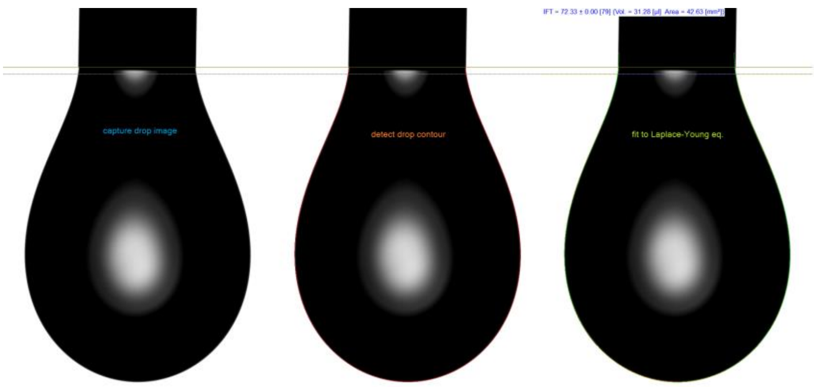
Critical Micelle Concentration (CMC) and Measurement

When a surfactant is continuously added to a solution, some physical properties of the solution, such as surface tension, conductivity, etc., change distinctly with the increasing concentration of the surfactant in the solution. These changes are resulted from the increase of free surfactant molecules which are present as free species in the solution and/or adsorbed at the surface/interface layer. At the beginning, the added surfactant molecules are preferentially adsorbed to the surface/interface to reduce the free energy of the surface/interface (and thus, of the whole system); as the concentration continues to increase, the surface/interface coverage of surfactant molecules approaches gradually its saturation. When this level of surfactant concentration is reached, additional surfactant molecules begin to self-organize into micelles in solution to reduce the total energy of the system. The critical micelle concentration (CMC) is the point of surfactant concentration at which micelles begin to form and all additional added surfactants go to formation of micelles.

Before reaching the CMC, surface tension is strongly affected by the surfactant concentration. After reaching the CMC, the surface tension is relatively stable regardless of the further increase in surfactant concentration. CMC is an important parameter for measuring and characterizing the surfactant and must be determined experimentally. Its value is also dependent of temperature, pressure, and of the presence of other surface-active substances and electrolytes. A screening procedure is often employed to find the optimal formulation under a given condition.

Among the methods which can be used for the determination of CMC, the method based on surface/interfacial tension (IFT) measurement is the most common one. Conventionally a force tensiometer based on the method of Du Noüy ring or Wilhelmy plate is employed thereby to determine the IFT. However, neither the Wilhelmy plate method nor the Du Noüy ring is optimally fit for working with solutions containing surfactants. The plate method encounters the problem of adsorption of surfactant molecules onto the *probe* metal (usually platinum) surface, which causes remarkable measurement error and may affect even the concentration of surfactants in solution. The ring method is in principle only applicable for one-component (i.e. pure) liquids. When surfactants are involved the ring is often difficult to be cleaned thoroughly, and it is in addition not possible to obtain the surface tension value that corresponds to a specific dynamic or equilibrated state.



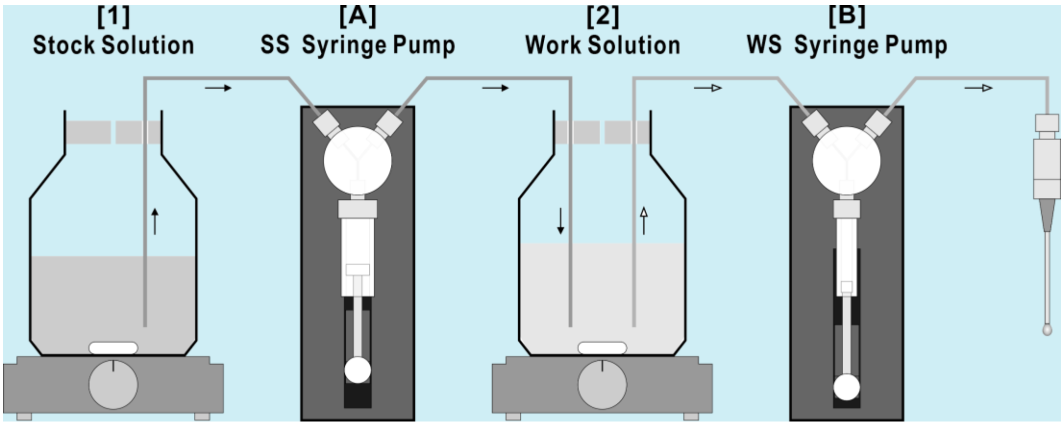
In sharp contrast to these traditional methods, the optical pendant drop analysis (PDA) method exhibits distinct advantages in almost every aspect regarding accuracy, reliability, convenience, and applicability to solutions containing various kinds of surfactants, as well as the degree of automation. Here some of its features, which are relevant to the determination of CMC:

1) High absolute and relative precision and accuracy: 0.1% (absolute) or 0.01% (relative);
2) Very broad measurement range: from ca. 10^{-3} to several thousands of mN/m;
3) Suited optimally for measurement of both surface and interfacial tension;
4) Covers a huge span of time-scale: from the moment shortly (ca. 50ms) after the interface is formed to nearly infinity. All time-dependent (IFT) values can be obtained from a single drop/interface;
5) The contact area between the formed liquid interface and the surface of the solid support is (negligibly) small, which greatly reduces the problems caused by the adsorption of surfactant molecules onto the solid surface;

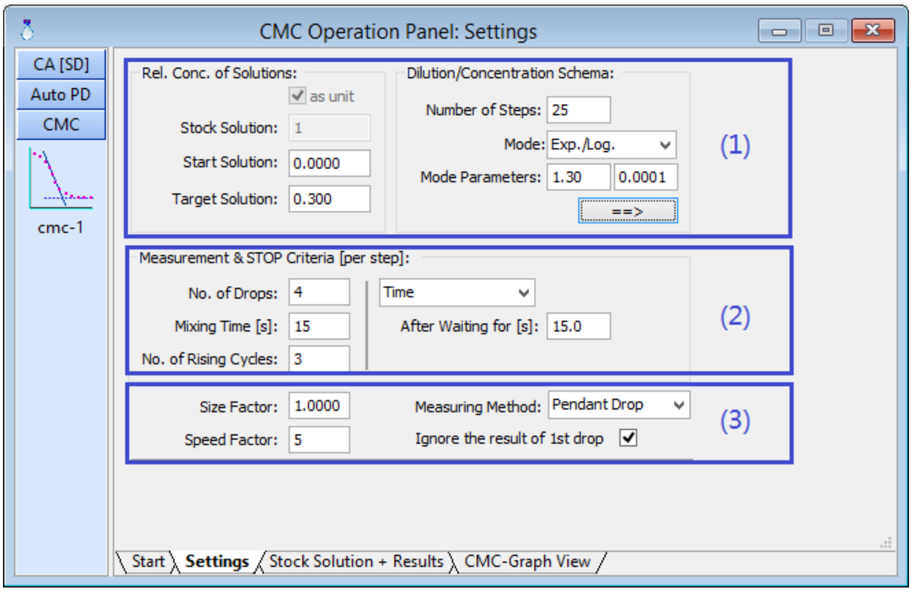
6) Can be fully automated: fully-automatic Pendant Drop Analysis (faPDA).

The CMC extension module, which is optional for all LSA-series, is based on the fully automatic Pendent Drop Analysis (faPDA) method and allows CMC measurement to be carried out completely automatically. Compared to the traditional force balance-based methods on the market, it provides a novel and fully automatic measuring method and equipment of excellent performance, powerful function, simple and flexible operation for the scientific research, product development, and industrial and production processes.

The CMC extension module consists mainly of a DUO-Syringe Pump and 1 or 2 magnetic stirrer(s) as well as the software package.



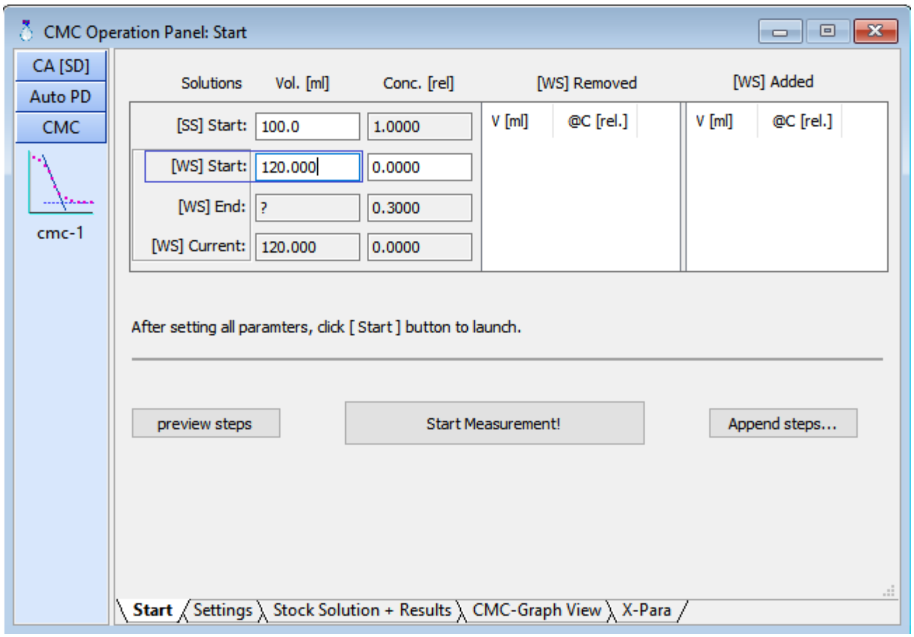
To perform a CMC measurement, here is what (all) you need to do:



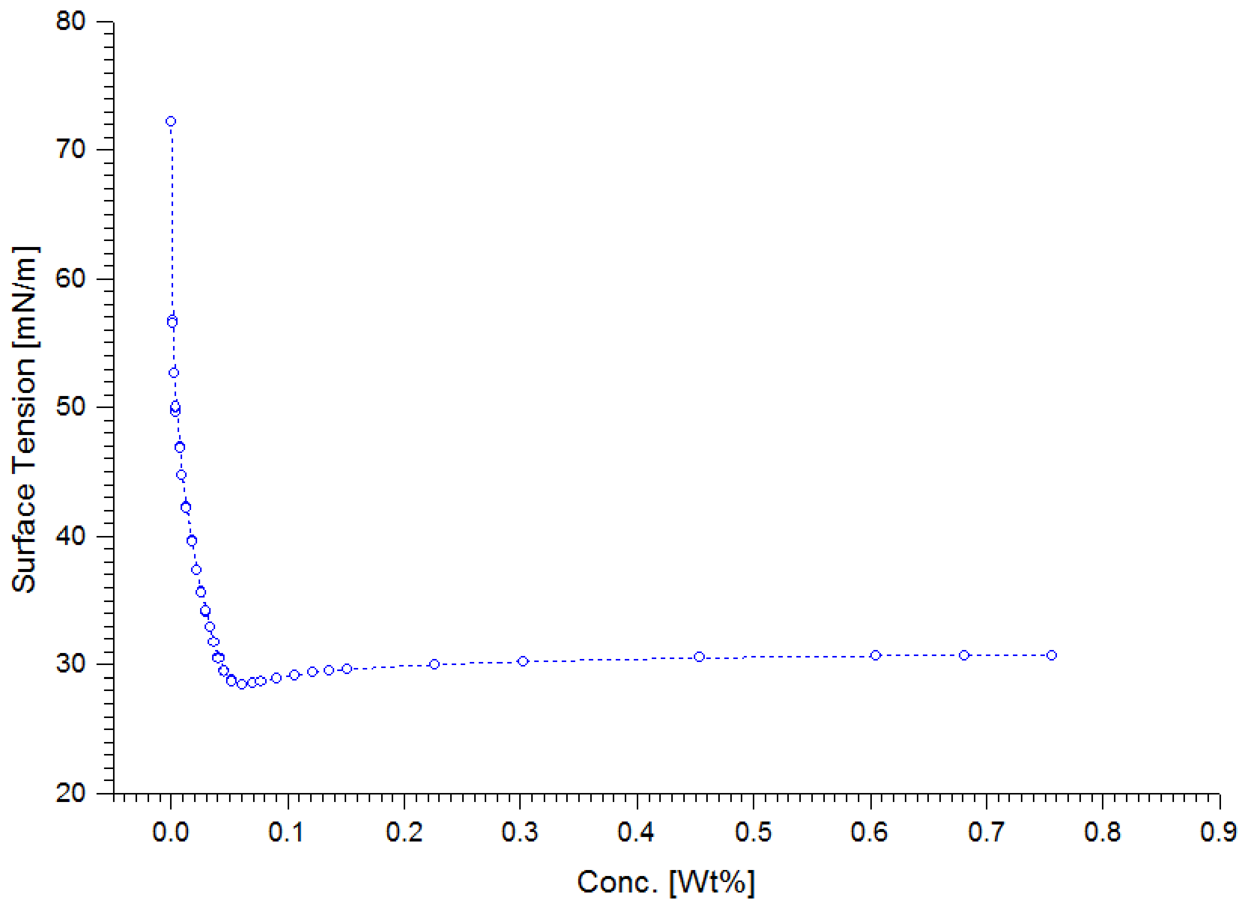
- ✓ Prepare a Stock Solution (SS) of knowing concentration and fill it into the container for SS;
- ✓ Fill a known volume of the start Working Solution (WS, usually pure solvent, e.g. pure water) into the container for WS, which is placed on a magnetic stirrer;
- ✓ Connect the tubing/fittings and set up the device;
- ✓ Enter the measurement parameters, among others, the number of concentration

nodes (CN) and the concentration changing schema (or their corresponding concentrations), number of repeats for each CN, and kind of measurement mode (static or dynamic);

- ✓ [Optionally] Click on the "preview steps" button to check up the settings made;
- ✓ Click on "Start Measurement!" button to launch the measurement, that's all!



The measurement can be run completely automatically without supervision. However, you may interrupt or pause the measurement procedure for whatever reason, and resume it later again. After a measurement has been completed, and it is found that the originally set endpoint of concentration is not high enough, you can use the "Append Steps" - function to add additional steps to extend the range of concentration, quite simply!



From the concentration-dependent IFT-curve, the value of CMC and other associated parameters can be easily determined.

Through the measurement of time- and concentration-dependence of IFT, not only the relationship of IFT with concentration, *IFT (c)*, in the quasi-equilibrium (static) state can be determined to obtain the corresponding (static) CMC value, but also its concentration-dependency at any time stage of surface/interface age can be measured to yield a comprehensive IFT/surfactant concentration/surface age - dependent, *IFT (c, t)*, network-like surface, which results in a time (surface age)-dependent CMC value curve, i.e. a dynamic CMC value curve, *CMC (t)*. The latter is of great importance in high-dynamic industrial processes like high-speed printing, foaming, etc.

In a nutshell, here are some distinct features of the CMC module based on faPDA:

- Fully-automatic, performable without supervision;
- Breakable and resumable;
- End-concentration extendable (after a measurement is completed);
- Suited for various kinds of surfactants;
- Not only static bust also dynamic CMC can be determined, in one pass.

Technical Data (CMC 10/20):

SFT/IFT Precision/Accuracy/Range:	ca. 0.01%; 0.1%; 10^{-3} – 2000 mN/m.
Concentration range of surfactant:	0 – ca. 70% of the stock solution.
Number of Concentration Nodes:	unlimited
Measurement Modes:	static CMC, dynamic CMC.
Measurement time length:	from ca. 30 min. to several hours (dependent of settings).
Package CMC 20 includes:	Software module, 2x Glass cuvette with cover, 1x Magnetic stirrer incl. stir bar, 1x ADUV 32