Task No. 3

THE INFLUENCE OF SELECTED PARAMETERS ON CRITICAL MICELLE CONCENTRATION OF IONIC SURFACTANTS

I.   Task purpose

The purpose of this task is estimation of the critical micelle concentration of ionic surfactant with different chain length and at various temperatures using the conductometric titration method.

II.   Basic issues

1.   Surfactants and their classification.

2.   Critical micelle concentration.

3.   Influence of various parameters on CMC.

4.   Conductometry.

References

1. P.W. Atkins, "*Physical chemistry*", 2001.
2. M.J. Rosen "*Surfactants and Interfacial Phenomena*" (3rd ed.). Hoboken, New Jersey: John Wiley & Sons, 2004.

Surfactants have a characteristic molecular structure consisting of a structural group that has very little attraction for the solvent, known as a *lyophobic group* (surfactant "tail"), together with a group that has strong attraction for the solvent, called the *lyophilic group* (surfactant "head"). This is known as an *amphipathic* structure – see Fig. 1.
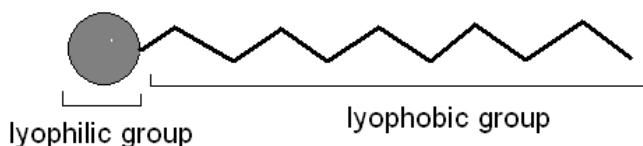

lyophilic group   lyophobic group

Fig. 1. Structure of surfactant molecule.

The word "amphiphile" was coined by Paul Winsor 50 years ago. It comes from two Greek roots: the prefix "*amphi*" means "double", "from both sides", "around", as in amphitheater or amphibian and the root "*philos*" expresses friendship or affinity, as in "philanthropist" (the friend of man), "hydrophilic" (compatible with water), or "philosopher" (the friend of wisdom or science).
An amphiphilic substance exhibits a double affinity, which can be defined from the physico-chemical point of view as a polar-apolar duality. A typical amphiphilic molecule consists of two parts: on the one hand a polar group which contains heteroatoms such as O, S, P, or N, included in the functional groups such as alcohol, thiol, ether, ester, acid, sulfate, sulfonate, phosphate, amine, amide etc… On the other hand, an essentially apolar group which is in general a hydrocarbon chain of the alkyl or alkylbenzene type, sometimes with halogen atoms and even a few nonionized oxygen atoms.

The polar portion exhibits a strong affinity for polar solvents, particularly water, and it is often called "hydrophilic" part or" hydrophile". The apolar part is called hydrophobe or lipophile, from the Greek roots "*phobos*" (fear) and "*lipos*" (grease). The following formula shows an amphiphilic molecule which is commonly used in shampoos (sodium dodecyl sulfate):

$$(CH_3- CH_2\ CH_2\ CH_2\ CH_2\ CH_2\ CH_2\ CH_2\ CH_2\ CH_2\ CH_2\ CH_2\ \text{-O-SO}_3)^- Na^+$$
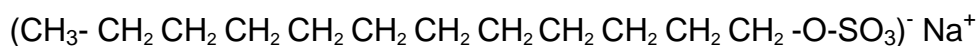
Sodium Dodecyl Sulfate.

Because of its dual affinity, an amphiphilic molecule does not feel "at ease" in any solvent, be it polar or non polar, since there is always one of the groups which "does not like" the solvent environment. This is why amphiphilic molecules exhibit a very strong tendency to migrate to interfaces or surfaces and to orientate so that the polar group lies in water and the apolar group is placed out of it, and eventually in oil.

The term *surfactant* is a blend of "*surface active agent*". It designates a substance which exhibits some superficial or interfacial activity. It is worth remarking that all amhiphiles do not display such activity; in effect, only the amphiphiles with

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more or less equilibrated hydrophilic and lipophilic tendencies are likely to migrate to the surface or interface. It does not happen if the amphiphilic molecule is too hydrophilic or too hydrophobic, in which case it stays in one of the phases.

A surfactant is a substance that, when present at low concentration in a system, has the property of adsorbing onto the surfaces or interfaces of the system and of altering to a marked degree the surface or interfacial free energies of those surfaces.

The term *interface* indicates a boundary between any two immiscible phases and the term *surface* denotes an interface where one phase is a gas.

The *interfacial free energy* is the minimum amount of work required to create that interface. The interfacial free energy per unit area is what we measure when we determine the interfacial tension between two phases. It is the minimum amount of work required to create unit area of the interface or to expand it by unit area. The interfacial (or surface) tension is also a measure of the difference in nature of the two phases meeting at the interface. The greater dissimilarity in their nature, causes the greater the interfacial tension between them.

The tail of surfactants can be:

a) hydrocarbon chain: aromatic hydrocarbons (arenes), alkanes (alkyl), alkenes, cycloalkanes, alkyne-based;

b) alkyl ether chain:
- ethoxylated surfactants: polyethylene oxides are inserted to increase the hydrophilic character of a surfactant;
- propoxylated surfactants: polypropylene oxides are inserted to increase the lipophilic character of a surfactant;

c) fluorocarbon chain: fluorosurfactants;

d) siloxane chain: siloxane surfactants.

Surfactant can have also two tails (double chained surfactants) and they tend to associate as a bilayer instead. It is worth noting that these bilayers are the structural skeleton of many biological membranes in plants and animals, as those produced by phospholipid association.

The structure of surfactants influences their properties like solubility in water or organic solvents. Increase in the length of the hydrophobic group decreases the solubility of the surfactant in water and increases its solubility in organic solvents. It causes closer packing of the surfactant molecules at the interface (provided that the area occupied by the hydrophilic group at the interface permits it), increases the tendency of the surfactant to adsorb at an interface or to form aggregates, called micelles, increases the melting point of the surfactant and of the adsorbed film and the tendency to form liquid crystal phases in the solution, and increases the sensitivity of the surfactant, if it is ionic, to precipitation from water by counterions. The introduction of branching or unsaturation into the hydrophobic group increases the solubility of the surfactant in water or in organic solvents (compared to the straight-chain, saturated isomer), decreases the melting point of the surfactant and of the adsorbed film, causes looser packing of the surfactant molecules at the interface (the cis isomer is particularly loosely packed; the trans isomer is packed almost as closely as the saturated isomer) and inhibits liquid crystal phase formation in solution, may decrease biodegradability in branched-chain compounds, and may increase thermal instability. Poly(oxypropylene)

units increase the hydrophobic nature of the surfactant, its adsorption onto polar surfaces, and solubility in organic solvents. Poly(oxyethylene) units decrease the hydrophobic character of the surfactant.

Surfactants can be classified by the presence of formally charged groups in its head. A non-ionic surfactant has no charge groups in its head. The head of an ionic surfactant carries a net charge. If the charge is negative, the surfactant is more specifically called anionic; if the charge is positive, it is called cationic. If a surfactant contains a head with two oppositely charged groups, it is termed zwitterionic.

Selected surfactants from several groups [1]:

A. Anionic:
- a) Sulfates:
  - alkyl sulfates: ammonium lauryl sulfate, sodium lauryl sulfate (SDS);
  - alkyl ether sulfates: sodium laureth sulfate, also known as sodium lauryl ether sulfate (SLES), sodium myreth sulfate;
- b) Sulfonates:
  - dioctyl sodium sulfosuccinate;
  - sulfonate fluorosurfactants: perfluorooctanesulfonate (PFOS), perfluorobutanesulfonate;
  - alkyl benzene sulfonates;
- c) Phosphates:
  - Alkyl aryl ether phosphate
  - Alkyl ether phosphate
- d) Carboxylates:
  - Alkyl carboxylates: Fatty acid salts (soaps): sodium stearate;
  - Sodium lauroyl sarcosinate;
  - Carboxylate fluorosurfactants: perfluorononanoate, perfluorooctanoate (PFOA or PFO).

B. Cationic:
- a) pH-dependent primary, secondary or tertiary amines (primary amines become positively charged at pH < 10, secondary amines become charged at pH < 4), e.g. octenidine dihydrochloride;
- b) Permanently charged quaternary ammonium cation:
  - Alkyltrimethylammonium salts: cetyl trimethylammonium bromide (CTAB), cetyl trimethylammonium chloride (CTAC);
  - Cetylpyridinium chloride (CPC);
  - Polyethoxylated tallow amine (POEA);
  - Benzalkonium chloride (BAC);
  - Benzethonium chloride (BZT);
  - 5-Bromo-5-nitro-1,3-dioxane;
  - Dimethyldioctadecylammonium chloride;
  - Dioctadecyldimethylammonium bromide (DODAB).

C. Zwitterionic (amphoteric): based on primary, secondary or tertiary amines or quaternary ammonium cation with:
- a) Sulfonates:

- 3-[(3-Cholamidopropyl)dimethylammonio]-1-propanesulfonate (CHAPS);

b) Carboxylates:
- Amino acids;
- Imino acids;
- Betaines;

c) Phosphates:

- Lecithin.

D. Nonionic
a) Fatty alcohols:
- Cetyl alcohol,
- Stearyl alcohol,

b) Polyoxyethylene glycol alkyl ethers (Brij): $CH_3–(CH_2)_{10–16}–(O\text{-}C_2H_4)_{1–25}–OH$:

- Octaethylene glycol monododecyl ether,;
- Pentaethylene glycol monododecyl ether;

c) Polyoxypropylene glycol alkyl ethers: $CH_3–(CH_2)_{10–16}–(O\text{-}C_3H_6)_{1–25}–OH$;

d) Glucoside alkyl ethers: $CH_3–(CH_2)_{10–16}–(O\text{-}Glucoside)_{1–3}–OH$:

- Decyl glucoside;
- Lauryl glucoside;
- Octyl glucoside;

e) Polyoxyethylene glycol octylphenol ethers: $C_8H_{17}–(C_6H_4)–(O\text{-}C_2H_4)_{1–25}–OH$:

- Triton X-100;

f) Polyoxyethylene glycol alkylphenol ethers: $C_9H_{19}–(C_6H_4)–(O\text{-}C_2H_4)_{1–25}–OH$:
- Nonoxynol-9;
g) Glycerol alkyl esters:
- Glyceryl laurate;
h) Polyoxyethylene glycol sorbitan alkyl esters: Polysorbates;
i) Sorbitan alkyl esters: Spans;
j) Block copolymers of polyethylene glycol and polypropylene glycol:
- Pluronic F-127.

Surfactants reduce the surface tension of water by adsorbing at the liquid-gas interface. They also reduce the interfacial tension between oil and water by adsorbing at the liquid-liquid interface. Many surfactants can also assemble in the bulk solution into aggregates (micelles). Micelles can possess various shapes (see Fig. 2): spherical (A), rod or cylindrical (B), liposome (C), lamellar (D).

When micelles form in water, their tails form a core that can encapsulate an oil droplet, and their (ionic/polar) heads form an outer shell that maintains favorable contact with water. When surfactants assemble in oil, the aggregate is referred to as a reverse

micelle. In a reverse micelle, the heads are in the core and the tails maintain favorable contact with oil – Fig. 2 E.
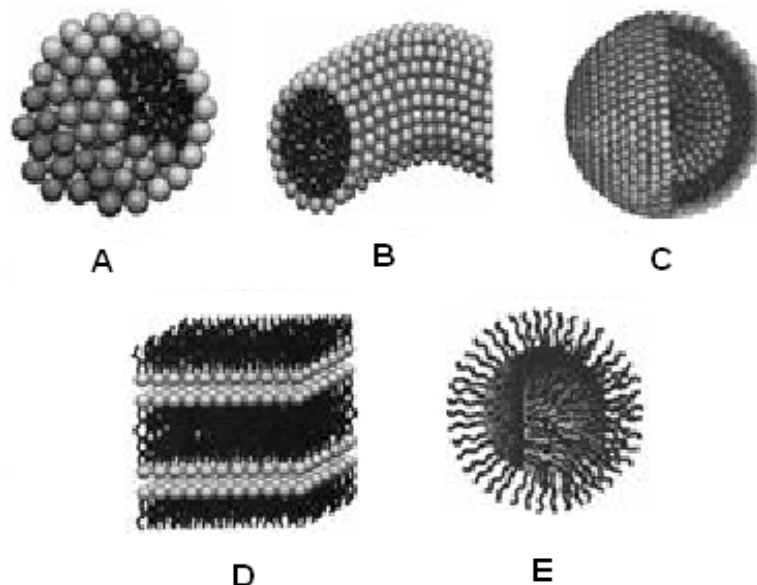

Fig. 2. Different forms of micelles: A - spherical, B - cylindrical, C – liposome, D – lamellar, E – reverse micelle.

Surfactants are soluble in water at a very low concentration, making a transparent solution of monomers. Increase of surfactant concentration causes the aggregation of monomeric molecules into the micelles. The specific concentration at which surfactant begins to form micelles is known as the *critical micelle concentration* (CMC). The CMC values of selected ionic surfactants are collected in Table 1.

In the case of ionic surfactants the significant term is the *Krafft point* (also known as *Krafft temperature*). It is the minimum temperature at which surfactants form micelles – see Fig. 3. Below the Krafft temperature, there is no value for the critical micelle concentration (CMC), i.e. micelles cannot form. The Krafft temperature is a point of phase change below which the surfactant remains in the crystalline form, even in aqueous solution. Surfactants in such a crystalline state will only solubilize and form micelles if another surfactant assists it in overcoming the forces that keep it crystallized.

The Krafft point increases with the increase in the number of carbon atoms in the hydrophobic group and decreases with branching or unsaturation in that group in a homologous series of ionic surfactants. Moreover, the substitution of triethyl for trimethyl in the head group of cationic alkyl trimethylammonium bromides leads to significant reduction in their Krafft point values.
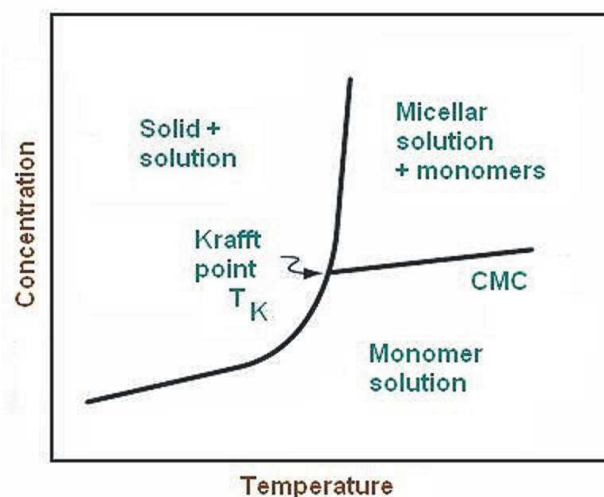
Fig. 3. Surfactant concentration *vs* temperature.

Table 1. CMC values of ionic surfactants [1].

Surfactant	Temp., °C	CMC, M
$C_{11}H_{23}COO^-Na^+$	25	$2.8 \cdot 10^{-3}$
$C_9H_{19}CH_2\ SO_3^-Na^+$	45	$4.0 \cdot 10^{-2}$
$C_9H_{19}CH(C_2H_5)SO_3^-Na^+$	45	$1.8 \cdot 10^{-2}$
$C_9H_{19}CH(C_4H_9)SO_3^-Na^+$	45	$6.8 \cdot 10^{-3}$
$C_9H_{19}CH(C_6H_{13})SO_3^-Na^+$	45	$1.7 \cdot 10^{-3}$
$C_9H_{19}CH(C_8H_{17})SO_3^-Na^+$	45	$2.4 \cdot 10^{-4}$
$C_9H_{19}CH(C_9H_{19})SO_3^-Na^+$	45	$8.9 \cdot 10^{-5}$
$C_{12}H_{25}CH_2\ SO_4^-Na^+$	25	$8.1 \cdot 10^{-3}$
$C_{14}H_{29}CH_2\ SO_4^-Na^+$	40	$2.2 \cdot 10^{-3}$
$C_8H_{17}N^+(CH_3)_3Br^-$	25	$2.9 \cdot 10^{-4}$
$C_{10}H_{21}N^+(CH_3)_3Br^-$	25	$6.4 \cdot 10^{-2}$
$C_{10}H_{21}N^+(CH_3)_3Cl^-$	25	$6.8 \cdot 10^{-2}$
$C_{12}H_{25}N^+(CH_3)_3Br^-$	25	$1.5 \cdot 10^{-2}$
$C_{12}H_{25}N^+(CH_3)_3Cl^-$	25	$2.2 \cdot 10^{-2}$
$C_{14}H_{29}N^+(CH_3)_3Br^-$	25	$3.2 \cdot 10^{-3}$
$C_{14}H_{29}N^+(CH_3)_3Br^-$	40	$4.2 \cdot 10^{-3}$
$C_{16}H_{33}N^+(CH_3)_3Br^-$	25	$8.5 \cdot 10^{-3}$
$C_{16}H_{33}N^+(CH_3)_3Cl^-$	25	$1.4 \cdot 10^{-3}$
$C_{10}H_{21}Pyr^+Br^-$	25	$4.4 \cdot 10^{-2}$
$C_{11}H_{23}Pyr^+Br^-$	25	$2.1 \cdot 10^{-2}$
$C_{12}H_{25}Pyr^+Br^-$	25	$1.0 \cdot 10^{-2}$
$C_{13}H_{27}Pyr^+Br^-$	25	$5.3 \cdot 10^{-2}$
$C_{14}H_{29}Pyr^+Br^-$	25	$2.7 \cdot 10^{-3}$
$C_{15}H_{31}Pyr^+Br^-$	25	$1.3 \cdot 10^{-3}$
$C_{16}H_{33}Pyr^+Br^-$	25	$6.4 \cdot 10^{-4}$

Pyr = Pyridyne

Critical micelle concentration influences many different factors like:
    a) the structure of surfactant;
    b) counterion   - in a case of ionic surfactant;
    c) addition of electrolyte   - salts;
    d) addition of non-electrolyte   - alcoholes;
    e) temperature;
    f) pressure.

For homologues series of cationic surfactants CMC depends linearly, on the number of carbon atoms in the hydrophobic chain (Fig. 4), according to following equation:

$$ln\ CMC = A \cdot N_C + B \qquad\qquad (1)$$

where A and B are the specific constants for homologous series and N_C is a number of carbon atoms in the hydrophobic chain

Generally, increase of a length of hydrophobic part of an ionic head of surfactant causes decrease of the CMC value.

For ionic surfactants an important factor in determining the ability of creating micelles is kind of counter ion emerging from the dissociation of surfactant. Competitive counterion hydration affects the association of surfactants and their CMC.
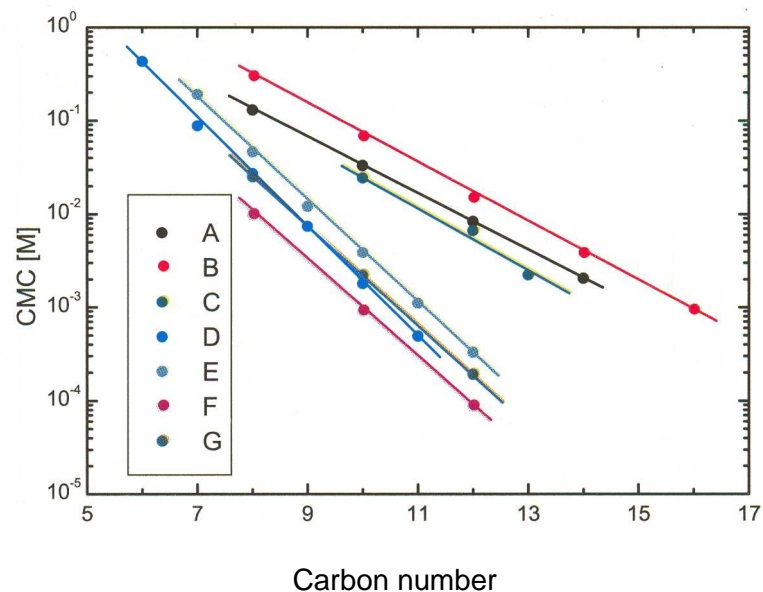

Fig. 4. Influence of carbon chain length of ionic surfactant on CMC for:

A - sodium alkylosulfate, B - alkylotrimethylammoniu bromide, C – N-alkylo-betaine, D –alkylmethylsulfoxide, E – alkyldimethyphosphine oxide, F - monoether methyl alkiloheksaoksyetylene glycol, G – alkylo-β- D –glucopyranoside. [2]

The influence of addition of an electrolyte on CMC depends upon the chemical structure of a surfactant (Fig. 5). For ionic compounds the addition of an electrolyte

with a common ion to the counter ion of a surfactant decreases CMC according to the empirical equation:

$$ln\ CMC= A \cdot ln(CMC+C_s) + B \qquad (2)$$

where: A and B are the specific constants dependent upon a type of surfactant, type of salt and temperature, C_S is the molality of added salt .
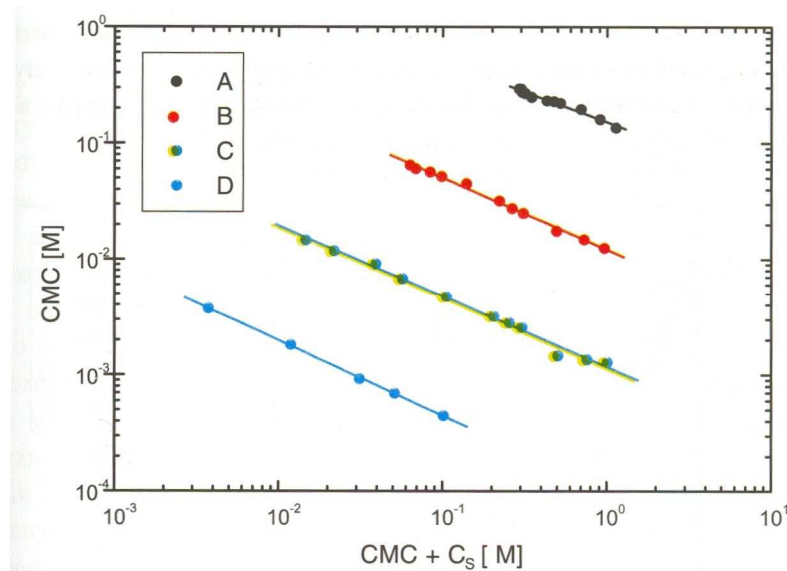

Fig. 5. Effect of salt concentration on CMC of ionic surfactant.

A – octyltrimethylammonium bromide, B - decyltrimethylammoniu bromide, C – N- dodecyltrimethylammonium bromide, D – tetradecylammonium bromide. [2]

The addition of electrolyte to the water solution of nonionic surfactant decreases the CMC value and is described by the Seczenov equation:

$$ln\ CMC=k_S\ C_E +\ ln\ CMC_0 \qquad (3)$$

where: C_E - the electrolyte concentration, k_S – the Seczenov constant, which depends mainly on temperature and type of an electrolyte, CMC_0 - the value of CMC for pure surfactant solution.

Surface behaviour of a surfactant solution can be modified also by the addition of nonelectrolyte, like urea or alcohols. The addition of lower alcohols decreases CMC (Fig. 6).
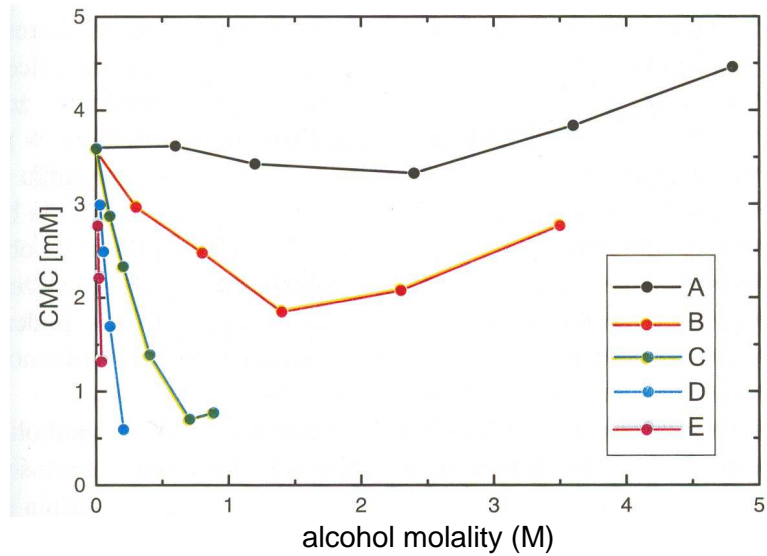
Fig. 6. Effect of alcohol concentration on the CMC of ionic surfactants in the water-alcohol solution.

A – etanol , B – n-propanol, C – n-butanol, D – n-pentanol, E – n-hexanol. [3]

Influence of temperature on CMC of ionic surfactants is quite complex and depends on the chemical structure of surfactant and temperature range**.** On the curves of CMC of ionic surfactants, the temperature minimum (T_{min}) occurs. Location of minimum shifts to lower temperature with the increasing hydrocarbon chain length.
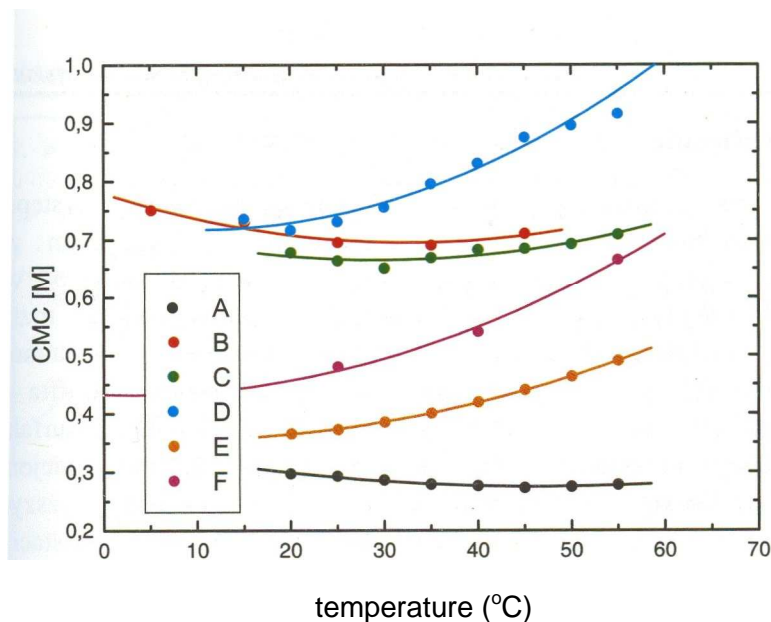

Fig. 7. Effect of temperature on CMC value of water solution ionic surfactants.

A – octyltrimethylammonium bromide, B - nonyltrimethylammoniu bromide, C –decyltrimethylammonium bromide, D – dodecyltrimethylammonium bromide, E - tetradecylammonium bromide, F - hexadecylammonium bromide. [4]
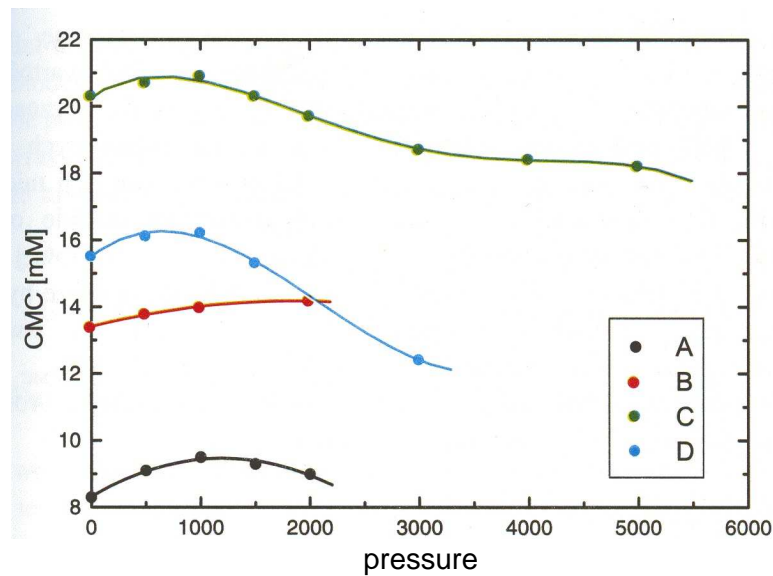
Fig. 8. Effect of pressure on CMC value of water solution ionic surfactants.

A – sodium dodecylosulfate, B - dodecylammoniu chloride, C – dodecyltrimethylammonium chloride, D – dodecyltrimethylammonium bromide. [5]

Effect of pressure on the CMC value of ionic surfactants is complex and depends both on the chemical structure of surfactant and range of applied pressure. Found that the CMC curves of the pressure exhibit the maximum sliding to lower pressure with lengthening the hydrocarbon chain.

Application of selected commercially available surfactants:

Sodium and Potassium Salts of Straight-Chain Fatty Acids, RCOO⁻M⁺ (Soaps) - Used in toilet soap bars and for degumming of silk, where alkaline solution is required. For industrial use in hard water, lime soap-dispersing agents (sulfonates and sulfates) are added to prevent precipitation of insoluble lime soaps.

Sodium and Potassium Salts of Tall Oil Acids - Mainly ''captive'' use or in situ preparation for various industrial cleaning operations.

Amine Salts - Triethanolamine salts are used in nonaqueous solvents and in situ preparation as an emulsifying agent (free fatty acid in oil phase, triethanolamine in aqueous phase). Ammonia, morpholine, and other volatile amine salts are used in polishes, where evaporation of the amine following hydrolysis of the salt leaves only water-resistant material in film. Long-chain amines and their salts, $RNH_3^+X^-$ are used as cationic emulsifying agents at pH below 7 - corrosion inhibitors for metal surfaces, to protect them from water, salts, acids. Saturated, very long-chain amines are best for this purpose, since these give close-packed hydrophobic surface films. Used in fuel and lubricating oils to prevent corrosion of metal containers, ore flotation collectors, forming non-wetting films on specific minerals, allowing them to be separated from other ores.

Quaternary Ammonium Salts - N-Alkyltrimethylammonium chlorides, $RN^+(CH_3)_3Cl^-$, are used as dye transfer inhibitors in rinse cycle fabric softeners. They

are also used as emulsifying agents for acidic emulsions or where adsorption of emulsifying agent onto substrate is. They are highly effective germicides for industrial use. Bis [long-chain alkyl] derivatives are less effective than monoalkyls; oxyethylenation drastically reduces germicidal effect; chlorinated aromatic ring increases it. N-Benzyl-N-alkyldimethylammonium halides $RN^+(CH_2C_6H_5)(CH_3)_2Cl^-$, are used as germicides, disinfectants and sanitizers. They are compatible with alkaline inorganic salts and nonionics and are used together with them in detergentsanitizers for public dishwashing (restaurants, bars). They are also used as hair conditioners (after shampoo rinses), since they adsorb onto hair, imparting softness and antistatic properties. The cetyl derivative is used in oral antiseptics. Cetylpyridinium bromide is used in mouth washes.

Sulfuric Acid Ester Salts - Sodium salts are most common. Sodium alcohol sulfate can be used in laundry powders, as a toothpaste foaming agent, as an emulsifier in food and cosmetic products, and as a dyestuff dispersion agent in aqueous solution. Magnesium lauryl sulfate is used where a less hydroscopic powder is needed and has greater solubility in hard water and higher alkali tolerance than the corresponding sodium salt. Diethanol, triethanol, and ammonium salts are used in hand dishwashing liquids and in hair shampoos and cosmetics, where their higher water solubility and slightly acidic pH make them desirable.

The world production of soaps, detergents and other surfactants was about 18 Mt (million tons) in 1970, 25 Mt in 1990 and 60 Mt in 2008 (not counting polymeric surfactants). Approximately 25 % corresponds to the North American market and 25 % to the European market. The raw materials are extremely varied and come from diverse origins, with a transformation ranging from a simple hydrolisis to multistep high pressure synthesis processes. With the single exception of rosin and tall oils the surfactant raw material market does not depends significantly on the surfactant manufacturing business. A consequence of this is that raw material costs can vary considerably because of factors external to the surfactant business. This volatile situation has produced changes and altered competitive margins in the surfactant industry [1].

The ionic surfactant is charged and it acts as an electrolyte and so obeys Ohm's law. That means that when a voltage (*V*) is applied across a cell containing the surfactant solution the flowing current (*I*) is proportional to *V*. *Ohm's law* can be written as:

$$V = I \cdot R \tag{2}$$
$$\text{or } I = V \cdot G \tag{2a}$$

where *R* is the resistance and *G* (=1/*R*) the conductance of the solution. The conductance of the solution depends upon the dimensions of the cell and the nature of the solution. The conductance of a solution contained in a cell of length *l* and area *A,* as is shown in Fig 9, is given by:

$$G = \frac{A}{l} \kappa \tag{3}$$

where κ is the *conductivity* of the solution and is independent of the shape of the cell. Conductivity has the units $\Omega^{-1} \cdot m^{-1}$ or $S \cdot m^{-1}$ where S is Siemens - the SI unit of

conductance. The glass cell has fixed electrodes, and the ratio *l/A* is constant, giving the cell constant *k*.
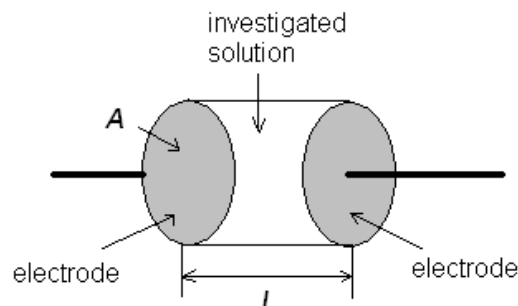

Fig. 9. Scheme of conductometric cell.

An approximate value can be obtained from the geometry of the cell. Eqn (2) can be written:

$$\kappa = G \cdot k \tag{4}$$

The cell constant is usually obtained by calibrating the cell using a 0.01 mol·kg^{-1} KCl solution at 298 K.

A very useful quantity is the *molar conductivity*. For a solution of concentration *c* the molar conductivity, Λ, is given by:

$$\Lambda = \kappa/c \tag{5}$$

Unity of molar conductivity is S·m^2·mol^{-1}.

Molar conductivity is a very convenient way of quantifying conductivity because it highlights the properties of the electrolyte. For instance, doubling the concentration of an electrolyte solution would be expected to double the number of ions and thus to double the conductivity. In this case the molar conductivity would be unchanged. In most cases, however, the molar conductivity actually decreases with increasing concentration owing to the influence of concentration on interactions between electrolyte ions or on an ionic dissociation process.

The molar conductivity of an electrolyte depends upon the extent to which the electrolyte dissociates into ions. Strong electrolytes (e.g. KCl) are almost completely ionised, whilst weak electrolytes (e.g. CH$_3$COOH) are ionised to only a small extent. Dilution of an electrolyte solution increases the extent of dissociation, and at infinite dilution the molar conductivity reaches a maximum value Λ_0.

At infinite dilution ion-ion interactions are eliminated, the anions and cations travel independently. Kohlrauch found that the molar conductivity of a salt could be separated into a component from each, called ionic conductivities (λ_0). The *Kohlrauch law of independent migration of ions* can be described as:

$$\Lambda_0 = \lambda^+_0 + \lambda^-_0 \tag{6}$$

For example, the molar conductivity of sodium chloride is the sum of the ionic conductivities of the sodium and chloride ions.

Below the CMC, the addition of surfactant to an aqueous solution causes an increase in the number of charge carriers and consequently, an increase in the conductivity. Above the CMC, further addition of surfactant increases the micelle concentration while the monomer concentration remains approximately constant (at the CMC level). Since a micelle is much larger than a surfactant monomer it diffuses more slowly through solution and so is a less efficient charge carrier. A plot of conductivity against surfactant concentration and method of critical micelle concentration estimation are shown in Fig. 10.
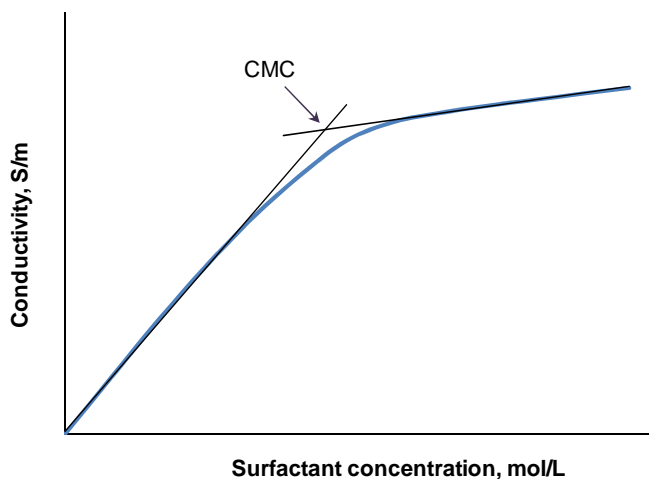

Fig. 10. Estimation of critical micelle concentration.

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[5] J. Osugi, M. Sato, N. Ifuku, Review of Physical Chemistry of Japan, 35 (1965) 33.

Experimental

A. Equipment and reagents

1. Instrumentation:
   - Multifunction meter CX-401 ELMETRON;
   - Magnetic stirrer with heating.
2. Equipment:
   - Glass vessel (100 mL) with magnetic stirrer;
   - Glass burette (50 mL).
3. Reagents:
   - 0.02 M cetyltrimethylammonium bromide (CTAB) in water solution;
   - 0.09 M dodecyltrimethylammonium bromide (DTAB) in water solution;
   - Distilled water.

B. Task performance

Conductivity measurements will be performed using the multifunctional meter CX-401 ELMETRON (see Fig. 11), after the instructions given by a teacher.

Fig. 11. Multifunction meter CX-401.

Measurements

Pour 50 mL of distilled water into a glass vessel. Using the multifunction meter CX-401 ELMETRON measure conductivity values after adding subsequently 1 mL of 0.02 M CTAB solution and waiting for the system equilibration during 1.5 minutes at 25°C. Repeat the measurements for DTAB surfactant.

Perform the same measurements for both surfactants at 40°C.
Collect the obtained data in Table:

$V_{titrate}$ [mL]	κ, S/m			
	25°C		40°C	
	CTAB	DTAB	CTAB	DTAB
0				
1				
2				
3				
…				

C. Analysis of the results

Draw plots $\kappa = f(V)$ for each investigated system.
Estimate the critical micelle concentration for each system taking into account the dilution of investigated solution after titrate addition.
Compare the obtained CMC values with the literature data and draw some conclusions about the influence of temperature and carbon chain length on critical micelle concentration of cationic surfactants.