

THE ELECTROCHEMISTRY OF SOAP

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INTRODUCTION

The surfactant industry is one of the most creative and antique chemical activities. Soap was known already by ancient Egyptians in 2500 b.C. Surfactants are widely used at home and in almost all industries: cosmetics, pharmaceuticals, oil recovery, laundry, mineral processing, pesticides, paper and metallurgical industry, among others. In the United States, the sales of cleaning products in 1995 were of 9,600 million dollars. About 21 % of these products were soaps [1]. Although the proportion of soaps in the surfactant industry is slowly diminishing in comparison with synthetic surfactants, the absolute amount of soaps produced increase with time due to the rapid increase of the surfactant industry [2]. In spite of their sensibility to acid media and polyvalent metal ions, soaps are the option for several applications because of their complete biodegradability, low price and toxicity among other properties. Some additives such as substances which complex the polyvalent cations may be used to avoid the soaps' disadvantages. For almost all the uses of soaps, it is preferable to employ inexpensive mixtures instead of pure, expensive soaps. The combination of several chain lengths and structures gives to the mixture abilities which are impossible to obtain with a single component. For instance, the best wetting effect is observed with detergents having 7 carbon atoms in their saturated chain (n_C , without considering the polar head group). The best solubilisation of fats and oils is obtained by surfactants having $n_C = 13$. The common solution is to use a 11 to 13- carbon atoms chain. The effects of using a mixture having $n_C = 11 - 13$ in average are better than those obtained with a single surfactant with this chain length, besides they are cheaper. Emulsions are better stabilised by mixtures than by single surfactants. Different applications need different n_C average values: the stabilisation of oil-in-water (O/W) emulsions need more hydrophilic mixtures (having low n_C average values) than the stabilisation of water-in-oil (W/O) emulsions, which need large n_C average values. Surfactants employed in hot media need larger n_C average values than those used in cold ones, therefore the importance of knowing of the n_C average value of a natural mixture is capital.

Natural oils and fats have different fatty acid in their structure. Since soaps are obtained by saponification of these compounds, ordinary soaps are mixtures of several different fatty acid salts. Because of the “liquid” nature of the micelle hydrocarbon core [3], mixtures of members of the same homologous series of surfactants (e.g., soaps) behave as ideal mixtures in solution [4], therefore it is possible to use average properties (such as number average molecular weight) to describe them.

Since soaps are salts of weak acids, they undergo hydrolysis. This hydrolysis is enhanced by the formation of micelles, which solubilise the formed fatty acid. For several applications, a high pH enhances the detergency. As an example, the optimal pH for wool cleaning is between 7 and 8, between 9 and 10 for cotton, and for technical purposes, the pH may be of 11 or higher [5]. Consequently, the knowledge of the hydrolysis properties of a given soap mixture is of practical importance. All of these properties are also of theoretical interest because they give information on micelle structure such as solubilisation capability, Stern layer properties and micelle composition.

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scitation and pictures from: **AN UNDERGRADUATE PHYSICAL CHEMISTRY EXPERIMENT ON SURFACTANTS: ELECTROCHEMICAL STUDY OF A COMMERCIAL SOAP.**

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In this exercise, pH and conductivity measurements are used to study the chemical composition of commercial soap, and the formation of micelles and aggregates in soap solutions.

The critical micelle concentration (*c.m.c*) depends on the number of carbon atoms in the hydrocarbon chain, n_C , according to Eq. (1):

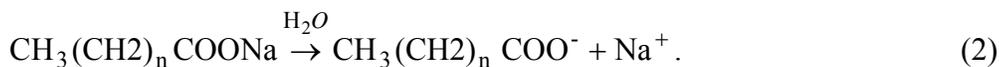
$$\log(c.m.c) = a + \Phi_{CH_2} \cdot n_C, \quad (1)$$

where a is a constant and Φ_{CH_2} is the Gibbs energy of the micelle formation of a methylene group. Because the lengthening of the carbon chain enhances micelle formation, Φ_{CH_2} is negative.

Soap	n_C	CMC % w/v	M g
Sodium octanoate	7	6.65	166.20
Sodium decanoate	9	1.75	194.25
Sodium dodecanoate	11	0.467	222.30
Sodium tetradecanoate	13	0.18	250.36
Sodium hexadecanoate	15	0.047	278.41
Sodium octadecanoate	17	0.0092	306.46

Table 1: Effect of some properties of soap to the critical micelle concentration.

Commercial soap is a sodium salt of fatty acids, $CH_3-(CH_2)_n-COONa$, that hydrolyses in water:



Then, a basic solution is formed, with some amount of fatty acid:



The fatty acid (HA) is a weak acid, and its conjugate ion (A^-) is a strong base, so an equilibrium constant can be written for Eq. (3), assuming that there are no other components in the solution:

$$K_b = \frac{[HA] \cdot [OH^-]}{[A^-]} \quad (4)$$

When it is known that $[HA] = [OH^-]$, and that for a strong base and weak acid's salt

$$K_b = \frac{K_w}{K_a}, \quad (5)$$

where K_w is the ionic product of water, $K_w = [H_3O^+] \times [OH^-]$, the concentration of the soap in the solution can be estimated from the pH measurements using Eq. (6):

$$[A^-] = |saippua| = \frac{K_a \cdot [OH^-]^2}{K_w} = \frac{K_a \cdot K_w}{[H_3O^+]^2} \quad (6)$$

to obtain

$$pH = -\log[H_3O^+] = \frac{1}{2} \log |saippua| - \frac{1}{2} \log K_a \cdot K_w \quad (7)$$

The degree of hydrolysis, β , of the soap can be estimated from Eq. (8):

$$\beta = \frac{OH^-}{[saippua]} \quad (8)$$

Normally, the degree of hydrolysis decreases as a function of concentration. In a soap solution, micelles can form around the hydrofobic fatty acid molecules to separate them from the water. Then, the equilibrium in Eq. (3) shifts to the product side and the degree of hydrolysis increases, until the number of micelles reaches its maximum and the degree of hydrolysis starts to decrease again (see Fig. 1).

It has been shown, that the concentration of the soap solution, where aggregates (dimers, precipitating fatty acid etc.) start to form, C_F , can be estimated from the minimum value of β :

$$C_F = \frac{K_b}{\beta_{\min}} = \frac{K_w}{K_a \cdot \beta_{\min}} \quad (9)$$

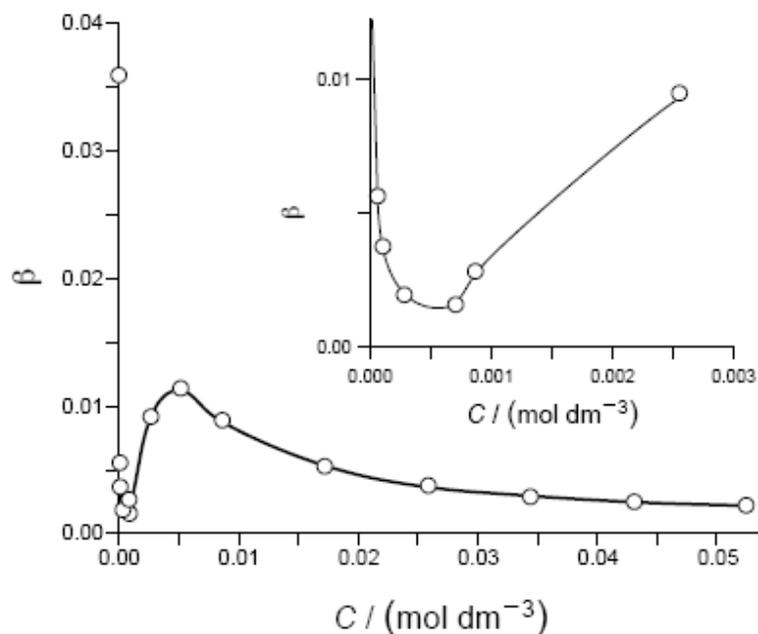


Figure 1: Degree of hydrolysis, β , of a soap solution as a function of concentration.

EXPERIMENTAL

Reduce commercial soap sample to small pieces with a cutter. Dehydrate the pieces in a laboratory oven at 110 °C for a day (for safety reasons, do not leave the oven on unattended overnight). Pulverize the dehydrated soap in a mortar. Put the powder into the oven at 110 °C until constant weight is attained. Weigh a portion of the anhydrous soap in an analytical balance to assure the milligram. Dissolve the soap in ion exchange water to obtain 750 ml of a solution of about 1 g per 100 ml (1 % w/v). Some heating may be necessary. Prepare solutions having decreasing concentration of soap between 1 g % and 0.001 g % by dilution with ion exchange water (see table for exact concentrations). Measure the conductivity and pH of each sample, starting from the most dilute sample. Work at 30 °C, using a water bath, to ensure solubility of the commercial soap.

Sample	C % (w/v)	Sample	C % (w/v)
1	1	8	0,025
2	0,75	9	0,015
3	0,5	10	0,01
4	0,25	11	0,0075
5	0,1	12	0,005
6	0,075	13	0,0025
7	0,05	14	0,001

Table 2: The concentrations of the measured samples

ANALYSIS OF THE RESULTS

Plot the conductivity κ as a function of the concentration and estimate the critical micelle concentration (*c.m.c.*) from the point of discontinuity. Plot the values in table (1) according to Eq.(1) and use it to determine the average number of carbons in the soap mixture's hydrocarbon chains, n_C , using the value of *c.m.c.* obtained. Note, that the value of n_C is probably not an integer. Use the molecular mass to calculate the real concentrations of the soap solutions (mol/l).

From the pH measurements, estimate the acidity constant K_a of the soap's fatty acid. Use Eq. (7) for the linear fit of the data that has a slope of ~ 0.5 . Calculate the degree of hydrolysis, β , for the soap using Eq. (8), when $[\text{OH}^-]=10^{\text{pH}-14}$, and draw a graph of β as a function of soap concentration. From the graph, determine the minimum value of the degree of hydrolysis, β_{\min} , and calculate the aggregation concentration C_F using Eq. (9).

Things to discuss in the report

According to your results, is it probable that aggregates form in the soap solution?