Acid-Soap Formation in Aqueous Oleate Solutions

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Surfactants have been considered in the past to form pre-micellar multimers such as dimers and acid soap. In a previous publication, we presented a thermodynamic model for the surface tension dependence on surfactant concentration taking into account pre-micellar aggregation and we considered the possibility of formation of dimers in alkaline potassium oleate solutions. In this paper, the surface tension data for potassium oleate solutions at two pH values is analyzed using the above model and the observed differences from predictions of the model are attributed to the formation of acid soaps in the neutral pH region. The formation constant for acid soap is estimated from this analysis to be $1.75 \times 10^7$ (kmole/m\(^3\))\(^{-1}\).

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\begin{align*}
\text{RH} + R^- - H^- + \text{M}^+ + \text{X}^- + \text{H}^+ + \text{OH}^- + \text{H}_2\text{O}.
\end{align*}

\text{Chemical equilibria such as}

\begin{align*}
\text{RH} + R^- - H^- + \text{M}^+ + \text{X}^- + \text{H}^+ + \text{OH}^- + \text{H}_2\text{O}.
\end{align*}

\text{and the relevant thermodynamic constants such as}

\begin{align*}
K_s = \frac{[R^-][\text{H}^-]}{[\text{RH}]}.
\end{align*}
where the terms in the brackets represent the activities of the species involved, can be written for this system. The Gibbs equation relating the chemical potential of the various species \( \mu_i \) to the surface tension \( \gamma \) is given by

\[
\frac{d \gamma}{RT} = \sum_i \Gamma_i \delta \mu_i.
\]  

where \( \Gamma_i \) is the surface excess of species \( i \). Considering the various chemical equilibria and mass balance in the system, the surface tension changes under constant pH and high ionic strength conditions can be related to the chemical potential of a single species by equations (1):

\[
\frac{d \gamma}{RT} = \frac{\Gamma \delta \mu}{RT}.
\]  

where

\[
\Gamma = \Gamma_H - \Gamma_R + 2 \Gamma_H - 2 \Gamma_R^2 - 2 \Gamma_R^2.
\]

\[
\alpha = \frac{1}{1 + \frac{1}{\Gamma H} + \frac{1 + K_H}{V(1 + K_H)^2 + 8 \pi \Gamma H}}.
\]

\[
\gamma = K_d K_a \Gamma_H (1 + K_d K_H),
\]

\[
K_d = \frac{[R^-]}{[R^+]},
\]  

\[
K_a = \frac{[R^+]}{[R^-][H^+]},
\]  

Note that when there is no association, i.e., \( K_d = 0 \) and \( K_a = 0 \) and \( \alpha = 0 \), \( \alpha \) is equal to unity. Under conditions of complete association, on the other hand, \( \alpha \) tends to \( \infty \) and \( \alpha \) becomes \( \frac{1}{2} \). Thus the value of \( \alpha \) between 1 and \( \frac{1}{2} \) reflects the degree of association. Note also that the slope of the surface tension vs log cT curve is proportional to the product of \( \Gamma T \) and \( \alpha \).

**EXPERIMENTAL**

**Materials**

Oleic acid (>99.9% as per manufacturer's chromatographic analysis) purchased from Applied Science Laboratories was in 1-g ampoules sealed under nitrogen atmosphere. Stock solutions of potassium oleate were prepared by saponifying the oleic acid with KOH. Special care was taken to prevent the oxidation of oleate solutions by preparing them using deaerated water and storing them under ni-
trogen atmosphere in the refrigerator. All the other chemicals used were of a.r. grade purchased from Fisher Scientific Co.

**Methods**

Surface tension was measured using the Wilhelmy plate technique with sand-blasted platinum as the sensor (1).

**RESULTS AND DISCUSSION**

Results obtained for the surface tension of potassium oleate solutions at pH 9.4 as a function of surfactant concentration are given in Fig. 2. For the purpose of comparison, surface tension results at pH 11.4 are also included in the same figure. The pH in these systems was maintained at a constant value using the KOH/K₂HPO₄ buffer. It can be seen that the surface tension at pH 9.4 is lower than that at pH 11.4 under all the tested oleate levels. Most interestingly, the observed decrease in $\delta \gamma/\delta \log c_T$ at pH 11.4 with an increase in oleate above a certain level is not evident at pH 11.4 at least up to oleate concentrations (2-3 kmol/m³) almost equal to CMC. Note that the decrease in $\delta \gamma/\delta \log c_T$ above a certain oleate level was considered to be due to oleate dimerization at pH 11.4. The absence of such a marked slope change at pH 9.4, however, cannot be taken as definite evidence for the absence of any aggregation under these conditions. Possible reasons for the differences in the dependence of surface tension on oleate concentration at the two pH levels is examined below using the thermodynamic equations presented earlier. The slope of the $\gamma$ vs log $c_T$ curve, as mentioned earlier, is proportional to the product $\Gamma_T \times a$ (see Eq. [2]). Since $\Gamma_T$ is not expected to decrease with an increase in oleate concentration, the decrease observed in $\delta \gamma/\delta \log c_T$ at pH 11.4 was attributed to a decrease in $a$. At pH 9.4, on the other hand, $\delta \gamma/\delta \log c_T$ does not exhibit such a decrease in the premicellar region. The constant slope above a certain oleate level at pH 9.4 suggests that the product, $\Gamma_T \times a$, remains constant in this case. This can happen under two conditions: (i) absence of any association ($a = 1$) and $\Gamma_T$ attains a constant saturation value, and (ii) an increase in $\Gamma_T$ is compensated by a decrease in $a$. Assuming case i to be valid for the present.
system. The value of $\Gamma_T$ at pH 9.4 is $4.75 \times 10^{-6}$ mole/m². The corresponding value of area per molecule of oleate is 35 Å². This value is found to be identical to the saturation area per molecule at pH 11.4 (19). The same value of area per molecule at pH 11.4 and 9.4 is, however, contrary to what can be expected on the basis of type of monolayers at these pH levels. While the monolayer will be fully ionized at pH 11.4, it can be expected to be only partially ionized at pH 9.4. The area per molecule at pH 9.4 should therefore be lower than that at pH 11.4: the lower values obtained for surface tension at pH 9.4 compared to the corresponding values at pH 11.4 under all the tested oleate levels also suggest this. In other words, the value calculated assuming $\alpha = 1$ is lower than the expected value at pH 9.4. Based on these considerations, it can be concluded that the observed constancy of $\sigma_T/\delta \log \gamma$ in the premicellar region at least up to about $2-3 \times 10^{-3}$ kmole/m³ oleate is the result of the compensatory effects of the increase in $\Gamma_T$ and the decrease in $\alpha$.

Determination of $\alpha$ requires a knowledge of $\Gamma_T$ at different levels of oleate. Because of the partially ionized nature of the monolayer at pH 9.4, the saturation value of $\Gamma_T$ should correspond to an area per molecule in the range of 20 to 35 Å². The former is for an unionized fatty acid monolayer and the latter is for an ionized oleate monolayer at pH 11.4. The results of monolayer studies reported in the literature, however, show that the lowest area per molecule for an unionized oleic acid monolayer is only 30 Å² (20). Using the value estimated for the dimerization constant ($K_d$) at pH 11.4 (11), the acid-soap formation constant ($K_{ads}$) was computed for different $\Gamma_T$ values corresponding to different molecular areas in the range 20 to 30 Å². The dependence of $K_{ads}$ on the value selected for the area per molecule is illustrated in Table I. The value corresponding to an area per molecule of 30 Å² represents the maximum possible value of $K_{ads}$. The minimum value of $K_{ads}$ should of course be higher than $K_d$ ($5 \times 10^3$ (kmole/m³)^{-1}). Since the monolayer is partially ionized at pH 9.4 the $K_{ads}$ value corresponding to the geometric average of the maximum and the minimum values of $K_{ads}$ ($1.75 \times 10^5$ kmole/m³) is suggested to be a reasonable estimate of the acid-soap formation constant. Based on the available information on $K_a$, $pK_{ads}$, $K_d$ and the data obtained in the current study, constants for the various chemical equilibria in oleate solution are

$$RH_3 \rightleftharpoons RH \quad pK_{ads} = 7.6$$
$$RH \rightleftharpoons R^- + H^- \quad pK_d = 4.95$$
$$2R^- \rightleftharpoons R_2^- \quad pK_a = -3.7$$
$$R^- + RH \rightleftharpoons R_2H^- \quad pK_{ads} = -5.25$$

Activities of various oleate species at any total oleate concentration can now be computed as a function of pH. As an example, the species distribution obtained for $3 \times 10^{-3}$ kmole/m³ total oleate is shown in Fig. 3. The following features are to be noted: (a) the pH of the onset of precipitation of oleic acid for $C_T = 3 \times 10^{-3}$ kmole/m³ total oleate is 7.9; (b) the activities of oleate monomer ($R^-$) and dimer ($R_2^-$) remain almost constant above the pH of precipitation of oleic acid and decrease rapidly below it; (c) the activity of acid soap increases with increases in pH in the oleic acid precipitation range and decreases above it. Similar diagrams can be computed for other oleate concentrations.

SURFACE ACTIVITY OF ACID SOAP AND ION DIMER

As discussed above, the observed dependence of surface tension on total oleate concentration can be considered to indicate the
formation of premicellar aggregates such as dimers and acid soaps. The role of those species will actually be determined by their surface activities in comparison to that of the monomeric species. The surface activities of these complexes, on the basis of charge and molecular size considerations, can be different from those of the monomers. While it is possible to estimate the surface activities of a homologous series of surfactants by considering the chain length and the free energy for transfer of -CH₂- groups from the bulk solution to the interface, the peculiar shapes of these complexes make it difficult to estimate their surface activities. For example, in the case of the acid soap, the molecular size has doubled even though the effective chain length has not necessarily doubled. Therefore a method involving the surface area of the molecule rather than the chain length is proposed here to estimate the surface activity of these complexes. The underlying assumption in this estimation is that the free energy change involved in the transfer of a hydrocarbon chain from the aqueous phase to the liquid–air interface is proportional to the surface area of the species. Estimates based on this approach show that the surface activity of the acid soap can be seven orders of magnitude higher than that of the oleate ion and five orders of magnitude higher than that of the neutral oleic acid molecule. Consequently, oleate solutions can be expected to be most surface active under conditions when acid soap is present in maximum amounts. The observed minimum in the surface tension of oleate solutions (see Fig. 4) is at the maximum in the hydrophobicity of number of oleate-treated oxide and silicate minerals in the pH range of 7 to 8 (21) are in accordance with the above considerations.

A precise comparison of the surface activity of the dimer with that of the monomer is difficult because of the presence of the ionic groups at the opposite ends of the dimer. Adsorption of the dimer at the solid–liquid interface can, however, be considered to be favored since such adsorption would lead to hydrophilic groups toward both the hydrophobic solid and the solution. Available results for the dependence of the wettability of solids as well as the flocculation/dispersion characteristics of hydrophilic particles on surfactant concentration do show them to become hydrophilic at high concentration (22). These observations are in accordance with the possible adsorption of doubly charged dimers at the solid–liquid interface.
SUMMARY

The formation of acid-soap oleate dimer has been investigated by analyzing the dependence of surface tension on total oleate concentration. While the surface tension vs log concentration curve obtained at pH 11.4 shows a decrease in slope with an increase in oleate above a certain level in the preemiscellar range, the curve at pH 9.4 does not exhibit such a decrease. The decrease in slope at 11.4 has been attributed to the formation of doubly charged dimers in the solution. Comparison of the values of the slopes at pH 9.4 to those at pH 11.4 indicates the presence of a significant association at pH 9.4 also. Using the surface tension data, the acid-soap formation constant has been estimated for the present system. Oleate species distribution has also been computed as a function of pH using the available thermodynamic constants and those determined in the present study. The treatment further provides a method to estimate the surface activity of complex molecules such as oleate acid soap.

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