

11.c Critical micellar concentration



A micellar solution consists of a dispersion of micelles in a solvent (most usually water). Micelles are formed by aggregated amphiphiles (i.e. molecules with both lyophilic and lyophobic part) that are oriented in direction given by minimum energy of the system. The spherical shape is the most frequent shape of the micelles. Micelles in a micellar solution are in equilibrium with free, unaggregated amphiphiles. Micellar solutions form when the concentration of amphiphile exceeds the critical micellar concentration. Micellar solutions (colloids) can be formed if we dissolve some high molecular weight substances (soaps, starches, surfactants, ...). The size of the micelles dispersed in the colloidal solution is in the range of 2-100 nm. Micellar solutions differ from true solutions in that they show a Tyndall effect.

Critical micellar concentration (CMC) can be determined from the breaks that show the dependencies of various physicochemical quantities (see **FIG. 1**) on the concentration of molecules forming the micelles. The CMC is temperature dependent similarly as solubility limit of crystalline substances (see **FIG. 2**).

In case the micelle releases by solvation simple ion (ie amphiphiles is ionogenic), it is suitable to use conductivity measurements (see instruction in chapter **6.c**) to determine CMC. Below the CMC value, the solute behaves as a simple electrolyte. The course of the molar conductivity λ as a function of the square root of the concentration is in agreement with Onsager's theory, according to which the molar conductivity of the uni-univalent electrolyte is:

$$\lambda = \lambda_0 - \text{const.} \cdot \sqrt{c} \quad (1.)$$

where λ_0 is the limiting molar conductivity, c is molar concentration of electrolyte.

After exceeding the CMC (see **FIG. 1**), the molar conductivity of the solution decreases more rapidly with increasing concentration and at even higher concentrations it either goes through a minimum or no longer changes with the concentration.

Another way to determine the CMC is to measure the surface tension of solutions. It is possible because the substances capable of forming associative colloids are surfactants. Until micelles are formed in the solution, the dependence of the surface tension on the concentration (see **FIG. 1**) corresponds to the Szyszkowski semi empirical equation (see Chapter Chyba! Nenalezen zdroj odkazů.):

$$\lambda_0 - \lambda = a \ln(1 + bc)$$

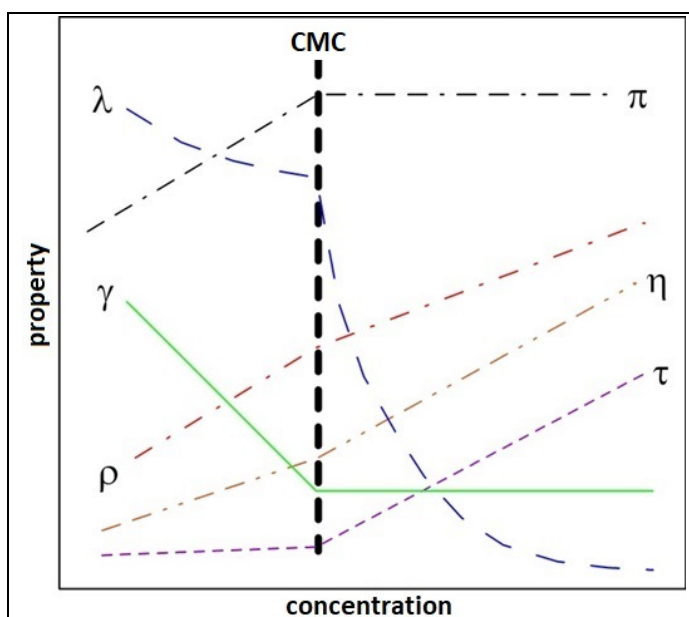


FIG. 1: Schematic representation of the dependences of various physicochemical quantities (ρ -density, π -osmotic pressure, η -viscosity, γ -surface tension, λ -molar conductivity, τ -turbidity) on the concentration of molecules forming micelles of colloidal solution

$$\text{if } bc \ll 1 \text{ then } \lambda_0 - \lambda = a bc \quad (2.)$$

where λ_0 is the surface tension of the solvent, λ is the surface tension of solutions of concentrations c at the same temperature, a and b are empirical constants.

Associative colloidal molecules are incorporated into the micelles if the CMC is exceeded. The concentration of free molecules in the solution remains the same as well as surface concentration. Thus surface tension does not change either.

The association colloid molecules may not always form spherical micelles. Under suitable conditions, for example at low temperatures, the molecules can form a solid phase with all the features of an ordered crystalline structure. The transformation temperature of micelles to the crystalline phase is called the Kraft point (see **Fig. 2**).

? **TASK:** Determine the critical concentration of the micellar surfactant (sodium lauryl sulphate is suitable) and its Kraft point in water by the conductivity method and by measuring the surface tension.



LABORATORY AIDS AND CHEMICALS: Stock solution of 0.1 M sodium lauryl sulphate (CAS No 151-21-3, $M_r = 288,38 \frac{g}{mol}$), 2 beakers (250 cm^3), 2 pipettes (20 cm^3), scale pipette (10 cm^3). Conductivity measurement: conductometer, conductivity electrode, thermostat, tempered vessel with tap outlet, thermometer. Capillary Stalagmometer (suitable outer diameter approx. 8 mm , inner diameter approx. 2 mm), thermometer, at least 2 weighing bottles with lid. Test tube, ice.



INSTRUCTIONS: The conductivity must be measured in a vessel at constant temperature (it is advantageous to use a temperature control for accurate measurements). Connect directly the outlet of the tempered vessel with the capillary by hose for simultaneous surface tension measurement.

1. Measurement of specific conductivity of water. Rinse thoroughly the vessel with capillary several times with distilled water. Monitor the conductivity. The assembly is ready for measurement if there is no significant decrease in conductivity. Pour about 60 ml of water and let it equilibrated. Record a stable value of specific conductivity of water, it should be close to pure distilled water.

2. Measurement of surface tension of water. Wipe the two marked weighing bottles dry with a swab and weigh. Use equilibrated water in previous conductivity measurement. Remove air bubbles between the tap of the conductive vessel and the end of the capillary. Adjust the drain cock of the conductive vessel so that the drops dripping from the end of the capillary count well. Place the first empty weighing bottle under the capillary and catch 20 drops of water. Capture the same number in the second weighing bottle.

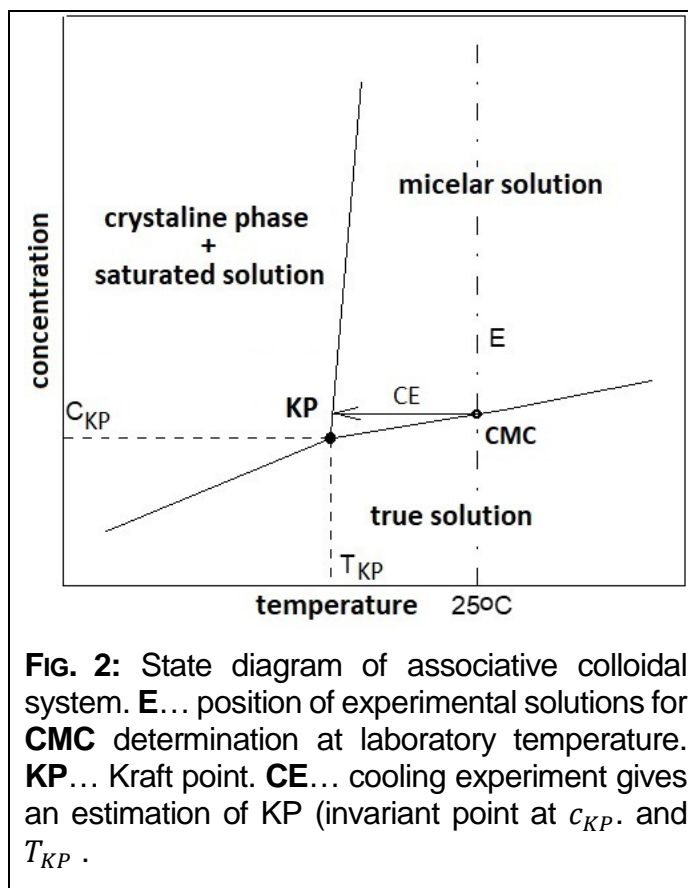


Fig. 2: State diagram of associative colloidal system. **E**... position of experimental solutions for **CMC** determination at laboratory temperature. **KP**... Kraft point. **CE**... cooling experiment gives an estimation of KP (invariant point at c_{KP} and T_{KP}).

Weigh the scales with water drops. The difference in the weight of the water must not be worse than half the weight of its drop, i.e. approx. 0,05g.

3. Measurement of specific conductivity and surface tension of solutions.

Proceed in the same way as in the case of measuring pure water. Pour about 60 ml of stock solution into a conductivity vessel. Measure the conductivity and the surface tension. Each subsequent solution is then prepared for further measurements as follows. Pipette 40 ml of the solution from a conductive vessel and mix it with 20 ml of water in a clean and dry beaker (i.e. 2/3 dilution). Drain the remaining contents of the conductivity vessel to waste and replace it without rinsing with a newly prepared diluted solution. Measure the conductivity and weight of 20 drops (a common mistake is incorrect drop counting or insufficient drying of the weighing bottle). By diluting to 2/3, we gradually obtain data for 12 different concentrations.

4. Simple measurement of Kraft point. Interpolate the CMC from the experiment (see **FIG. 2**). Prepare a solution with interpolated concentration and measure twice its conductivity and weight of 20 drops. Pour the solution into a test tube. Insert the thermometer. Sink the tube in a beaker with water with crushed ice. Note the temperature when the crystalline particles appear. Repeat the transformation effect at heating and cooling twice.



REPORT: Table 1: values of concentration c , $c^{1/2}$, measured specific conductivity κ and molar conductivity Λ . **Graph 1:** dependence Λ on $c^{1/2}$. **Next:** tabulated value of water surface tension γ^0 , averaged weight of empty weighing bottles and 20 drops of water. **Table 2:** values c , average weights of 20 drops of solutions, surface tension γ of solutions. **Graph 2:** dependences of γ on c . **Next:** Interpolate critical micellar concentration from the breaks on both curves. State the temperature and composition corresponding to the Kraft point.