Exercise 9

TESTING THE PROCESS OF MICELLIZATION OF IONIC SURFACTANTS

Keywords: colloidal state, classification of colloid systems, structure and stability of colloids, micellar systems, first and second law of thermodynamics, Gibbs Free Energy, condition of spontaneity of isothermal-isobaric process, electrical conductivity (conductance) of electrolyte solutions.

A surfactant or surface active agent is a substance that, accumulating on the interface of the phases, significantly changes the surface properties of the liquid in which it is dissolved, even at low concentrations. These substances have molecules with an asymmetric structure, consisting of two parts with extremely different properties: non-polar or weakly polar (of hydrocarbon origin) and strongly polar (ion-forming or dipole). The surfactant molecule was assumed to be represented as a circle representing the polar group and a section of the line representing the hydrophobic group. The non-polar (hydrophobic) part is insoluble in water and highly polar liquids, but easily soluble in oils (lipophilic) and in non-polar liquids. The polar part, on the is hydrophilic and therefore lipophobic. Due to the different behavior towards different phases, such molecules are also called amphipathic. These molecules exhibit a specific behavior of forming colloidal-sized structures. These structures are formed either at the interface or in the bulk phase of the surfactant solution, where they are ordered (aggregated) in a schematic manner shown in Fig. 1.

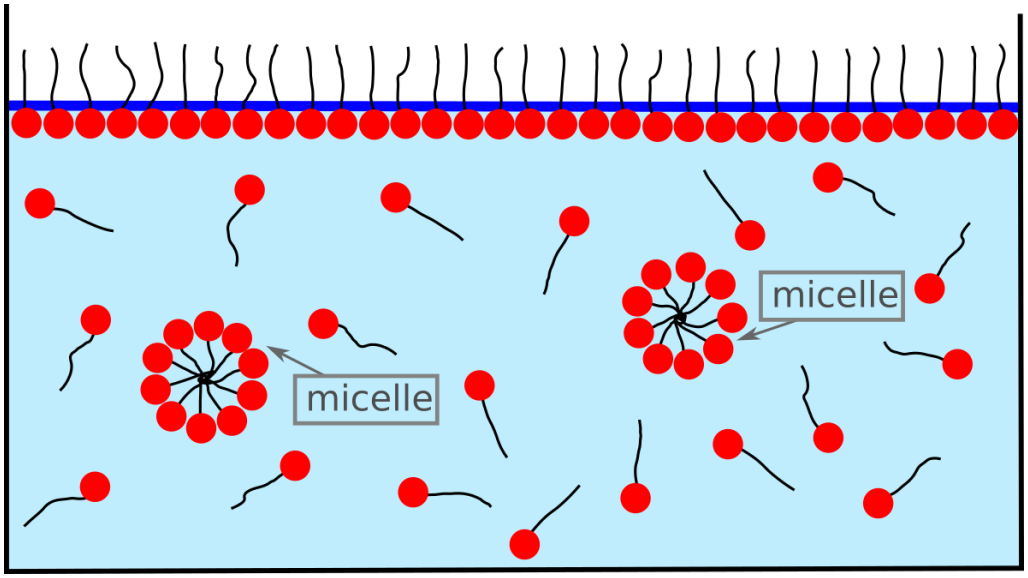

Fig. 1 Colloidal structures of surfactant molecules at the interface and in the bulk phase of an aqueous solution

The following considerations concern the formation of colloidal structures by surfactant molecules in the bulk phase of the solution.

- In very dilute solutions, surfactant molecules exist as single individuals (monomers).
- Exceeding a certain concentration, the molecules spontaneously associate to form aggregates of colloidal size (Fig. 1), called micelles. The surfactant concentration at which the micellization process begins is called the critical micelle concentration (CMC).

- Above the CMC, the cluster of surfactant molecules is a thermodynamically stable form, remaining in dynamic equilibrium with single molecules. This means that at a certain micelle size, the minimum free enthalpy of the system is reached.

The reduction of the free enthalpy as a result of the micellization process taking place in the aqueous medium, $\Delta_{mic}G$, is mainly the result of a positive entropy change, $\Delta_{mic}S$. This finding may initially seem surprising, as micellization reduces the number of kinetically independent surfactant molecules. Enthalpy changes, $\Delta_{mic}H$ accompanying the micellization process, can be both positive and negative, but their contribution to the free enthalpy ($\Delta_{mic}G = \Delta_{mic}H - T\Delta_{mic}S$) is smaller than the contribution of the entropic term.

The increase in the entropy of the system caused by the formation of micelles is related to the tendency of water molecules to form ordered structures being a result of dipole interactions and hydrogen bonds. As a result of thermal fluctuations, these structures, present in pure water, are subject to numerous disturbances. Admixtures of other substances may affect the durability and size of these structures. For example, in the immediate vicinity of hydrocarbon chains, the ordering of H_2O molecules takes place and leads to the formation of a spatial structure of water that is less susceptible to disturbances. Polar or ionic groups cause the opposite effect - a disturbance of the ordered structure of water.

Aggregation of the surfactant with the hydrophobic part reduces the contact area of its hydrocarbon fragments with water molecules, and thus the transition of a certain number of water molecules from a more ordered structure around these fragments to a less ordered structure in the bulk phase. Thus, micelles will form when the decrease in free enthalpy resulting from the exclusion of water molecules from the micelle core (i.e. from its hydrophobic interior) exceeds the increase in free enthalpy. The free enthalpy increase may be caused by entropy decrease due to the "ordering" of surfactant molecules into micelles and an increase in repulsion electrostatic, hydration and steric effects between the ionic (polar) groups of the surfactant resulting from the proximity of these groups in the micelle. $\Delta_{mic}G$ is a function of the number of individual surfactant molecules in the solution and the number of surfactant molecules in the aggregate (n), called the aggregation number. The $\Delta_{mic}G$ minimum is reached at a certain micelle size. The formation of micelles can also be considered from the point of view of the law of mass action. Assuming that the resulting micelles have the same size, and n is the number of aggregations, the micellization process can be represented by the equation:

$$nS \rightleftarrows S_n$$

Moreover, if the total surfactant concentration is denoted by c, and the degree of aggregation (i.e. the fraction of the total surfactant concentration contained in the micelles) by α, then the equilibrium constant K of the reaction between the two states of aggregation can be written as follows:

Assuming a certain value of K, it is possible to estimate the effect of surfactant concentration on the degree of aggregation for different values of n. When n is small, micelle formation occurs gradually, when $n \approx 50$ or more, aggregation occurs suddenly (Fig. 2).

When the number of aggregations is large, the introduction of successive portions of surfactant into the solution will initially increase the concentration of single surfactant molecules. When the CMC value is exceeded, the concentration of single molecules practically stops increasing, instead the concentration of micelles now increases. Reaching CMC is therefore accompanied by a step change in

the dependence of some physical properties of surfactant solutions on their concentration. They include e.g. electrical conductivity, turbidity, surface tension, viscosity, osmotic pressure. In addition, above the CMC, surfactant solutions show the ability to bring into solution substances that are sparingly soluble or insoluble in a given solvent (solubilization). For example, in the case of aqueous solutions, non-polar substances accumulate in the hydrophobic core of the micelles. Substances whose molecules contain a polar group, but which are not hydrated enough to dissolve in water, accumulate in the so-called the palisade layer (i.e. between the hydrophilic groups and the first few carbon atoms of the hydrophobic group of the surfactant) in such way that the polar groups face the aqueous phase.

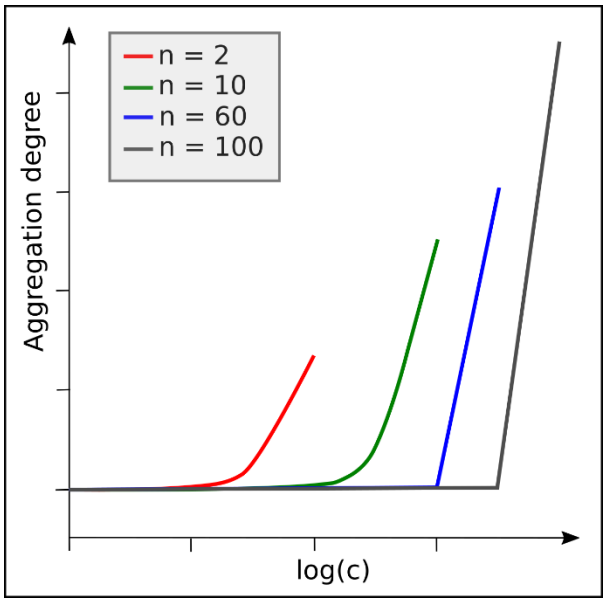

Fig. 2. Influence of surfactant concentration on the degree of its aggregation

Step changes in the properties of surfactant solutions accompanying micellization can be used to determine the CMC. Typically, the measured property is graphically represented as a function of concentration; the CMC is determined as shown in Figure 3.

The CMC value can also be determined by the solubilization method. For this purpose, water-insoluble dyes are often used by observing the color change of the solution associated with the solubilization of the dye in the micelles.

The factors affecting micellization, and thus also the CMC value, are primarily:

1. The structure of the surfactant. Generally, in aqueous media, the CMC decreases when the hydrophobicity of the surfactant increases. Ionic surfactants also have significantly higher CMC values than non-ionic surfactants containing the same hydrophobic groups.

2. The presence of an electrolyte in the solution. In aqueous solutions, the presence of an electrolyte reduces the CMC of a given surfactant, and this effect is particularly pronounced in the case of ionic surfactants. The electrolyte reduces the thickness of the ionic atmosphere around the ionic groups of the surfactant and, as a result, reduces the mutual electrostatic repulsion between them in the micelle. This, in turn, allows to increase the number of aggregations and lower the CMC.

3. The presence of various organic substances there in the solution. These substances either become incorporated into micelles, creating the so-called mixed micelles and lowering the CMC, or changing the interactions between the surfactant and the solvent (e.g. urea, formamide) increasing the CMC

4. Temperature. A temperature increase, on the one hand, reduces the hydration of hydrophilic groups of the surfactant, and on the other, causes disturbances in the ordering of water molecules surrounding the hydrophilic groups. Due to the opposing effect of these two effects on the micellization process, CMC is generally only slightly temperature dependent.

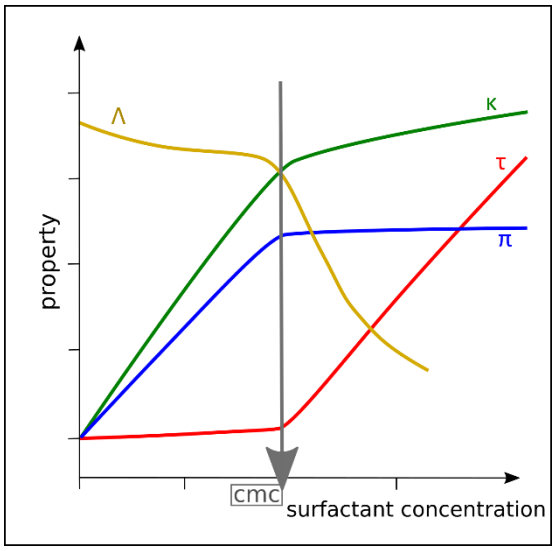

Fig. 3. Schematic representation of the dependence of some physical properties of the surfactant solution on its concentration (κ – electrolytic conductivity, τ – turbidity, π – osmotic pressure, Λ – molar conductivity)

Exercise

The aim of the exercise is to determine the CMC values of two ionic surfactants based on conductance measurements of their aqueous solutions at different concentrations.

Reagents

- $8{,}00 \cdot 10^{-2}$ M aqueous solution of sodium dodecyl sulphate (SDS, $CH_3\ (CH_2)_{11}\ OSO_3\ Na$, molar weight 288,38 D)
- $8{,}00 \cdot 10^{-3}$ M aqueous solution of cetyltrimethylammonium bromide (CTAB, $[CH_3\ (CH_2)_{15}\ N+\ (CH_3)_3]\ Br^-$, molar weight 364,46 D)

Performing the exercise

- Place a clean and dry beaker on a magnetic stirrer,
- Fix the probe with conductivity electrodes in it (so that the distance from the bottom of the beaker is approx. 2 cm)
- Pour a precisely measured 0.1 dm^3 of distilled water
- Add 0.001 dm^3 of the surfactant solution (V_S) from the burette. Each time, after introducing a portion of surfactant and thoroughly mixing, measure (after turning off the stirrer) the conductance G of the solution in the beaker. Put the results in table 1.

Table 1. Results of measurements and data analysis

surfactant	V_s [dm³]	G [S]	c_s [mol/dm³]	a_1	b_1	a_2	b_2	c_k^{CMC}

- The total volume of added surfactant solution should be 0.025 dm^3.

Results elaboration

- Calculate the final concentration (c_S) of the surfactant in the beaker after each addition of a portion of concentrated surfactant solution from the equation :

$$c_k = \frac{c_p V^S}{V + V^S}$$

, where c_p concentration of the added surfactant, V_s volume of the added surfactant solution,

- For each of the tested surfactants, plot the graph G = f(c_S),
- Find the inflection point of the resulting curve
- Using the least squares method, fit two straight lines to the obtained experimental points
  - Before the inflection point $y = a_1x + b_1$
  - After the inflection point $y = a_2x + b_2$

$$c_k^{CMC} = \frac{b_1 - b_2}{a_2 - a_1}$$

- Calculate the intersection of the fitted lines from equation The intercept obtained will be the c_K^{CMC} estimate.