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AN UNDERGRADUATE PHYSICAL CHEMISTRY EXPERIMENT ON SURFACTANTS: ELECTROCHEMICAL STUDY OF A COMMERCIAL SOAP.

Pablo C. Schulz *

Departamento de Quimica, Universidad Nacional del Sur, Bahía Blanca, Argentina.
pschulz@criba.edu.ar

Danièle Clausse

Département du Génie Chimique, Université de Technologie de Compiègne, Compiègne,
France.

* To whom correspondence should be addressed.

LAB DOCUMENTATION

Some additional information on surfactant industry and soaps that are not commonly in texts is added below to enhance the students' curiosity.

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.

Since the CMC is not really a unique concentration but a concentration range (C_1, C_2) [6], the critical micelle concentration (CMC) values obtained by different techniques and dissimilar treatments of the data may differ among them, even if the same experimental data is used with different theoretical treatments. This is due to the fact that different techniques are sensible to diverse components of the sample, e.g., surface tension is sensible to the concentration of monomeric surfactant molecules in the aqueous phase, conductivity is sensible to the ensemble of charged entities in solution, pH measurement is sensible to the hydrolysis equilibrium of non-micellised soap anions, and dye solubilisation, to the existence of aggregates having a hydrophobic moiety capable of

characteristic may have unlike sensitivity, e.g., one of them may detect the presence of micelles at a smaller concentration than the other.

Additional information on surfactants for students:

The following lectures are recommended to the students:

- Hiemenz P.C., Rajagopalan R., Principles of Colloid and Surface Chemistry, 3rd Ed., Dekker, New York, chapter 8, pp 355 – 380 (1997)
- Evans, D.F., Wennerström H., The Colloidal Domain, Wiley-VCH, New York, chapter 1, pp. 5-18, and chapter 4. pp. 157-211 (1999)

Students must know the general principles of conductivity and pH measurements.

THEORY ON ELECTROCHEMICAL DATA TREATMENT AND INTERPRETATION

Conductivity of surfactant solutions:

Plots of specific conductivity (κ , S.cm⁻¹) as a function of the concentration (C) generally give two straight lines: one for concentrations lower than the critical micelle concentration (CMC) and the other at concentrations higher than the CMC. The CMC is the concentration at which the two lines intersect. The appearance of a third straight line or a curvature in the high concentration zone of the κ vs. C line is evidence that the micelles change their structure (e.g., if they undergo a sphere-to-rod-like transformation). Since the CMC is not really a unique concentration but a concentration range (C₁,C₂) [6], at the CMC region the experimental points may not follow the straight lines but a curve connecting the straight lines. This can be seen magnifying this zone of the plot.

To obtain the average molar weight (M) and average number of carbon atoms (n_C) of an unknown soap mixture, the specific conductivity of the solutions having different concentrations in weight/volume percent of that mixture may be plotted as a function of concentration, and the CMC value (in w/v %) may be found and compared with that of pure saturated soaps (Table I). There are some differences in soaps' CMC when the counterion is changed, but commercial soaps are mainly sodium salts. Comparison is very easy because the logarithm of the CMC is a linear function of n_C [8]:

$$\log \text{cmc} = a + \Phi_{\text{CH}_2} \cdot n_C \quad (1)$$

Table I			
Critical micelle concentration of saturated soaps [7].			
Soap	n_C	CMC	M
-----	---	% w/v	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

in which a is a constant related with the nature of the polar group, and Φ_{CH_2} is the Gibbs free energy for micellisation by methylene group in kT units (k being the Boltzmann constant and T the absolute temperature). Since the increase in hydrocarbon chain length facilitates micellisation, Φ_{CH_2} is negative. The average value of n_C may be obtained by interpolation of a plot of n_C vs. $\log CMC$ (w/v %), made with the data of Table I. The average n_C value may not be an integer. Once n_C is known, all concentrations may be transformed to $\text{mole} \cdot \text{dm}^{-3}$. Since the molar weight M is proportional to n_C , an interpolation gives the average molar mass of the soap mixture.

The micelle ionisation degree $\alpha = 1 - \beta = 1 - m/n$, in which m is the number of counterions in the micelle Stern layer and n the aggregation number, may be computed from specific conductivity measurements by Evans' equation [9]:

$$1000(d\kappa/dC)_2 = n^{2/3} \alpha^2 [1000(d\kappa/dC)_1 - \lambda_X] + \alpha \lambda_X \quad (2)$$

where $(d\kappa/dC)_1$ and $(d\kappa/dC)_2$ are the slopes of the κ vs. C straight lines prior and after the CMC, and λ_X is the equivalent conductivity of the counterion. This equation is a function of the aggregation number n . However, this dependence is very weak and a reasonable n value may be used without a significant error.

Following a theory on micelle formation [10], the largest spherical micelle formed by a surfactant having n_C carbon atoms in its chain has a hydrocarbon core radius equal to the length of the chain, l (nm) = $0.15 + 0.1265n_C$; the volume of the micellised surfactant

the aggregation number is $n = 4\pi l^3/3v$. To obtain the volume of a whole micellised molecule the head group volume V_{hg} must be added, being 0.0213 nm^3 for sodium carboxylate, obtained from the partial molar volume of micellised sodium dodecanoate, $V = 207.3 \text{ cm}^3\text{mol}^{-1}$ [11]. Thus, knowing the number of carbon atoms in the hydrocarbon chain of the surfactant molecule, a reasonable value of n may be estimated and used in equation (1).

There are several methods to work with conductivity measurements, and all of them have pros and cons. The most common methods of plotting conductivity data are:

*** *The equivalent (or molar) conductivity:***

$$\Lambda (\text{S.cm}^2\text{eq}^{-1} \text{ or } \text{S.cm}^2\text{mol}^{-1}) = 1000 \kappa/C \quad (3)$$

which is commonly represented as a function of \sqrt{C} , but in some cases (especially if (C_1, C_2) is large or for very small micelles) it is preferable to plot Λ vs. $\log C$ [7]. This latter representation gives a best determination of the CMC when the slope change in the Λ vs. \sqrt{C} plot is not clear. The Λ vs. $\log C$ graph also shows some details that may be obscured in the classical Λ vs. \sqrt{C} plot: if the system shows a stepwise aggregation mechanism, each step of aggregation (formation of dimmers or premicelles, micelles, sphere-to-rod-like micelle transformation) is marked by a sudden fall of the curve [7].

Some surfactant systems form premicellar aggregates such as dimmers [12] and small fully ionised aggregates (oligomers), some of them having slight solubilisation power [7,13]. The Λ vs. $\log C$ plot enables to detect their formation better than the traditional Λ vs. \sqrt{C} one. This latter representation gives a deviation of the experimental points from the Debye – Hückel – Onsager line at concentrations lower than the CMC, which may be completely masked by the hydrolysis [14].

*** *The differential conductivity*** $\Lambda^d = 1000dk/dc$, plotted as a function of the average concentration C_{av} [15] or the square root of the average concentration, $\sqrt{C_{av}}$ [16], is computed from the specific conductivity data by:

$$\Lambda^d = 1000(\kappa_{i+1} - \kappa_i)/(C_{i+1} - C_i) ; \quad C_{av} = (C_{i+1} + C_i)/2 \quad (4)$$

C_i and C_{i+1} being two successive concentrations having specific conductivities κ_i and κ_{i+1} , respectively. Classical differential conductivity plots show two straight, almost horizontal lines, one of them at $C < \text{CMC}$ and the other at $C > \text{CMC}$, connected by a sigmoid curve. The inflection point is taken as the CMC. If the pre-CMC line is not horizontal, this may be an indication of pre-micellar association. The larger the (C_1, C_2) interval, the larger the concentration interval containing the sigmoid curve is. A square, abrupt step must replace the sigmoid curve if the aggregation number of micelles is infinite, thus small micelles must give an elongated sigmoid [15b]. Some differential conductivity curves have a maximum at the CMC instead of the sigmoid curve. This indicates the formation of highly charged micelles [15c]. A constant Λ^d value above the CMC indicates that micelles do not change their structure significantly. A curvature appears when micelles grow or change from spherical to rod-like with increasing concentration, and /or if intermicellar interactions are important [15b]. The Λ^d value at the minimum of the post-CMC curve is taken as Λ^M , the molar conductivity of micelles [16a], that is:

$$\Lambda^M = \alpha(Fu^{\text{mic}} + \lambda_x) \quad (5)$$

where α is the micelle ionization degree, u^{mic} the micelle electrical mobility and F the Faraday constant.

Additional comments on conductivity:

The differential conductivity plot illustrates a frequent characteristic of micelles: their reduced contribution to the conductivity in comparison with that of monomers, due to the capture of counterions in the Stern layer. When a soap micelle forms, it includes n surfactant ions (A^-) and m counterions (Na^+). Since $m < n$, the micelle has negative charge. It migrates to the anode carrying the attached counterions. The charge transport through the solution by each micelle is its neat negative charge $(n-m)$ plus that of the free counterions in the Gouy-Chapman diffuse layer, $(n-m)$. This gives $2(n-m)$ charge carriers by micelle, instead of $2n$ when the micelle is not formed. In consequence, the molar differential conductivity of soap solutions must decrease. This derivation is oversimplified, because the effect of size and shape of micelles were not taken into account, but the general conclusions are correct. However, there are some examples of systems having high $\Lambda^{d,M}$

values, when very small, highly charged micelles form at the CMC. This situation appears when fully (or almost fully) ionised micelles are formed at the CMC. A micelle having n charges has higher mobility than the n monomeric surfactant ions, because the viscous opposition to the movement of ions depends on the surface of the kinetic entities. The surface of a micelle is lower than the sum of the n surfactant ions.

The same data give different CMC values when different mathematical treatments are employed. This is shown by the different representation of the conductivity data. For this reason both, the physicochemical method and the theoretical treatment of the obtained data must be indicated when CMC values are reported.

pH measurements in surfactant solutions:

Since sodium soaps are salts (NaA) of a weak fatty acid (HA) and a strong base, their hydrolysis give alkaline solutions:



Therefore, there is some fatty acid HA in solution in equilibrium with soap anions A^- and OH^- ions. If only these components are present and the formed HA is soluble in water, the pH vs. log C plot must be a straight line with slope + 0.5:

$$C = \frac{K_a K_w}{[H^+]^2} \rightarrow pH = -\log [H^+] = 0.5 \log C - 0.5 \log K_a K_w \quad (7)$$

in which K_a and K_w are the acidity (ionization) constant of the fatty acid and the self-ionization constant of water. Thus, from the intercept of this line the ionization constant of the acid may be obtained.

In some cases, the fatty acid solubility in water is very low, and solid HA may be formed. In other cases, a complex known as “acid soap” of composition $HNaA_2$ is formed, which is also a solid. Both solids may be so finely divided that they rest in suspension in the aqueous phase for a long time. Lucassen [17] studied these phenomena by combination of the hydrolysis equilibrium with the solubility of the fatty acid S_{HA} , and the equilibrium constant of formation of the acid soap:

$$K_{HNaA_2} = [Na^+][H^+][A^-]^2 \quad (8)$$

which is the solubility product. When only HA precipitates:

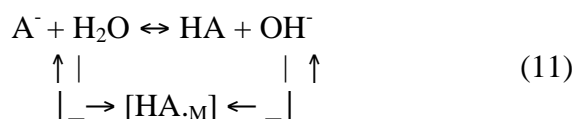
$$[H] = \frac{S_{HA}K_A + K_W}{C} \quad (9)$$

S_{HA} can be obtained from the last equation with the pH values at very low total concentration of the soap. If the acid soap precipitates, a straight line having a slope of +3 must be obtained in the pH – log C plot:

$$pH = 3 \log C + pK_{NaHA2} \quad (10)$$

and the value of K_{NaHA2} can be obtained from the intercept. However, this slope may be less than +3 if the proportion of surfactant molecules forming acid soap is large. At the limiting case in which all the soap forms acid soap, the slope is +1. Lucassen's theory is for pre-micellar solutions and it only mentions that the slope of the pH – log C plot becomes zero in presence of micelles. It also can be negative at higher concentration.

Stainsby and Alexander developed another theory of surfactant hydrolysis [18]. This theory is for somehow complementary to Lucassen's. It explains the characteristic shape of the hydrolysis degree ($\beta = [OH^-]/C$) vs. C plot for soap solutions by the solubilisation of the strongly hydrophobic fatty acid molecules by micelles. If no micelles are present, β decreases with increasing concentration, as in common (non-surfactant) hydrolysable salts solutions. Micelles solubilise the formed HA molecules and extract them from the aqueous moiety. This shifts the hydrolysis equilibrium to the formation of more HA and OH^- , producing a sudden increase in β . But micelles have a limited solubilisation capacity, and when that capacity is saturated, the hydrolysis becomes proportional to the concentration of micelles and a maximum of β is obtained, followed by a diminution. The involved equilibria are:



in which $HA.M$ is the fatty acid dissolved in micelles. Thus a distribution constant of HA

β vs. C equal to the experimental ones and that the position of the maximum is related to the CMC value:

$$C_{\max} = 2\text{CMC} \quad (12)$$

where C_{\max} is the concentration at the maximum of β . They also found that the distribution constant of HA between micelles:

$$K_F = [\text{HA}_M]/[\text{HA}_s] \quad (13)$$

where $[\text{HA}_M]$ is the concentration of acid in micelles per unit volume of micelles and $[\text{HA}_s]$ is the concentration of acid per unit volume of aqueous solution. K_F is related to the density of micelles ρ , the hydrolysis constant $K_h = K_w/K_a$, and the value of the hydrolysis degree at the maximum, β_{\max} :

$$\beta_{\max}^2 = K_h K_F / 4\rho \quad (14)$$

The micelle density ρ can be computed as:

$$\rho = M/v_{\text{Mmolec}} N_A \quad (15)$$

where M is the molar average weight, v_{Mmolec} is the micellised molecule volume and N_A is Avogadro's number.

Finally, they found that the hydrolysis degree at the minimum β_{\min} is related to the concentration at which the first aggregates form, C_F . These aggregates may be dimers, solid HA or acid soap:

$$K_h = C_F \beta_{\min} \quad (16)$$

Additional comments on pH measurement:

In pH studies, the values of the carboxylic acid solubility S_{HA} and the concentration in which small aggregates first form, C_F are frequently similar, especially in pure surfactant

systems. The difference between C_F and S_{HA} in our mixed soap system may be due to the different approaches to develop the two theories. Lucassen theory [17] was developed for solutions without micelles having a coexistence of water soluble and insoluble species with the hydrolysis one. The Stainsby and Alexander theory [18] was developed taking into account the solubilisation power of micelles. Thus, this latter theory probably detects the formation of the most hydrophobic of the fatty acids formed by hydrolysis, whereas that of Lucassen takes into account the effect of all fatty acids formed. Therefore, there is no difference when a pure soap solution is studied. But Stainsby and Alexander theory does not determine the nature of the aggregate formed at C_F . Another possibility is that this aggregate was the $NaHA_2$ complex. In view of the very small value of K_{NaHA_2} , this may also be a plausible interpretation.

Examples of students' results

Table II is an example of the data obtained by one of the students.

The κ vs. C least squares lines obtained with all the students data were:

Before the CMC:

$$\kappa \text{ (S.cm}^{-1}\text{)} = 0.0213 C(\text{mol.dm}^{-3}) + 8 \times 10^{-6}; \quad R^2 = 0.9999$$

After the CMC:

$$\kappa \text{ (S.cm}^{-1}\text{)} = 0.0645 C(\text{mol.dm}^{-3}) + 0.000185; \quad R^2 = 0.9999$$

The pH vs. $\log C$ values obtained by our students gave the following least squares equations:

Straight line A:

$$\text{pH} = 0.4988 \log C + 9.5292; \quad R^2 = 0.9653$$

Straight line B:

$$\text{pH} = 2.3133 \log C + 15.372; \quad R^2 = 0.9653$$

Example of students' data

C	κ	pH
%w/V	mS.cm ⁻¹	-
0.000444	0.0093	7.79
0.00112	0.011	7.38
0.00222	0.0137	7.50
0.00440	0.019	7.58
0.00667	0.025	9.38
0.0112	0.040	7.82
0.0178	0.053	8.00
0.0222	0.064	8.34
0.037	0.103	9.08
0.052	0.138	9.31
0.0667	0.176	9.36
0.133	0.275	9.76
0.222	0.369	9.88
0.444	0.550	9.95
0.667	0.741	9.97
0.780	0.815	9.98
0.889	0.922	9.99
1.11	1.09	10.00

CAS number of chemicals: KCl [7447-40-7].

INSTRUCTIONS TO STUDENTS TO FOLLOW IN THE EXPERIMENT

Sample preparation

Reduce commercial soap sample to small pieces with a cutter. Dehydrate the pieces in a laboratory oven at 110 °C 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 double - distilled water to obtain 500 ml of a solution of about 1 g % w/v. Some heating may be necessary. Prepare solutions having decreasing concentration of soap between 1 g

% and 0.001 g % are prepared by dilution with double - distilled water. About five samples by concentration decade (e.g.: 0.001 – 0.0025, 0.005, ...0.01, 0.025, ...0.1, 0.25, etc.) may be sufficient. Work at 30 °C to ensure solubility of the majority of commercial soaps.

Measurements

Calibrate the conductimeter with a KCl solution of known specific conductivity (κ , S.cm⁻¹). Measure the κ of all samples, starting by the most diluted.

Calibrate the pH-meter with buffer of pH 7.00 or 8.00. Measure the pH of all samples, starting by the most diluted.

Data treatment

Conductivity

Plot a $n_C - \log \text{CMC}$ (% w/v) figure using the data of Table I.

Using a worksheet (such as Excel), create a table with the columns C (in % w/v) and κ (in S.cm⁻¹). Draw a κ vs. C (% w/v) plot and find the CMC (in % w/v) by the intersection of the traight lines. Use this CMC to find the average n_C value in the $n_C - \log \text{CMC}$ (% w/v) figure. With this value, find the average molar weight of the commercial soap, M_{av} . Create another column in the worksheet, with $C(\text{mol.dm}^{-3}) = 10C(\% \text{ w/v})/M_{av}$. Represent κ vs. $C(\text{mol.dm}^{-3})$, and an amplification of the region around the CMC to see the curvature. If the primary experimental data does not show points in the CMC zone, an additional short series of about five samples in this zone may be prepared and measured. Find the equations of the straight lines prior and after the CMC, and compute the ionisation degree of soap micelles with equation (2). Use the λ_{Na+} value obtained from the *Handbook of Chemistry and Physics*, (CRC Press).

Create a new column with equivalent conductivity Λ (S.cm²eq⁻¹) and plot it as a function of $\log C$ and \sqrt{C} .

Create a column with the differential conductivity and the average concentration using equation (4). Obtain Λ^M and compute u^{mic} with equation (5). Determine the equivalent conductivity of the carboxylate ions.

pH

Create a table with the columns C (mol.dm^{-3}) and pH in the worksheet. Plot pH vs. $\log C$ and analyse the different portions of the curve, to obtain the values of K_a , K_{NaHA2} and S_{HA} using equations 7 to 10.

Create a column to obtain $[\text{HO}^-] = 10^{\text{pH}-14}$ and use this concentration to compute the hydrolysis degree β in a subsequent column. Plot β vs. C and find K_F and C_F with equations 12 to 16.

Discussion

Analyse the results in the light of the theory. Is there a curvature in the CMC zone of the κ vs. C plot, indicating a wide critical micellisation interval? From the Λ vs. $\log C$ and the Λ^d vs. C_{av} plots, determine if there is premicellar aggregation.

Compare the values of S_{HA} and C_F .

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