DETERMINATION OF FREE ENERGY OF MICELLIZATION OF SODIUM DODECYL SULFATE

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Task VI-S

DETERMINATION OF FREE ENERGY OF MICELLIZATION OF SODIUM DODECYL SULFATE

I. Aim of the task

The aim of the task is the experimental determination of critical micelle concentration (CMC) of sodium dodecyl sulfate (SDDS) by spectrophotometric method and the calculation of its free energy of micellization.

II. Introduction

1. The micellization process. Critical micelle concentration of surfactants (CMC) and methods of its determination.
2. Types of micelles.
3. Thermodynamics of micellization.
4. UV-Absorption Spectroscopy Method.

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III. Theory

III. 1. The micellization process. Critical micelle concentration (CMC) of surfactants and methods of its determination

Surface active agents (surfactants) are the chemical compounds which consist of two parts of different properties: the hydrophilic head and the hydrophobic chain. They possess two characteristic physicochemical features. Even at their low concentration they tend to **adsorb** at different interfaces, e. g. the water-air one, effectively reducing the high surface tension of water (which is the most common solvent). At their higher concentration or more exactly over the so-called **critical micelle concentration (CMC)** surfactants spontaneously form the molecular aggregates of different shapes and sizes in the bulk phase of the solution. The critical micelle concentration can be determined on the basis of the measurements of various physicochemical properties of the solution (e. g. electrical conductivity, surface tension, light scattering, density or viscosity). At this concentration there is a break in almost every measurable physical property that depends on size or number of particles in the solution and it is shown by all types of surfactants: nonionic, anionic, cationic and zwitterionic in aqueous media [1].

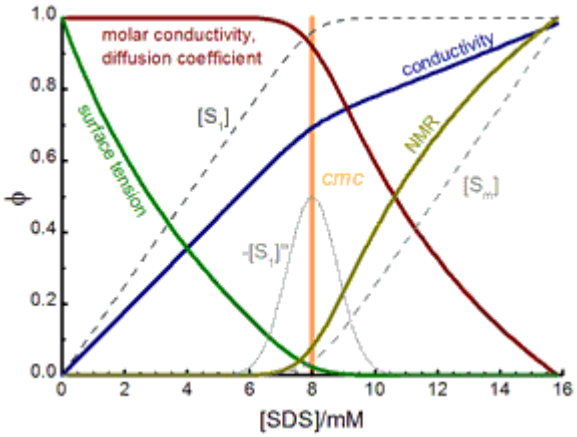


Fig. 1. The dependence between various physicochemical properties of the solution and surfactant (sodium dodecyl sulfate) concentration [2].

When surfactant molecules are dissolved in water, their hydrophobic groups distort the water structure and therefore increase the free energy of the system [1]. That is the reason why surfactant molecules adsorb at the interface in such a way that their hydrophobic chains are directed away from the solvent and the hydrophilic groups are oriented towards the aqueous phase. Because of that process, the free energy of the solution is minimized.

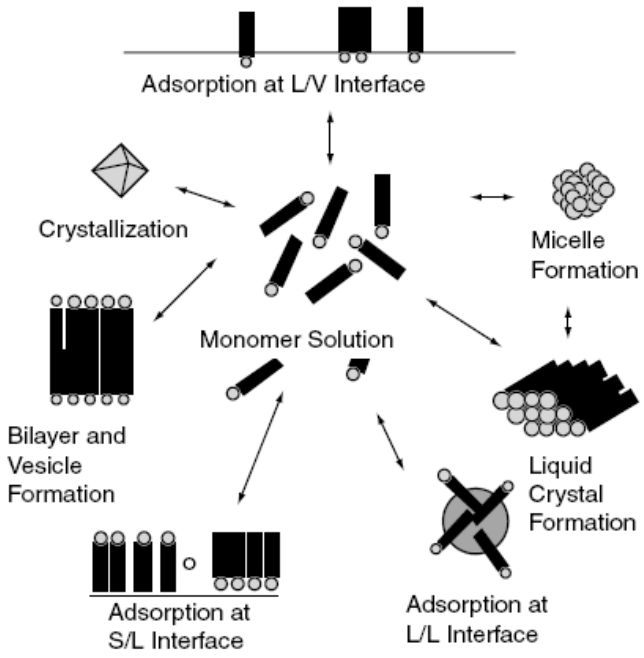


Fig. 2. The surface activity of surfactants [3].

The distortion of the solvent structure can also be decreased (and the free energy of the solution reduced) by the aggregation of the surfactant molecules into micelles with their hydrophobic groups directed toward the interior of the aggregate and their hydrophilic groups directed toward the solvent.

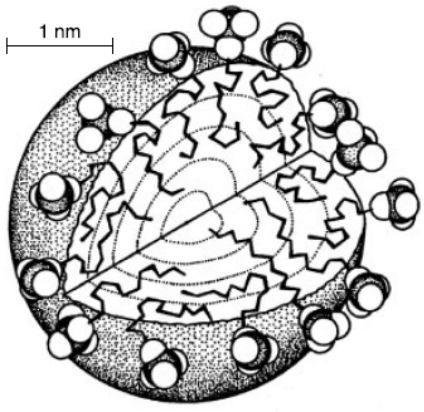


Fig. 3. Illustration of spherical micelle of sodium dodecyl sulfate [4].

Micellization is an alternative mechanism to adsorption at the interfaces for removing hydrophobic groups from contact with water and reducing the free energy of the system. If the distortion of the solvent structure solvent by the liophilic group is low (e.g., in water, when the hydrophobic group of the surfactant is short), then there is little tendency for micellization

to occur. This is often the case in nonaqueous solvents, and therefore micelles of the size comparable to those formed in aqueous media are seldom found in other solvents [1].

Table 1. List of CMC values of selected surfactants [5].

Surfactant	CMC[a]
Dodecylammonium chloride	$1.47 \cdot 10^{-2}$ M
Dodecyltrimethylammonium chloride	$2.03 \cdot 10^{-2}$ M
Decyltrimethylammonium bromide	$6.5 \cdot 10^{-2}$ M
Dodecyltrimethylammonium bromide	$1.56 \cdot 10^{-2}$ M
Hexadecyltrimethylammonium bromide	$9.2 \cdot 10^{-4}$ M
Dodecylpyridinium chloride	$1.47 \cdot 10^{-2}$ M
Sodium tetradecyl sulfate	$2.1 \cdot 10^{-3}$ M
Sodium dodecyl sulfate	$8.3 \cdot 10^{-3}$ M
Sodium decyl sulfate	$3.3 \cdot 10^{-2}$ M
Sodium octyl sulfate	$1.33 \cdot 10^{-1}$ M
Sodium octaonate	$4 \cdot 10^{-1}$ M
Sodium nonaonate	$2.1 \cdot 10^{-1}$ M
Sodium decaonate	$1.09 \cdot 10^{-1}$ M
Sodium undecaonate	$5.6 \cdot 10^{-2}$ M
Sodium dodecaonate	$2.78 \cdot 10^{-2}$ M
Sodium p-octylbenzene sulfonate	$1.47 \cdot 10^{-2}$ M
Sodium p-dodecylbenzene sulfonate	$1.2 \cdot 10^{-3}$ M
Dimethyldodecylamineoxide	$2.1 \cdot 10^{-3}$ M
$CH_3(CH_2)_9(OCH_2CH)_6OH$	$9 \cdot 10^{-4}$ M
$CH_3(CH_2)_9(OCH_2CH)_9OH$	$1.3 \cdot 10^{-3}$ M
$CH_3(CH_2)_{11}(OCH_2CH)_6OH$	$8.7 \cdot 10^{-5}$ M
$CH_3(CH_2)_7C_6H_4(CH_2CH_2O)_6$	$2.05 \cdot 10^{-4}$ M
Potassium perfluorooctanoate	$2.88 \cdot 10^{-2}$ M

[a] *in mol/dm^3 (M) or mol/kg H_2O (m)*

The critical micelle concentration of surfactant is not a fixed value but it may change under the influence of many factors. Among these factors are [1]:

- the structure of surfactant,
- the presence of electrolyte in the solution,
- the presence of organic additives in the solution,
- the presence of a second liquid phase,
- temperature.

III. 2. Types of micelles

Micelles of a surfactant formed in its solution can have different shapes and sizes. Various properties of the surfactant solution, e. g. its viscosity, cloud point or capacity to solubilize water-insoluble material result from their shapes. The major types of micelles are [1]:

- relatively small, **spherical** structures (aggregation number <100),
- elongated **cylindrical**, **rod-like** micelles with hemispherical ends (prolate ellipsoids),
- large, flat, **lamellar** micelles (**disc-like** extended oblate spheroids),
- **vesicles** – more or less spherical structures consisting of **bilayer** lamellar micelles arranged in one or more concentric spheres.

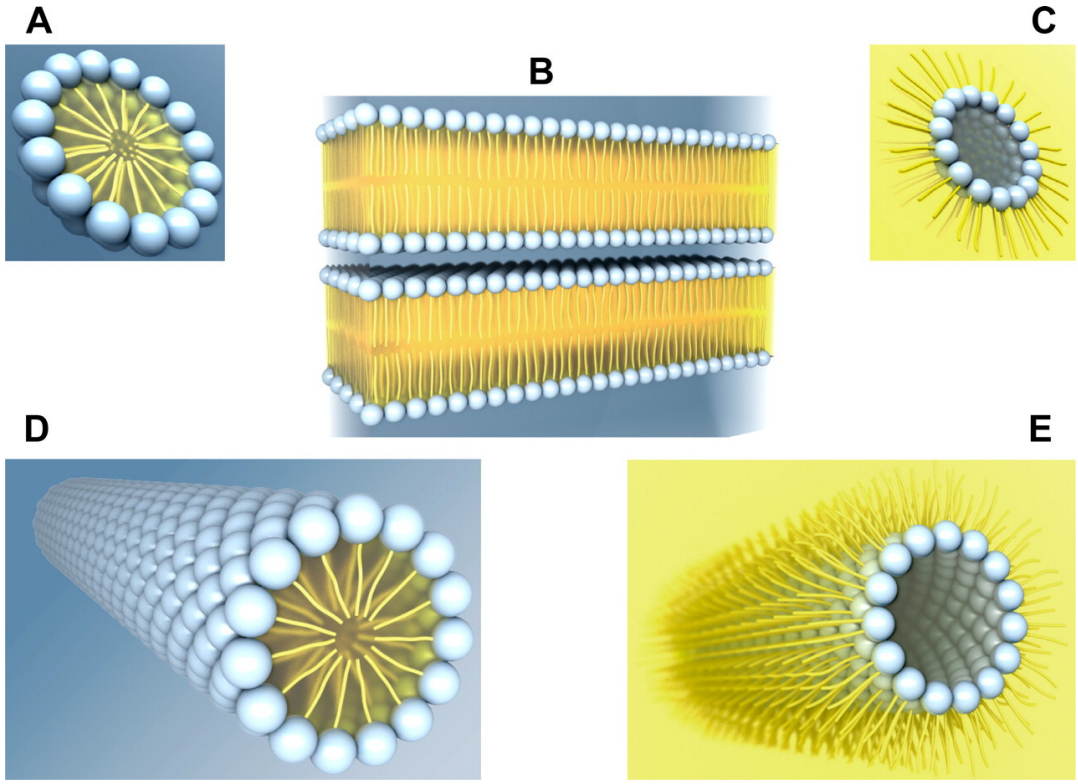
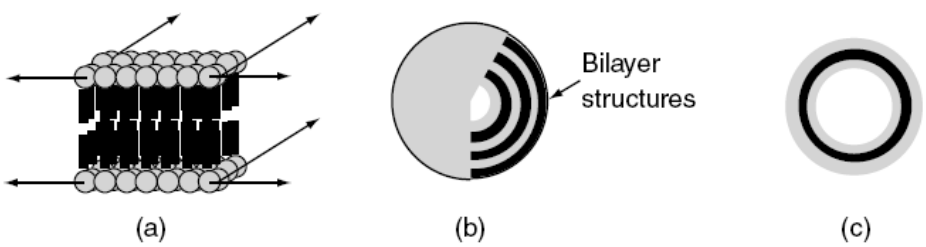


Fig. 4. The most important micelle shapes: (A) normal spherical; (B) lamellar (bilayer); (C) inverted spherical; (D) cylindrical; (E) inverted cylindrical [6].



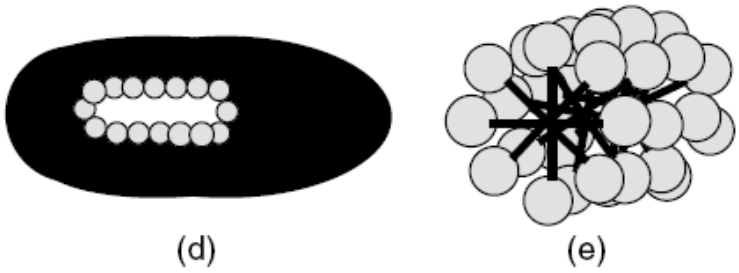


Fig. 5. Other possible micelle shapes: (a) extended bilayer structures;(b) closed multiple bilayer vesicles; (c) closed single bilayer vesicles;(d) oblate ellipsoidal; (e) prolate cylindrical or rod-shaped [3].

In aqueous media, the surfactant molecules are oriented, in all these structures, with their polar heads predominantly directed toward the aqueous phase and their hydrophobic groups away from it. In vesicles, there will also be an aqueous phase in the interior of the micelle. The interior region of the micelle, containing the hydrophobic groups, has a radius approximately equal to the length of the fully extended hydrophobic chain. The water molecules can probably penetrate into the micelle beyond the hydrophilic head groups and the first few methylene groups of the hydrophobic chain adjacent to the hydrophilic head are often considered as a hydration sphere of the micelle. Thus the interior region of the micelle can be divided into two parts: an outer core that may be penetrated by water and an inner core from which water is excluded.

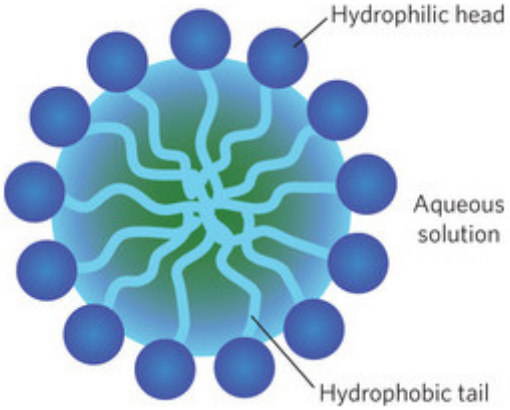


Fig. 6. The structure of spherical micelle in the aqueous solution [7].

In nonpolar solvents, **reversed micelles** of surfactant are formed. The polar heads of surfactant form the interior region of the micelle surrounded by an outer region containing the hydrophobic groups and nonpolar solvent. Such micelle contains usually a few water molecules which stabilize it. Dipole–dipole interactions hold the hydrophilic heads together in the core.

The shape, size and aggregation number of the micelle depend on different factors such as surfactant structure and concentration in the solution, temperature or the presence of

various additives in the liquid phase. Because of these factors, the micelle structure can change from spherical through rod- or disc-like to lamellar.

Israelachvili, Mitchell, and Ninham developed a theory of micellar structure, based upon the geometry of various micellar shapes and the space occupied by the hydrophilic and hydrophobic groups of the surfactant molecules. The micelle shape can be determined by the **'packing parameter'** $V_H / l_C a_0$ where V_H is the volume occupied by the hydrophobic groups in the micellar core, l_C is the length of the hydrophobic group in the core and a_0 is the cross-sectional area occupied by the hydrophilic group at the micelle–solution interface [1].

Table 2. Dependence of the micelle size on the value of the packing parameter [8].

Packing parameter	General surfactant type	Expected aggregate structure
0.33	Single-chain surfactants with large head groups	Spherical or ellipsoidal micelles
0.33-0.5	Single-chain surfactants with small head groups, or ionics in the presence of large amounts of electrolyte	Large cylindrical or rod-shaped micelles
0.5-1.0	Double-chain surfactants with large head groups and flexible chains	Vesicles and flexible bilayer structures
1.0	Double-chain surfactants with small head groups or rigid, immobile chains	Planar extended bilayers
>1.0	Double-chain surfactants with small head groups, very large and bulky hydrophobic groups	Reversed or inverted micelles

According to Tanford [1]:

$$l_C \leq 1.5 + 1.265n \text{ (Å)} \quad (1)$$

and

$$V_H = 27.4 + 26.9n \text{ (Å}^3\text{)} \quad (2)$$

where n is the number of carbon atoms of the chain embedded in the micellar core (the total number of carbon atoms in the chain, or one less).

Fig. 7. Illustration of the quantities in the packing parameter [3].

The value of l_C depends on the extension of the chain and for saturated, straight chains it may be 80% of the fully extended chain. The value of a_0 depends on the structure of the hydrophilic group, electrolyte content, temperature, pH and the presence of additives in the solution. Such additives as medium-chain alcohols (which are solubilised in the vicinity of head groups) increase the value of a_0. In the case of ionic surfactants, a_0 decreases with the increase of the electrolyte concentration in the solution because of the compression of the electrical double layer and with the increase of the surfactant concentration because that increases the content of counterions in the solution. This decrease of a_0 value favours the change in the shape of the micelle from spherical to cylindrical. Some ionic surfactants form long, wormlike micelles in aqueous solutions, especially in the presence of electrolyte or other additives which decrease the repulsion between ionic heads. When the value of the packing parameter is about 1, a surfactant can form normal lamellar micelles in the aqueous solvent or reverse micelles in the nonpolar solvents. When the value of $V_H / l_C a_0$ increases much over 1, reverse micelles in the nonpolar solvents become less asymmetrical and more spherical in shape.

In aqueous solutions, surfactants having bulky or loosely packed hydrophilic groups and long, thin hydrophobic groups form rather **spherical micelles**, while those with short, bulky hydrophobic groups and small, close-packed hydrophilic groups tend to form **lamellar** or **cylindrical micelles**. Surfactants which have two long alkyl chains (e.g. fatty acid esters of sucrose, especially diesters) can (under the influence of sonification in the aqueous media) form **vesicles**. Vesicles are curved, closed lamellar bilayers and for their formation the value of the packing parameter must be close to 1.

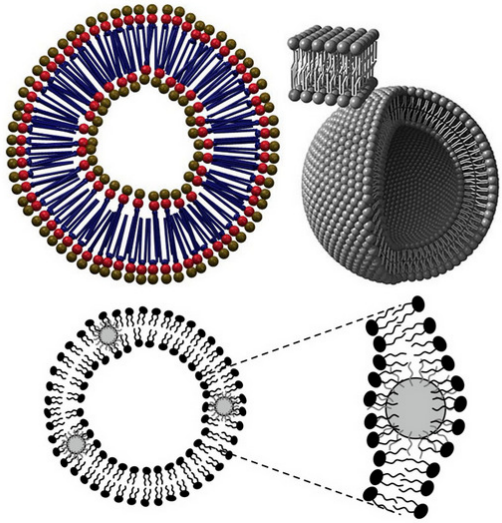


Fig. 8. Lipid vesicles [9].

When there is a sufficient number of micelles in the solution, they start to pack together in a number of geometric arrangements, which depend on the shape of individual micelles. These arrangements are called **liquid crystals**. They have the molecular arrangement of solid

crystals but the mobility of liquids. They increase considerably the viscosity of the solution. Spherical micelles form cubic liquid crystals, cylindrical micelles pack to form hexagonal liquid crystals, and lamellar micelles form lamellar liquid crystals.

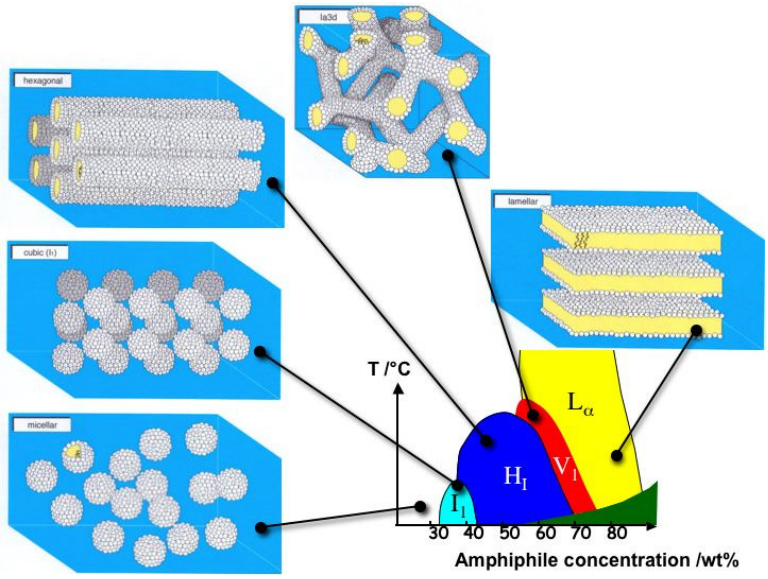


Fig. 9. Scheme of the amphiphiles aggregation into micelles (then into lyotropic liquid crystalline phases) as a function of concentration and temperature [10].

III. 3. Thermodynamics of micellization

As it was mentioned at the beginning, micelle formation is a highly important process in everyday life (detergency) as well as in many fields of industry (froth flotation) and medicine (drug delivery). Based on a great amount of data it can be stated that this process is spontaneous, so the free enthalpy (or Gibbs free energy) of this process should be negative. It is known that:

$$\Delta G = \Delta H - T\Delta S \tag{3}$$

If ΔG has a negative value, then $\Delta H - T\Delta S < 0$ and $T\Delta S > \Delta H$, so the contribution of entropy to the Gibbs free energy has to have a high positive value. There are two processes which strongly affect the ΔG value:

a) the addition of surfactant to water is connected with the ordering of water molecules around the hydrophobic groups of the surface active agent which causes the relatively low motion possibility of the hydrophobic tail of surfactant in the presence of polar water molecules. This process causes the negative change of entropy.
b) the hydrophobic parts of surfactant molecules in the micelles are oriented towards the aggregate and as a consequence, water molecules surrounding the hydrophobic tail of surfactant take a less structured orientation again so the entropy of the solvent increases.

Entropy of micellization has a positive value $\Delta S = S_{micelle} - S_{solution}$, because the entropy of micellar system is higher than that of the solution in which the micelles do not form. The attraction of the hydrophobic groups during micellization accompanied by the increase of the entropy of the polar solvent is called the **hydrophobic interaction.**

Because the micellization process usually occurs at the constant: temperature, pressure and volume of the system, it can be stated that the free enthalpy of micellization is equal to the free energy of micellization (Gibbs free energy is equal to Helmholtz free energy $\Delta G = \Delta H$). To deal with micelle formation, two general approaches are applied [4]. The first approach treats micelles as a single phase and is called **phase separation model**. Here, micelle formation is considered as a phase separation phenomenon and the CMC is the saturation concentration of the amphiphile in the monomeric state whereas the micelles constitute the separated pseudophase. Above CMC, a phase equilibrium exists with a constant activity of surfactant in the micellar phase. In the second approach, micelles and single surfactant molecules or ions are considered to be in the association–dissociation equilibrium. This is called **the mass action model**. In its simplest form, a single equilibrium constant is used to treat the micellization process.

III. 3.1. Phase separation model

In the phase separation model, the chemical potential of surfactant in the micellar state is assumed to be constant, at any temperature, and can be treated as the standard chemical potential (μ_m^0) [4]. In the equilibrium between micelles and monomers of surfactant it can be expressed in the following form:

$$\mu_m^0 = \mu_1^0 + RT \ln a_1 \tag{4}$$

where μ_1^0 is the standard chemical potential of the surfactant monomer, a_1 is its activity in the solution, R is the gas constant and T is the absolute temperature.

Knowing that $a_1 = f_1 \cdot X_1$ (where f is the activity coefficient and X_1 is the surfactant mole fraction in the solution), the following equation is obtained:

$$\mu_m^0 = \mu_1^0 + RT \ln f_1 \cdot X_1 \tag{5}$$

In the equilibrium state the difference between the standard chemical potential of surfactant in the micelle and in the monomeric form is equal to the standard free energy of micellization per mol of monomer:

$$\Delta G_m^0 = \mu_m^0 - \mu_1^0 = RT \ln f_1 \cdot X_1 \tag{6}$$

The micellization process occurs usually at low surfactant concentration (in very dilute solutions), so $f_1 \approx 1$ and:

$$\Delta G_m^0 = RT \ln X_1 \tag{7}$$

If X_1 is equal to the mole fraction of surfactant at which the micellization occurs (X_1^{CMC}), then:

$$X_1^{CMC} = \frac{CMC}{CMC + \omega} \tag{8}$$

where CMC is the critical micelle concentration of surfactant in mol/dm^3 and ω is the number of water moles in 1 dm^3 of the solution.

In most cases the value of the critical micelle concentration of surfactant is lower than 1 x 10^{-2} M, then $X_1^{CMC} = CMC/\omega$ and Eq. (8) can be written in the following form:

$$\Delta G_m^0 = RT \ln \frac{CMC}{\omega} = RT \ln CMC - RT \ln \omega \tag{9}$$

Eq. (9) is usually applied in the simpler, shorter form:

$$\Delta G_m^0 = RT \ln CMC \tag{10}$$

III. 3.2. Mass action model

In the mass action model, a dissociation-association equilibrium between the surfactant monomers and the micelles is assumed. The equilibrium state of the transfer of n molecules of nonionic surfactant from the monomeric (S) to micellar (S_n) form and reversely ($nS \leftrightarrow S_n$) can be described by the equilibrium constant (K_m) in the following form [4]:

$$K_m = \frac{[S_n]}{[S]^n} \tag{11}$$

The standard free energy of the surfactant transfer from the monomeric to the micellar form per monomer ($\Delta G/n$) is given by the following equation:

$$-\Delta G_m^0 = \frac{\Delta G}{n} = \frac{RT}{n} \ln K_m = \frac{RT}{n} \ln[S_n] - RT \ln[S] \tag{12}$$

For many micellar systems, n >50 and the term $\frac{RT}{n} \ln[S_n]$ may be neglected, so:

$$\Delta G_m^0 = RT \ln[S] = RT \ln \frac{CMC}{\omega} = RT \ln CMC - RT \ln \omega \tag{13}$$

If we neglect the term $RT \ln \omega$, we obtain Eq. (10).

The mass action model can be also applied to the ionic surfactants, in which micelles attract a substantial proportion of counterions into an attached layer [4].

For the surfactants of the type AB, which dissociate in water in the ions A^+ and B^-, the following equation is fulfilled:

$$K_m = \frac{[B_n^{p-}]}{[B^-]^n [A^+]^{(n-p)}} \tag{14}$$

The standard free energy of micellization of surfactant AB is related to the equilibrium constant K_m and can be expressed in the following form:

$$-\Delta G_m^0 = \frac{RT}{n} \ln \frac{\left[B_n^{p-}\right]}{\left[B^-\right]^n \left[A^+\right]^{(n-p)}} \tag{15}$$

For n >50, the term $\frac{RT}{n} \ln\left[B_n^{p-n}\right]$ may be neglected, so:

$$\Delta G_m^0 = \left(2 - \frac{p}{n}\right) RT \ln\left[B^-\right] = \left(2 - \frac{p}{n}\right) RT \ln X_1^{CMC} = \left(2 - \frac{p}{n}\right) RT \ln \frac{CMC}{\omega} \tag{16}$$

where p/n is the dissociation degree of the surfactant AB in the micelle.

For many ionic surfactants, the degree of dissociation equals approximately 0.2, so:

$$\Delta G_m^0 = 1.8 \ln \frac{CMC}{\omega} \tag{17}$$

Assuming that the micelle is undissociated and neglecting the term $(2 - p/n)RT \ln \omega$ we obtain the common expression for the calculation of free energy of micellization of ionic surfactants of the AB type:

$$\Delta G_m^0 = 2RT \ln CMC \tag{18}$$

Thermodynamic functions which characterize the process of micelle formation can be presented as a sum of the contributions of particular structural elements of the surfactant molecule:

$$\Delta G_m^0 = \Delta G_m^0(CH_3) + (N-1)\Delta G_m^0(CH_2) + \Delta G_m^0(HG) \tag{19}$$

where $\Delta G_m^0(CH_3)$ is the contribution of the terminal CH_3 group, $\Delta G_m^0(CH_2)$ is the contribution of the methylene group, $\Delta G_m^0(HG)$ is the contribution of the polar group to the changes of the free energy of spherical micelle formation, N is the number of carbon atoms in the unbranched hydrocarbon chain. Assuming that for the ionic surfactant the contribution of the structural elements of its polar group (i.e. ion and counterion) is additive, Eq. (19) can be written in the following form:

$$\Delta G_m^0 = \Delta G_m^0(CH_3) + (N-1)\Delta G_m^0(CH_2) + \Delta G_m^0(+) + \Delta G_m^0(-) \tag{20}$$

where $\Delta G_m^0(+)$ is the contribution of cation and $\Delta G_m^0(-)$ is the contribution of anion.

For better understanding of the micellization process of a given surfactant, the standard enthalpy (ΔH_m^0) and entropy (ΔS_m^0) of micellization should be known.

If ΔH_m^0 is constant in the studied temperature range, the standard entropy of micellization of a nonionic surfactant can be determined from the following equation [8]:

$$\Delta S_m^0 = -\frac{d\Delta G_m^0}{dT} = -RT \frac{d \ln(CMC)}{dT} - R \ln(CMC) \tag{21}$$

If ΔS_m^0 is constant in the studied temperature range, then [8]:

$$\Delta H_m^0 = -\frac{T^2 \frac{d\Delta G_m^0}{dT}}{dT} = -RT^2 \frac{d\ln(CMC)}{dT} \quad (22)$$

Table 3 presents the values of the contributions of the chosen structural elements of the ionic surfactant molecule to the free energy of the micelle formation.

Table 3. The contribution of the chosen structural elements to ΔG_m^0 [11].

Structural element	Temperature [°C]	Contribution [kJ/mol]
(CH_2) group in the homologous series $C_nH_{2n+1}OSO_3^-$	25	–1.569
(CH_2) group in the homologous series $C_nH_{2n+1}SO_3^-$	40	–1.766
(CH_2) group in the homologous series $[C_nH_{2n+1}N(CH_3)_3]^+$	25	–1.757
(CH_2) group in the homologous series $C_nH_{2n+1}N(CH_2CH_2OH)_2O$	25	–2.059
terminal (CH_3) group	25	–3.39
$–COO^-$	25	–1.08
$–OSO_3^-$	25	–5.234
Na^+	25	1.135
K^+	25	0.364
Cl^-	25	2.646
Br^-	25	1.943

III. 4. UV-Absorption Spectroscopy Method

As it was noted earlier, there are many methods of determination of the critical micelle concentration (CMC) of surfactants. One of them is the **UV-absorption spectroscopy method**. It is based on tautomerism of **1-phenyl-1,3-butadione (BZA)**. BZA can occur in two tautomeric forms: ketonic and enolic. In aqueous solution, BZA exists as a mixture of both forms: the keto form comprises about 62.5%. The content of enolic form is much greater in the nonpolar solvents, such as cyclohexane, than in the polar or hydrogen-bond donor solvents, such as water or short-chain alcohols.

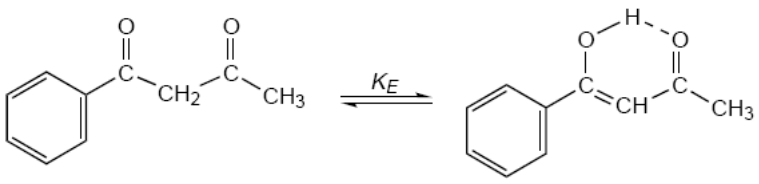


Fig. 10. BZA transition from the ketonic to enolic form [12].

If a surfactant is added to the aqueous solution in the concentration lower than its CMC, BZA is present in the solution mainly in the keto form. When the surfactant concentration increases above its CMC, its micelles start to form in the solution and BZA molecules migrate to the hydrophobic core of the micelle in which they exist mainly in the enol form. The transition of BZA from the ketonic form (in the aqueous solution) to the enolic one (in the interior of the micelle) occurs sharply at the surfactant concentration equal to its CMC and can be tracked by the measurement of the absorption of UV light.

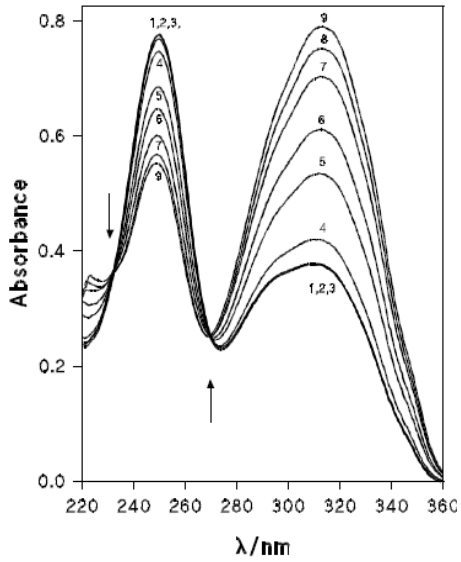


Fig. 11. The dependence of BZA absorbance in the surfactant solutions of different concentrations [12].

Figure 11 shows the effect the increasing surfactant concentration on the UV-absorption spectrum of the aqueous BZA solutions. In the diluted solutions of surfactant below its CMC (curves 1-3), so when the surfactant molecules are present in the monomeric form in the solution, no changes of BZA absorbance are observed. Above the CMC, the absorption band centered at λ=312 nm (due to the enolic form) increases and in parallel, the absorption band centered at 250 nm (mainly due to the keto form) diminishes.

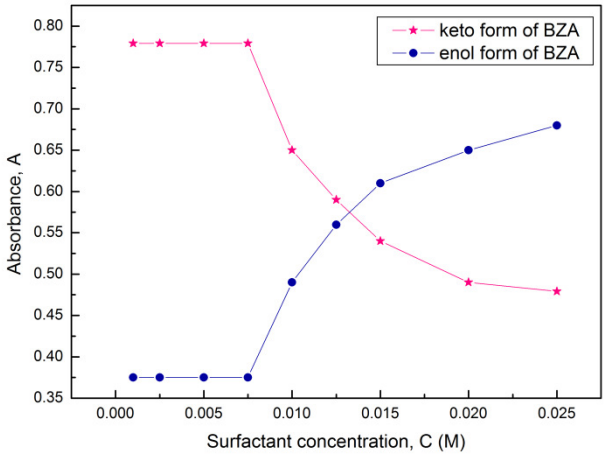


Fig. 12. The dependence between the solution absorbance and the surfactant concentration [13].

IV. Experimental

A. Devices and materials

1. **Device:** spectrophotometer Helios
2. **Equipment:**
   - quartz cell – 2 u,
   - measuring flask: 10 cm^3– 2 u,
   - graduated pipette: 2 cm^3– 1 u,
   - full pipette: 0.5 cm^3 – 1 u.
3. **Materials:**
   - aqueous solution of 1-phenyl-1,3-butadione (BZA),
   - aqueous solution of sodium dodecyl sulfate (SDDS) ($C_{12}H_{25}SO_4Na$): 0.1 M.

B. Program

1. Preparation of the aqueous solutions of sodium dodecyl sulfate and the aqueous solutions of sodium dodecyl sulfate with BZA.
2. Absorbance measurements of the aqueous solutions of sodium dodecyl sulfate with BZA using the Helios spectrophotometer.

C. Use of devices

Fig. 13 presents the spectrophotometer Helios.

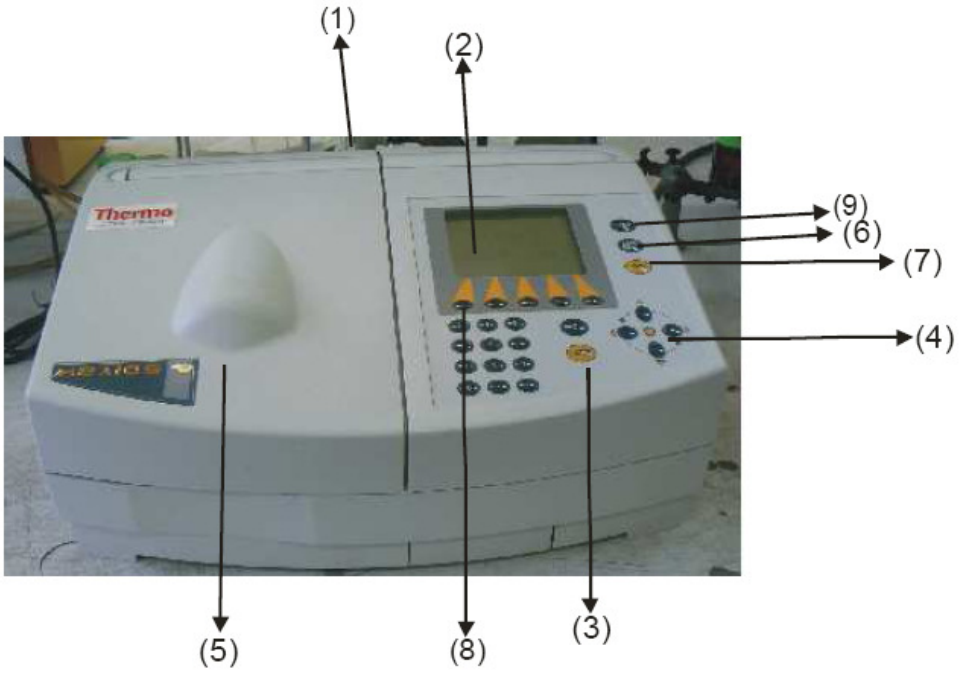


Fig. 13. Spectrophotometer Helios [13].

1. Turn the instrument on. The power switch is at the back of the instrument (1). Wait about 3 minutes until the instrument is ready and the optical tests are done.
2. On the display (2), choose [**MENU**] by pressing one of the function keys (8), then choose [**METODY**] *(methods)* and confirm by pressing [**ENTER**] (3).
3. Use the arrow keys (4) to choose [**WIDMO BZA**] *(BZA spectrum)*, then press [**ENTER**] (3).
4. Choose [**WCZYTAJ**] *(load)*, then press [**ENTER**] again.
5. Wait until the instrument is ready (the message [**aparat zajęty proszę czekać**] disappears], then open the sample compartment (5) and put the cell with the SDDS solution in the holder.
6. **Do not touch the transparent walls of the cell!**
7. Close the sample compartment and press [**ZERO BASE**] (6).
8. When the measurement is finished (the message [**aparat zajęty proszę czekać**] disappears], remove the cell with a standard solution from a holder and insert a cell with the studied solution (SDDS+BZA), then press [**RUN**] (7).
9. When the measurement is finished (the message [**aparat zajęty proszę czekać**] disappears], choose [**POKAŻ WYNIKI**] *(show results)* by pressing one of the function keys (8).
10. Write down the results for the appropriate wavelengths from the instrument display (2).
11. Rinse the cells by the next standard solution (with the increasing SDDS concentration) and the SDDS+BZA one, respectively, and pour the solutions into the cells.
12. Measure the absorbance of the solutions according to the steps described above.
13. After all the measurements, press [**HOME**] (9) and turn the instrument off by pressing (1).
14. Clean the cells and flasks with the running water, then rinse them with the distilled water.

D. Methods

1. Prepare the standard solution by pouring (with the pipette) 0.1 cm^3 of the stock solution (0.1 M) of sodium dodecyl sulfate to the measuring flask (10 cm^3) marked as (**0**). Then fill the flask to the mark with distilled water. After the measurement, rinse the flask with distilled water before the preparation of the next solution.
2. Prepare an aqueous solution of SDDS with BZA. For that purpose pour (with the pipette) 0.1 cm^3 of the stock solution (0.1 M) of sodium dodecyl sulfate to the measuring flask (10 cm^3) marked as (**1**). Then add 0.5 cm^3 of BZA and fill the flask to the mark with distilled water. After the measurement, rinse the flask with distilled water before the preparation of the next solution.
3. Measure the absorbance of the solutions using Helios spectrophotometer according to the steps described in the previous paragraph.
4. Similarly to point 1, prepare the next standard solutions by pouring (with the pipette) to the measuring flask (10 cm^3) marked as (**0**): 0.25; 0.5; 0.75; 1; 1.25; 1.5; 2 and 2.5 cm^3 of

the stock solution (0.1 M) of sodium dodecyl sulfate, respectively. Then fill the flask to the mark with distilled water.

5. Similarly to point 2, prepare the next aqueous solutions of SDDS with BZA by pouring (with the pipette) to the measuring flask (10 cm^3) marked as (**1**): 0.25; 0.5; 0.75; 1; 1.25; 1.5; 2 and 2.5 cm^3 of the stock solution (0.1 M) of sodium dodecyl sulfate, respectively. Then add 0.5 cm^3 of BZA and fill the flask to the mark with distilled water.
6. After all the measurements, pour the solutions to the sink, then clean the cells and flasks with the running water and rinse them with the distilled water.

NOTICE: For each measurement use the standard solution of SDDS at the same concentration as in the studied solution (the solution of SDDS with BZA)!

E. Results and conclusions

1. Calculate the concentration (C) of the prepared solutions of sodium dodecyl sulfate (SDDS).
2. Draw the curves of the dependence between the solution absorbance and the concentration of sodium dodecyl sulfate ($A = f(C)$) for both absorbance peaks.
3. At the inflection point of the curve ($A = f(C)$), read the value of SDDS concentration (which corresponds to the critical micelle concentration (CMC) of SDDS).
4. Calculate the average value of critical micelle concentration of SDDS on the basis of two obtained values of CMC.
5. Using the appropriate equation (18), calculate the free energy of micellization of SDDS.
6. Using Eq. (20) and the data from Table 3 calculate the theoretical value of free energy of micellization of SDDS and compare it with the experimental value determined in the previous point.