

# Determination of the critical micelle concentration

## THEORY

### ➤ CONDUCTOMETRY

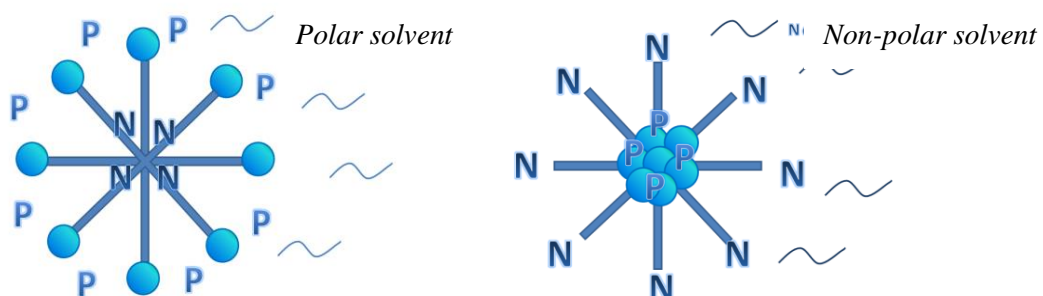
Electrical conductivity is a physical characteristic, which describes the ability of materials to conduct electric current. Substances, which conduct electric current easily, has high conductivity value, on the contrary, conductivity of substances, which do not conduct current, is zero. The symbol for conductivity is  $\gamma$  and SI base unit is siemens per meter ( $S \cdot m^{-1}$ ); method derived from measurement of conductivity is conductometry.

The conductivity depends on the amount of present ions and on their mobility to electrodes of measuring device. Conductometry can therefore be used for the determination of concentrations of substances in solution, to determine the purity of a solution or for conductometric titration. The test of conductivity is also part of the Pharmacopoeia, where it is used e.g. to verify the purity of *aqua purificata*.

### ➤ CRITICAL MICELLE CONCENTRATION

The critical micelle concentration of tensides can be determined by **measuring the electrical conductivity**. Tensides are surface-agents, which have a bipolar chemical structure. One part of the molecule has a polar character, the second one has nonpolar character. According to the type of polar group they are divided into ionic and non-ionic tensides. Ionic tensides can be divided according to the charge of hydrophilic group to anionic, cationic and ampholytic tensides.

Reaching a certain concentration of tenside in the solution leads to the association of tenside molecules to the so-called micelles. The appropriate part of the tenside molecule is oriented to the solvent: in a polar solvent (e.g. water) polar part of the molecule is oriented to the solvent, in a non-polar solvent non-polar part of molecule is oriented to the solvent (see figure). The critical micelle concentration is the concentration at which micelles are formed. Tensides are used in pharmaceutical technology as excipients (emulsifiers) for the preparation and production of liquid, semi-solid and also solid dosage forms.



Ionogenic tensides at lower concentrations form a true solution and they behave like simple electrolytes. Among other things it means that they conduct electric current. Kohlrausch's law of independent migration of ions:

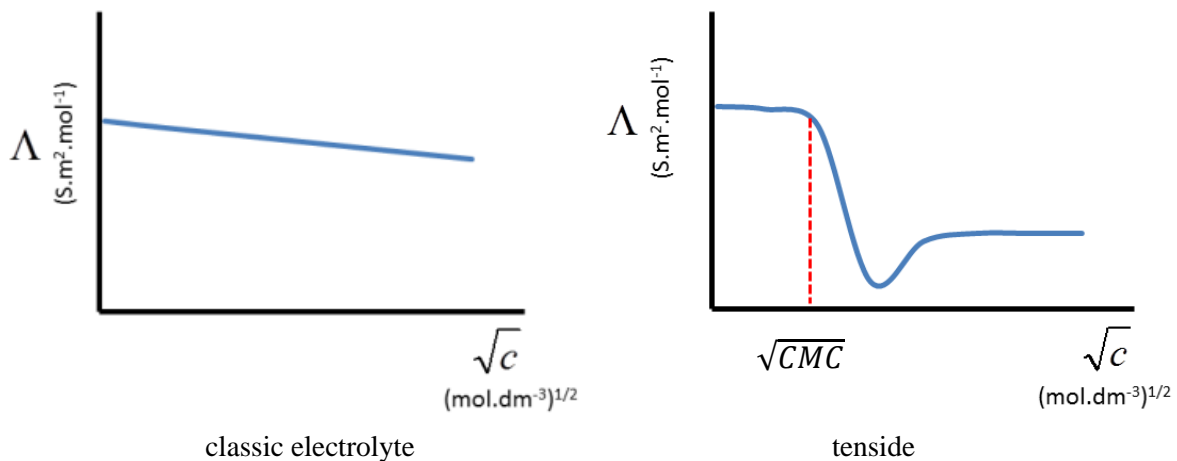
$$\lambda = \lambda_0 - a \cdot \sqrt{c},$$

where  $\lambda$  is molar conductivity,  $\lambda_0$  is molar conductivity at infinite dilution,  $c$  is concentration and  $a$  is empirical constant.

Molar conductivity can be calculated using conductivity and concentration, unit is  $\text{S} \cdot \text{m}^2 \cdot \text{mol}^{-1}$ .

$$\lambda = \frac{\gamma}{c}$$

The dependence of molar conductivity on the square root of concentration for classical electrolyte is linear. In point of critical micelle concentration (CMC) there is significant decrease in molar conductivity due to the association of tenside molecules into micelles and reduction in mobility of bound ions. For the dependence of the molar conductivity on the square root of the surfactant concentration: we can determine the square root of the critical micelle concentration in the point where the curve starts to drop.



Critical micelle concentration can be also determined using surface tension values measured by means of **stalagmometric method**. Surface tension can be defined as the force per unit length, symbol is sigma  $\sigma$  and unit is  $\text{N} \cdot \text{m}^{-1}$ .

Because the surface tension force and the force of gravity are in balance just before drip a drop from the stalagmometer, so method of drops weighing can be used for determining surface tension of unknown liquid. The ratio of weight of a certain number of drops  $n$  for control liquid  $m_1$  and for measured sample  $m_2$  equals the ratio of the surface tension of these liquids. As a control liquid is often used distilled water, appropriate value of surface tension is listed in the tables.

$$\frac{m_1}{m_2} = \frac{\sigma_1}{\sigma_2} \rightarrow \sigma_2 = \frac{m_2}{m_1} \cdot \sigma_1$$

Critical micelle concentration can be determined by means of graphical representation of the dependence of surface tension on the solution concentration. It is a coordinate for  $x$  axis of a point, in which two lines intersect.

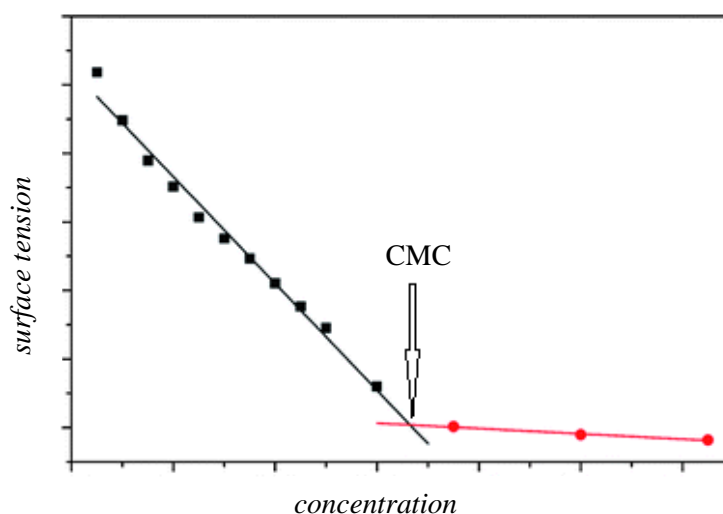


Table for determining the surface tension of distilled water (do not write to protocol)

Temperature ( $^{\circ}\text{C}$ )	Surface tension ( $\text{N} \cdot \text{m}^{-1}$ )
18	0.07305
19	0.07290
20	0.07275
21	0.07259
22	0.07244
23	0.07228
24	0.07213
25	0.07197

### TASK

- Determine the critical micelle concentration of Septonex using conductometry and stalagmometry. Compare the results of both methods with each other.

### EQUIPMENT AND CHEMICALS

- Conductometer; stalagmometer; 18× 50ml volumetric flask; 100ml volumetric flask; 1000ml volumetric flask; graduated pipette (5, 10, 25 ml); 2× manual propipetter; stand; 4× beaker; spoon; weighing boat; weighing bottle with cap; Septonex ( $M_r = 422.48$ ); KCl ( $M_r = 74.551$ ); unknown samples A, B, C.

## PROCEDURE

- Prepare stock solution of Septonex with concentration  $0.002 \text{ mol} \cdot \text{dm}^{-3}$  into 1000ml volumetric flask – by weighing the required amount of substance on the analytical balance. Then prepare 9 calibration solutions with concentrations from  $3 \cdot 10^{-4}$  to  $11 \cdot 10^{-4} \text{ mol} \cdot \text{dm}^{-3}$  into 50ml volumetric flasks by means of dilution of the stock solution. Mix the solutions thoroughly.
- Use prepared solutions for both methods, stalagmometry and conductometry (it is not necessary to prepare new solutions).

### ➤ CONDUCTOMETRY

- Switch the conductometer on by press the button on/off and wait to equilibrate and stabilize the device. Then carry out the measurement in the following manner: at first dry the conductivity probe with a cellulose wadding, then insert the probe into the beaker with the sample and write down the value on the display, including units.
- Prepare the solution of 0.01M KCl into 100ml volumetric flask by weighing the required amount of substance on an analytical balance. Verify the functionality of the device by the measurement of **conductivity of 0.01M KCl**. Consult the result with the teacher.
- Using measurement of conductivity **identify unknown samples A, B, C** by assigning to the following options: tap water, aqueous solution of salt, *aqua purificata*. The limit value of conductivity for *aqua purificata* is  $5.1 \mu\text{S} \cdot \text{cm}^{-1}$  (25 °C) according to Pharmacopoeia. Decide, if the sample meets the conditions set by the Pharmacopoeia.
- Then measure **conductivity of prepared solutions of Septonex**, rinse the probe with distilled water, dry the probe with a cellulose wadding and switch the device off by the pressing button on/off.

### ➤ STALAGMOMETRY

- Weight empty weighing bottle with cap.
- Beaker with sample (**distilled water and all solutions of Septonex**) placed under the stalagmometric tube and pipette measured solution using manual propipetter above the line of stalagmometer. Place the weighing bottle under the stalagmometric tube, in order to see drip individual drops. Let drip **30 drops** into the weighing bottle and determine their weight on the analytical balance by the difference of weight (filled weighing bottle vs. empty weighing bottle). At first always rinse the stalagmometer with measured solution and then measurement can be carried out, **twice for each sample**. Use the average values of the measured weight  $m$  in the formula for calculating the surface tension.
- After the measurement rinse the stalagmometer with distilled water.

## PROTOCOL

- Calculation of dilution / sample weight for preparation of all solutions.
- Measured values of conductivity  $\gamma$  for all solutions, calculated values of molar conductivity  $\lambda$  in unit  $\text{S} \cdot \text{m}^2 \cdot \text{mol}^{-1}$ .
- Graph of the dependence of molar conductivity  $\lambda$  on the square root of concentration  $\sqrt{c}$ ; determination of the critical micelle concentration based on graph.
- Measured values of weights of 30 drops  $m$  for all solutions, their means, calculated values of surface tension  $\sigma$ .
- Graph of the dependence of surface tension  $\sigma$  on the concentration of solution  $c$ ; determination of the critical micelle concentration based on graph.