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EXERCISE 9

Micellization of ionic surfactant

Ionic surfactants are amphiphilic molecules with a hydrophilic charged head-group and a hydrophobic hydrocarbon tail, as schematically shown in Fig.1. When dissolved in aqueous media, the salt (i.e., surfactant and counterion) dissociates into the bulk. If the tail is not too long, the driving force for solvation of the head-group will be strong enough to dissolve the whole molecule, even though the tail is not soluble in water. Owing to electrostatic repulsion between the head-groups, a homogenous solution with dissolved surfactant molecules is obtained.

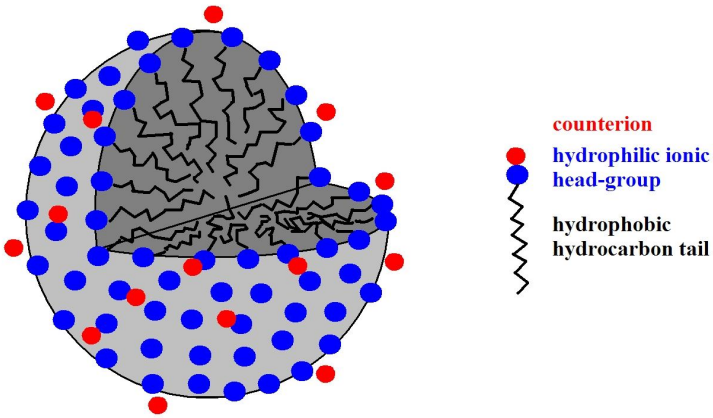


Fig. 1. Schematic picture of an ionic surfactant molecule and a micelle it forms.

Increasing the surfactant concentration results in two different effects. First, the increasing surfactant concentration leads to an increased ionic strength of the bulk. This in turn causes a decrease in the electrostatic repulsion between the head-groups due to screening of the charges. Second, an increase in the surfactant concentration is unfavorable for the hydrophobic tails, which on their own do not dissolve in water. The latter effect works against dissolving more

surfactant molecules. Eventually, the driving force for dissolution will be completely balanced by the forces working against the dissolution of the hydrophobic tails. At this moment, two scenarios are possible: either, if the hydrocarbon chain length is long enough, a macroscopic phase separation will appear, or micelles will be formed. In this latter case, this special concentration at which micelles start to be formed is a parameter specific for each surfactant and it is called the *critical micelle concentration*, often abbreviated as the *cmc*. It is worthwhile to stress that micelle formation is not a macroscopic phase separation, but the formation of a thermodynamically stable, microheterogenous supramolecular system, with surfactant molecules aggregated in micelles dissolved in the aqueous bulk.

Above the *cmc* the concentration of free surfactant molecules (i.e., monomers which are not associated with micelles) is practically constant. This results from thermodynamics. To understand this let us consider the following reversible process, in which molecules S agglomerate:

$$n\mathrm{S} \Leftrightarrow \mathrm{S}_n \tag{1}$$

where n is the number of molecules in the agglomerate (micelle). The equilibrium constant K for this process is given by:

$$K = \frac{[\mathrm{S}_n]}{[\mathrm{S}]^n} \tag{2}$$

Typically, for micelles n ranges between 10's and 100's. The larger n becomes the more sharp and steep increase of the micelle concentration with the surfactant concentration is observed, as shown in Fig. 2. The micelle formation is commonly considered as a quasi-phase separation.

The formation of micelles can be followed by several methods based on the fact that in the vicinity of the *cmc* there is a sharp change in the experimental observables (see Fig. 3).

There are many methods available in literature for the determination of the *cmc*: surface tension, spectrophotometry, kinetics, conductance, osmotic pressure etc. In the case of ionic surfactants the *cmc* can be easily found from the dependence of the solution conductance on the surfactant concentration. The tendency of the conductance to rise with the increasing surfactant concentration in the solution decreases at *cmc* owing to the lower mobility of larger micelles.

Another characteristic property of a surfactant is its *micellar aggregation number,* N_{agg}. This value, giving the average number of surfactant molecules in the micelle, depends on the hydrocarbon tail length, the kind of counterion, and the ionic strength (as does also the *cmc*).

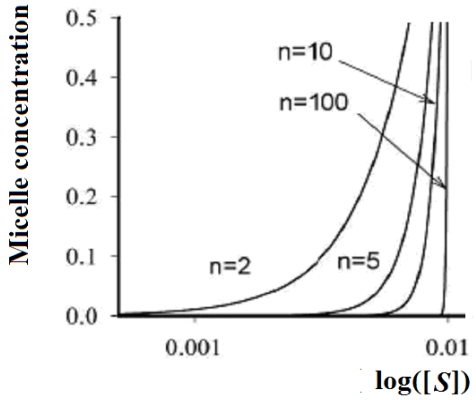


Fig. 2. Shapes of micelle concentration vs. log([*S*]) dependencies for different aggregation numbers

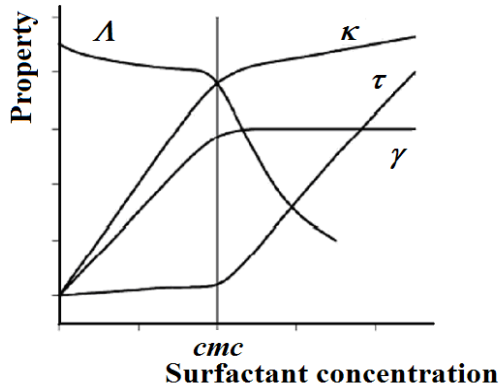


Fig. 3. Effect of surfactant concentration on various physical properties (Λ – then molar conductivity, κ – the specific conductivity, τ – the turbidity, γ – the surface tension)

Fluorescent probe techniques, have been largely employed for the determination of N_{agg}. Both steady-state and time-dependent fluorescence measurements have been applied to the determination of this parameter. Steady-state measurements usually rely on the decrease (quenching) of fluorescence of a probe associated with the micelle through the presence of a second species, the quencher. The basic idea underlying this method for determining N_{agg} is that in a system containing both fluorescent probe and quencher molecules, solubilized in an excess of micelles, the quenching will decrease with an increasing number of micelles because of a decreased probability of finding both probe and the quencher molecule in the same micelle. Below, let us consider this idea in more detail.

An apolar fluorescent molecules added into a micellar solution can be solubilized in the micelles. If the concentration of micelles exceeds that of fluorescent probes, then the solution will contain micelles of two types – those with probes and those without. If the fluorescent probe concentration is sufficiently low, each tagged micelle will contain only one probe. By this procedure, we obtain a known concentration of tagged micelles. When the sample is irradiated by constant low intensity light, a steady fluorescence intensity, I_0, can be measured. If now an apolar fluorescence quencher is added into this solution, a rapid non-radiative relaxation of the fluorescent state occurs, provided that the excited fluorescent molecules come sufficiently close to the quencher. Hence, the fluorescence intensity measured in the presence of the quencher, I_q, decreases.

We can assume that both the probe and quencher molecules are stationary in their host micelles during a time longer than the excited state lifetime, which means that migration of probe and quencher does not occur. Furthermore, the quenching should be very effective, that is, the detected emission emanates from micelles without quenchers only.

Assuming, that probes and quenchers both are distributed randomly between micelles, the probability of finding a micelle that contains the probe but lacks the quencher can be calculated.

If the concentration of micelles equals c_M, the average number of quenchers per micelle, $\bar{q}$, is

$$\bar{q} = \frac{c_q}{c_M} \tag{3}$$

where c_q denotes the quencher concentration. If quenchers are distributed among micelles according to the Poisson equation, then the probability $P(p)$ of finding p quenchers associated with a given micelle is:

$$P(p) = \left(\bar{q}\right)^p \cdot \frac{\exp\left(-\bar{q}\right)}{p!} \tag{4}$$

In particular, $P(0)$, which signifies the probability of finding an empty micelle, is:

$$P(0) = \exp\left(-\bar{q}\right) \tag{5}$$

since 0!=1. When we assume that the fluorescence can be observed only for probes residing in micelles containing no quenchers at all, we write:

$$I_q = P(0) \cdot I_0 \tag{6}$$

or

$$I_q = I_0 \exp\left(\frac{-c_q}{c_M}\right) \tag{7}$$

where I_0 is the fluorescence intensity in the absence of quenchers and provided the probes and quenchers are distributed independently.

The micelle concentration is given by:

$$c_M = \frac{c_S^{total} - c_S^{free}}{N_{agg}} \tag{8}$$

where c_S^{total} and c_S^{free} denote the total surfactant concentration and the concentration of surfactant monomers not associated with micelles, respectively. Since above the *cmc* the monomer concentration is practically constant we can assume $c_S^{free} = cmc$. Hence, we have:

$$\ln\left(\frac{I_q}{I_0}\right) = -\frac{c_q \cdot N_{agg}}{c_S^{total} - cmc} \tag{9}$$

and, after the rearrangement, we can obtain the following dependence:

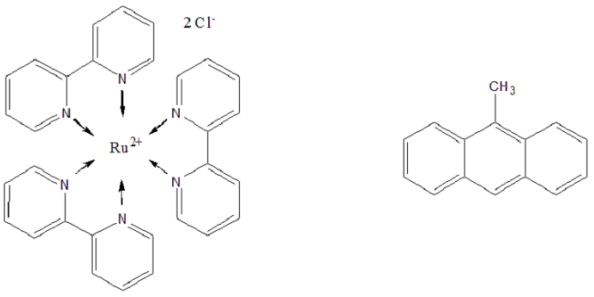
$$\left(\ln\left(\frac{I_0}{I_q}\right)\right)^{-1} = \frac{c_S^{total}}{c_q \cdot N_{agg}} - \frac{cmc}{c_q \cdot N_{agg}} \tag{10}$$

which allows the determination of N_{agg} from the slope and the intercept of a linear fit of $\left(\ln\left(I_0/I_q\right)\right)^{-1}$ versus c_S^{total}.

Experimental

The goal of the experiment is to determine the critical micelle concentration (*cmc*) and micellar aggregation number (N_{agg}) of anionic surfactant: sodium dodecyl sulfate, $CH_3(CH_2)_{11}OSO_3Na$, (molecular weight 288.38), abbreviated

further as SDS. For the *cmc* determination the method based on the conductance measurement is applied, whereas for the determination of N_{agg} the way described by Turro and Yekata [3] is used. In the last case, the tris(2,2'-bipyridyl)ruthenium(II) chloride (snonyms: dichlorotris(2,2'-bipyridyl) ruthenium(II) or tris(2,2'-bipyridyl)dichlororuthenium(II)) is used as the fluorescent probe and the 9-methylanthracene as the fluorescence quencher. The chemical formulae of these two compounds are presented in Fig. 4.



tris(2,2'-bipyridyl)ruthenium(II) chloride (PR) 9-methylanthracene (QU)

Fig. 4. Chemical formulae of fluorescent probe and fluorescence quencher used in the experiment

Materials and apparatus

1. Determination of cmc

- stock solution of SDS in water ($8.00 \cdot 10^{-2}$ mole/dm^3)
- conductometer equipped with a conductivity cell
- magnetic stirrer and a stir bar
- 25 cm^3 burette,
- beaker of 200-250 cm^3 and 2 beakers of 50-100 cm^3,
- pipette of 100 cm^3 and rubber pipette filler,
- wash bottle

2. Determination of N_{agg}

- aqueous solution of SDS of concentration $1 \cdot 10^{-2}$ mole/dm^3,
- aqueous solutions of SDS of concentrations $1 \cdot 10^{-2}$, $2 \cdot 10^{-2}$, $3 \cdot 10^{-2}$ and $4 \cdot 10^{-2}$ mole/dm^3, containing tris(2,2'-bipyridyl)ruthenium(II) chloride (PR) in concentration $7{,}2 \cdot 10^{-5}$ mole/dm^3,
- methanolic solution of 9-methylanthracene (QU) of concentration $5 \cdot 10^{-3}$ mole/dm^3,

- spectrofluorometer JASCO FP 6200 and fluorescence cuvettes,
- 20 bottles of capacity ~ 20 cm^3,
- adjustable volume automatic pipettes
- wash bottle with distilled water and methanol
- acetone and blow-dryer (hair-dryer)

Procedure

1. Determination of cmc

Place a beaker, containing a volume V = 100 cm^3 of water, on the magnetic stirrer. Introduce, by the stepwise addition of small portions (1 cm^3), 25 cm^3 of the surfactant stock solution. Use a burette for the addition and monitoring of the volume added. After introduction of each portion of the surfactant stock solution into the beaker wait 1 minute and then measure the conductance, G, of the resulting solution.

2. Determination of N_{agg}

►Absorption spectra of tris(2,2'-bipyridyl)ruthenium(II) chloride (further in the text referred as PR) and 9-methylanthracene (further in the text referred as QU), dissolved in aqueous SDS solution of concentration $1 \cdot 10^{-2}$ mole/dm^3, are represented in Figs 5 and 6. Choose the excitation wavelengths, λ_{ex}, for the recording of emission spectra of the two compounds (in the case of QU choose the wavelength of the longest-wavelength absorption band of PR (λ_{ex}= 450 nm)).

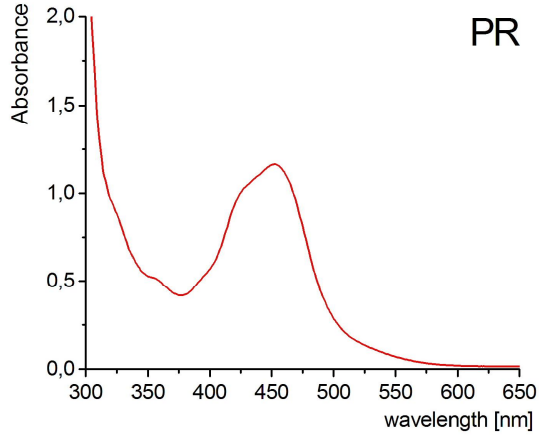


Fig. 5. Absorption spectrum of PR ($7{,}2 \cdot 10^{-5}$ mole/dm^3)

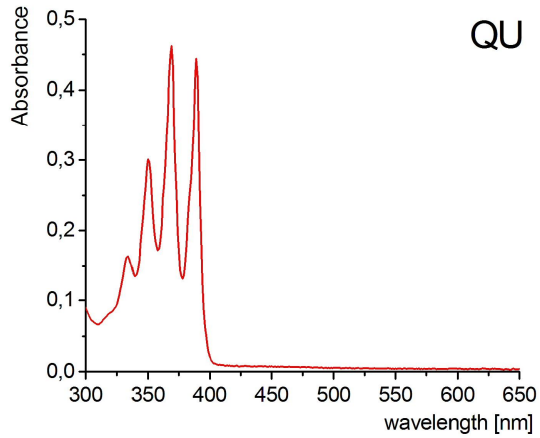


Fig. 6. Absorption spectrum of QU($1{,}0\cdot10^{-4}$ mole/dm^3)

► Record emission spectra of PR and QU (to this end use the obtained PR solution in aqueous SDS solution of concentration $1\cdot10^{-2}$ mole/dm^3, and QU solution obtained by mixing 0.1 cm^3 of methanolic stock solution of QU with 5 cm^3 of aqueous SDS solution of concentration $8\cdot10^{-2}$ mole/dm^3). Set the emission scan to start at a wavelength 15 nm longer than your excitation beam. The reason of that is that a small amount of the light from the excitation is scattered by the cuvette and the sample. This scattered radiation (called Rayleigh scatter) has the same wavelength as the excitation beam. To measure an emission spectrum, follow the instructions below.

Obtaining an emission spectrum

1. Turn "ON" the power switch located on the rear panel of the spectrofluorometer. When the power is turned "ON", the power lamp is illuminated. The light source requires approximately 5 minutes to stabilize.

2. Turn on the computer and the monitor.

3. Find [Spectra Manager] as shown in Fig. 7, and open it. The window shown in Fig. 8 will appear.

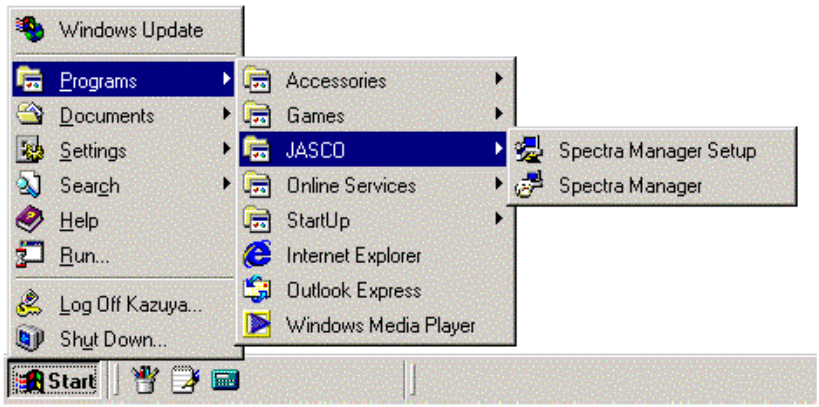


Fig. 7. Finding the [Spectra Manager]

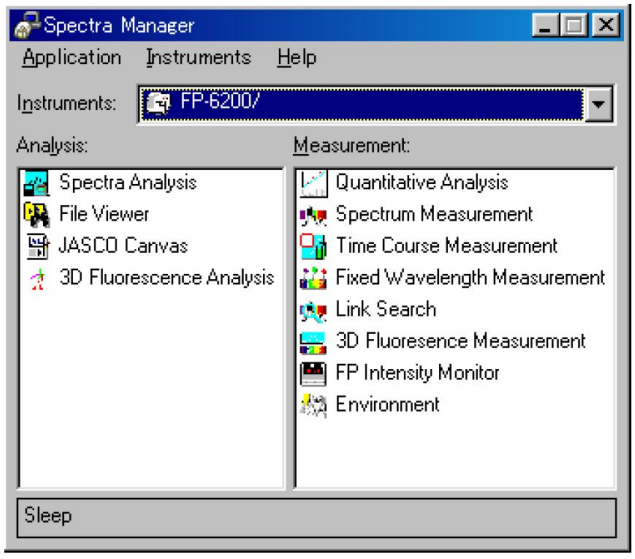


Fig. 8. [Spectra Manager] window

4. Double click on [Spectrum Measurement] from the [Spectra Manager]. The following window (Fig. 9) appears:

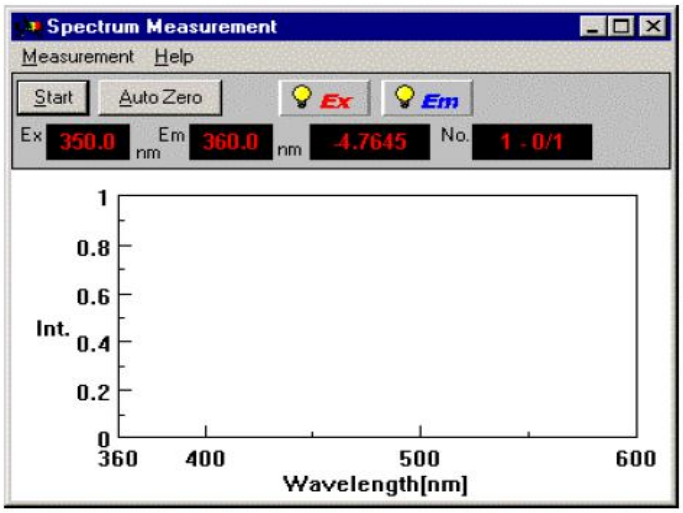


Fig. 9.[Spectrum Measurement] window

5. Select the [Measurement] menu to display the following menu (Fig. 10):

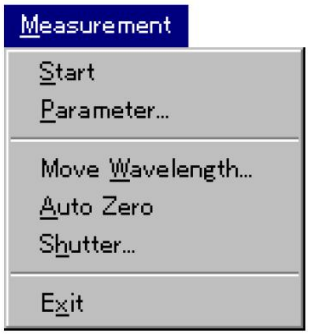


Fig. 10. [Measurement] menu

6. Open the [Parameter] dialog box (shown in Fig. 11), set the proper parameters and next close the box. (Excitation Wavelength: 450 nm, Start: 500 nm, End: 850 nm)

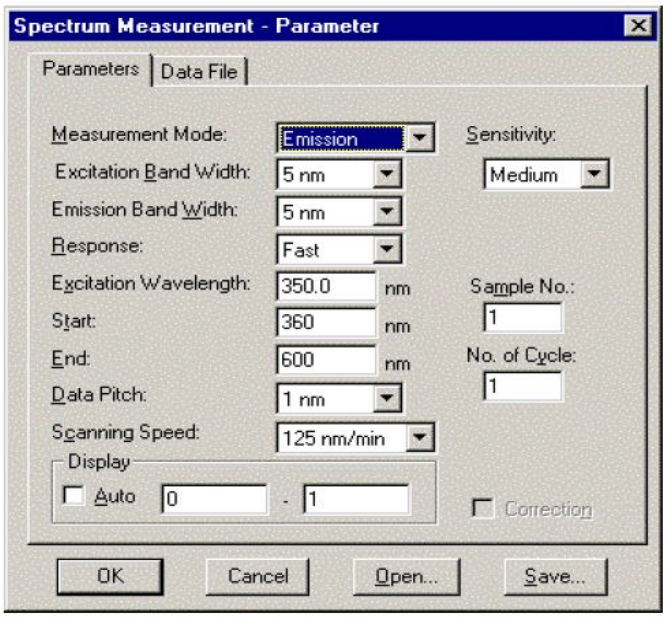


Fig 11. [Parameters] dialog box

7. Click the Ex button (Ex shutter button) and the Em button (Em shutter button). The yellow lamp icon indicates that the Ex and Em shutter are open.
8. Fill the clean and dry fluorescence cuvette (such a cuvette is transparent on all four sides) with the proper solution.
9. Wipe the surfaces of the cuvette and carefully place it in the holder in the sample compartment of the spectrofluorometer. Close the lid.
10. Execute [Measurement]-[Start] (or click the <Start> button). The sample is measured and the measurement progression appears. When measurement is complete, the [Spectra Analysis] program starts automatically and the spectrum is displayed in the active window.
11. Save the obtained data. To this end execute [File]-[Save As] when the [Spectra Analysis] program is active.

►In order to check whether the maximum band wavelength of PR fluorescence spectrum can be used as the analytical wavelength overlay the

obtained emission spectra. To this end you can use [Spectra Analysis] program: execute [File]-[Overlay] to display the corresponding dialog box.

►To 5 cm^3 of each SDS solution containing PR add 0,1 cm^3 of methanol and record the fluorescence spectra of prepared samples. Read (and note down) values of I_0 (at 625 nm). You can use [Spectra Analysis] program to find I_0. When you execute [View]-[Peak] the following menu will appear:

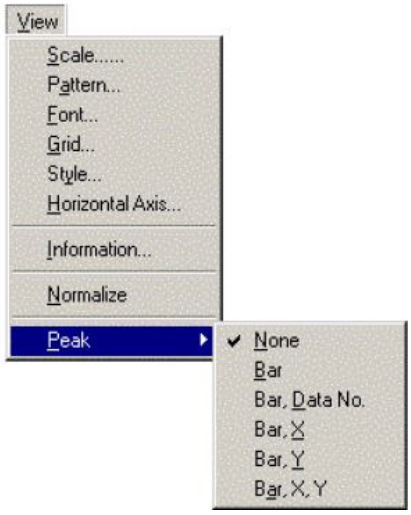


Fig. 12. Peak display menu

Click [Bar, X,Y]. Vertical bar appears. Set the bar at the analytical wavelength value and read the fluorescence intensity.

►To 5 cm^3 of each SDS solution containing PR add 0,1 cm^3 of methanolic stock solution of QU and record the fluorescence spectra of prepared samples. Read (and note down) the fluorescence intensities, I_q, at the analytical wavelength chosen.

► Exit all programs and shutdown both the PC and spectrofluorometer

► In order to determine the QU concentration in examined solutions prepare two samples by adding: 1/ 0.1 cm^3 of methanol and 2/ 0.1 cm^3 of methanolic stock solution of QU to 5.00 cm^3 of aqueous SDS solution of concentration $1 \cdot 10^{-2}$ mole/dm^3 and measure the absorbance of these solutions at wavelength 388 nm. The concentration of QU can be determined using the molar absorptivity ε=7500 $M^{-1}cm^{-1}$ [5].

Calculations

1. Determination of cmc

► Calculate the surfactant concentration in the solution from equation:

$$c_S^{total} = \frac{c_S^{stock} V_S^{stock}}{V + V_S^{stock}} \tag{11}$$

where V_S^{stock} is the volume of the added surfactant stock solution of concentration c_S^{stock}.

► Plot the obtained G values against c_S^{total}. The plot should contain two rectilinear regions as shown in Fig. 13. By linear regression analysis, find the best slopes a_1, a_2 and intercepts b_1, b_2 for each linear region. The *cmc* value can be found from the intersection of the two straight lines. Calculate this point from the following equation:

$$cmc = \frac{b_1 - b_2}{a_2 - a_1} \tag{12}$$

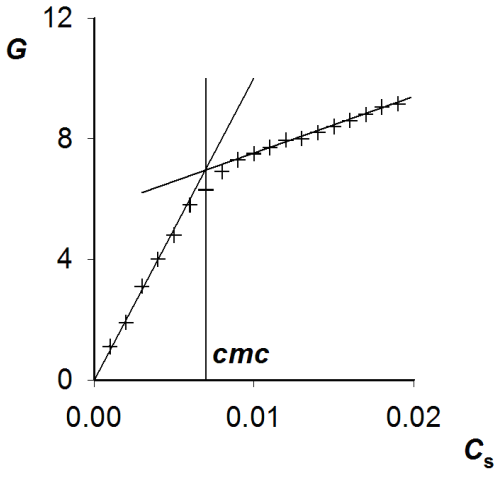


Fig. 13. Conductance, G, versus surfactant concentration, c_S^{total}. This figure illustrates a way of the *cmc* determination.

2. Determination of N_{agg}

► On the basis of the obtained I_0 and I_q values for different SDS concentrations plot $\left(\ln\left(I_0/I_q\right)\right)^{-1}$ versus c_S^{total}.

► Estimate the slope and the intercept of the obtained line using the linear least squares regression procedure.

► Calculate N_{agg} and cmc values from equation 10 using the fitted parameters.

► Confront the obtained cmc value with that determined by the conductance method.

References

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