air bubbles were formed at each concentration, and multiple images were taken of each bubble for analysis. Surface tension was calculated from the drop shape using a MATLAB code. The average values and standard deviations were obtained for all images (more than 20 images) at each concentration.

For higher-concentration experiments, the surface tension was measured using the normal Wilhelmy plate method on a Sigma 710 tensiometer (NIMA KSV), fitted with an automatic dispenser. The starting solution contained 0.33 M of Na$^+$ with an initial pH of 14.45. The stock solution was prepared by adding acid into the above solution to bring the concentration to 0.3 M. The mixture was then pumped gradually onto a measurement beaker, allowing the surface tension at acid concentrations ranging from 0 to 0.27 M to be obtained at a constant concentration of Na$^+$.

### RESULTS

#### General Observation

The surface tension data for both cases are presented together in Figure 4. For constant concentrations of Na$^+$ (0.33 M), the solubility was greater than 0.3 M. In this instance, the acid is fully ionized and soluble. The region around CMC ($\sim 0.2$ M) demonstrated a typical dip of anionic surfactants. For the acid-only solution, low acid solubility precluded the measurement of surface tension above 1.8 mM, which is 2 orders of magnitude lower than the basic case. It should be noted that the lowest surface tension, around 0.85 mM, might not correspond to the critical micelle concentration. Instead, the region may indicate surface aggregation or limited solubility.

#### Solubility and Association Constant

The surface tension in Figure 4 indicates that the surface is not saturated for $C_A < 0.9$ mM. Hence, pH data up to 0.8 mM were used to quantify the ionization constant. The ionization constant was obtained (Figure 5) by fitting the experimental data to the following equation:

$$\text{pH} = \log(C_{H_2O}) = \log \left(\frac{1}{C_A k_a + \frac{k_2}{4} - \frac{k_2}{2}}\right)$$

The ionization constant, $k_a$, was obtained as $1.7 \times 10^{-5}$ M with a corresponding $pK_a$ of 4.77, in good agreement with the $pK_a$ of 4.96 reported for nonanoic acid and consistent with the current literature on carboxylic acids.

#### Modeling Surface Tension

The interference of micelles or aggregates with surfactant adsorption remains a controversial issue in the literature. On the basis of the neutron reflectometry analysis of anionic surfactants,16 the adsorption should remain unsaturated to $\sim 80\%$ of CMC. Because the theoretical model in this study was only applicable to unsaturated adsorption, the lower ranges (up to 0.2 M and 0.9 M for constant Na$^+$ and acid-only conditions, respectively) were selected for modeling.

First, the surface tension in Figure 4 is recalculated as a function of $C_A$ for acid-only solutions. Under the constant Na$^+$ condition, $C_A$ and $C_{AH}$ are solved numerically, as shown in Figure 6a.

Consequently, the measured surface tension (from Figure 4) is expressed as a function of $C_A$ for both cases. Polynomial fittings are then applied to the data (Figure 7). The slope of the...
surface tension data was then obtained by differentiating the polynomial functions.

Under the acid-only condition, the slope is used to calculate the adsorbed concentration, $\Gamma_A + \Gamma_{AHP}$ as in eq 10. Under the condition of constant $\text{NaOH}$, we have

$$\beta = \frac{D}{d \ln (C_A)}$$

It can be seen that both correlations are linear as $\beta_1 = 1.00$ and $\beta_2 = 1.04$ (Figure 6b). By substitution into eq 20, we have

$$-\frac{1}{RT} \frac{d\gamma}{d \ln C_A} = \Gamma_{Na} + \frac{\beta_2}{\beta_1} \left( \Gamma_{AHP} + \Gamma_A - \Gamma_{Na} \right)$$

Combining with the isotherms, one obtains

$$-\frac{1}{RT} \frac{d\gamma}{d \ln C_A} = \Gamma_{Na} + \frac{\beta_2}{\beta_1} \left( \Gamma_{max} \left\{ \frac{K_A C_A + K_{AHP} C_{AHP}}{1 + K_A C_A + K_{AHP} C_{AHP}} \right\} \right)$$

Equations 10 and 26 were applied to both curves simultaneously. The fitting parameters are $\Gamma_{max}$, $K_A$, and $K_{AHP}$. The best-fitted results are tabulated in Table 1.

The data for both conditions are shown in Figure 8. Different values of $\lambda_s$ (0.3, 0.5, and 1 nm) were used. It can be seen that the variation has a limited impact on adsorption constants.

The model describes both cases successfully, excepting the low acid concentration at constant $C_{Na}$. The differences may arise from variation in $\lambda_s$. Although $C_{Na}$ is constant, the values of $\Gamma_A$ and $\Gamma_{OH}$ vary correspondingly (Figure 9). Consequently,
the value of \( \lambda_s \) changes with acid concentration. However, a proper valuation of \( \lambda_s \) would require detailed quantification of ionic pairings, which can only be obtained via molecular simulations. In any case, the variation of \( \lambda_s \) should be limited to a distance of a few angstroms and has a minimal impact on the adsorption constant. With \( \lambda_s \) fixed at 3, 5, and 10 Å, the adsorption constants vary only marginally, as shown in Table 1. The deviation between eq 26 and experimental data at low \( C_A \) (in Figure 8) can also be explained by the variation of \( \lambda_s \). At low acid concentrations, the interfacial layer is dominated by Na\(^+\) and OH\(^-\), which form H-bonds with surface water. The disruption of H-bonds affects the surface tension and thus deviates the data from modeled prediction.

### DISCUSSION

The final values shown in Table 1 are physically realistic. First of all, the value of \( \Gamma_{\text{max}} \) should be related to the size of the surfactant. The obtained value was in the same order of \( \Gamma_{\text{max}} \) as reported for all comparable surfactants. The value of \( K_{\text{AIt}} \) was significantly higher than \( K_A \) as expected. As both species have

| \( \lambda_s \) (nm) | \( \Gamma_{\text{Na}} \) (mol/m\(^2\)) | \( \Gamma_{\text{max}} \) (mol/m\(^2\)) | \( K_A \) (M\(^{-1}\)) | \( K_{\text{AIt}} \) (M\(^{-1}\)) |
|------------------|-----------------|-----------------|-----------------|-----------------|
| 0.3              | \( 9.9 \times 10^{-9} \) | \( 1.97 \times 10^{-3} \) | 30.300          | 8273.287        |
| 0.5              | \( 1.65 \times 10^{-7} \) | \( 1.97 \times 10^{-3} \) | 30.328          | 8274.058        |
| 1                | \( 3.30 \times 10^{-7} \) | \( 1.97 \times 10^{-3} \) | 30.397          | 8275.996        |

Figure 7. Surface tension as a function of \( C_A \) for nonanoic acid.

Figure 8. Modeling nonanoic acid adsorption.
the same alkyl tail, the increased adsorption constant corresponds to the decreased hydrophilicity of the group. In this instance, the ratio between the equilibrium constants of the carboxylic and carboxylate groups is given by $K_{\text{AH}}/K_A \sim 272$. In the literature, the surface energies for carboxylic and carboxylate states have been obtained via a thermodynamic equilibrium model. The reported ratios are 14 and 213 for CHO0H and CH3CO0H, respectively. The reported ratios are significantly higher (~20,000 times) for propionic and butyric acids, which may be explained by the uncertainties in the activity coefficients. Furthermore, both propionic and butyric acids have an apparent CMC, whereas acetic and formic acids show a gradual reduction in the surface tension of the pure acid solution. As mentioned earlier, the thermodynamic method requires the surface tension of the pure surfactant22 and fits very well for short-chain acids. Because C8H17COOH is a solid at room temperature, a direct comparison between the two models is not possible. Nevertheless, the order of magnitude between the two adsorption constants in this work is consistent with the surface energies determined from the thermodynamic model.

The modeling results indicated that AH is more surface active than $A^-$. This is consistent with the general hydrophobicity/hydrophilicity balance. The degree of ionization within the interfacial zone can be related back to the surface charge and should be collaborated with a surface potential. The proposed model can be applied to other pH conditions, for instance, in the intermediate pH range. Furthermore, different cations can be used to quantify the impact of water hardness on soap dissociation. The theoretical framework can be also extended to dynamic adsorption, by combining the diffusion process and chemical reaction kinetics. The chemical reaction can be the physical nature of the “barrier-limited” adsorption, which has been proposed in the literature over the last three decades. In addition to the air/water interface, the above framework can be applied to oil/water interfaces. In this case, the adsorption constant is related to the balance between oleophilicity and hydrophilicity of the surfactant molecules.

### CONCLUSIONS

A new model was proposed for the adsorption of carboxylic acid at the air/water interface. The model was successfully applied at two physical conditions simultaneously, and the adsorption constants for both neutralized and ionized acids were successfully quantified. The ratio of the adsorption constants of the carboxylic acid to its carboxylate form was calculated to be ~272 for nonanoic acid. The model lays important groundwork for modeling soap adsorption for the air/water and oil/water interfaces. By extending the method, the adsorption and action of carboxylic detergents can be comprehensively described at different pHs.

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