

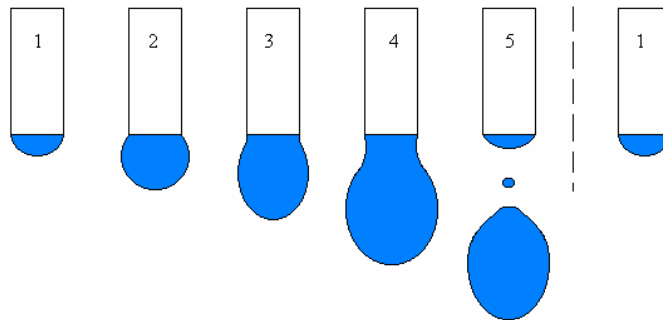
## Application note #4: At-line monitoring of surface tension of process liquids

### What is at-line monitoring?

At-line monitoring is manual batch sampling of process liquids at a production line in an industrial environment by the operator. The Attension Volumetric Tensiometer AL-20 is a bench-top tensiometer for checking the levels of chemical additives in process liquids by measuring surface tension. The surface tension of a water-based solution correlates with the amount of surfactants. Thus, based on the information from the measurement the operator can start or stop dosing chemicals into the process.

### Measuring principle

Volumetric dynamic surface tension measurement is based on the drop volume technique. When liquid flows gently through a tube, which is directed downwards, the liquid forms a drop at the tip. The drop grows to a certain volume after which it falls off. The maximum volume of the drop is proportional to the surface tension of the liquid.



In AL-20, a drop chamber is used to observe the drop rate of the liquid being measured. The liquid is pumped through the capillary at a constant rate, and each drop falling through the chamber is detected by an optical detector. The time interval between drops is detected and the average drop volume is calculated: the greater the time interval, the larger the drops and the higher the surface tension.

The surface tension of a water based solution is calculated by using the following equation

$$\gamma = \frac{\Delta\rho g V}{2\pi r_{cap} f}$$

where  $\Delta\rho$  = density difference between pure water and air

$g$  = gravitational constant

$V$  = drop volume

$r_{cap}$  = capillary radius

$f$  = calibration constant

The factor  $f$  is determined by calibrating the instrument with pure water. If the density of the sample differs from that of water, the surface tension displayed by AL-20 should be adjusted by the density ratio of the sample liquid and pure water according to the following equation

$$\gamma_{corrected} = \gamma_{displayed} \frac{\rho_{sample}}{\rho_{water}}$$

It should not be supposed that the drop volume technique is as accurate as the optical or force-based tensiometers, but it is useful for a sufficiently accurate determination when a quick and easy technique is needed. Additionally, measurements of dynamic surface tension is highly relevant for transient engineering processes where the system is continuously running and there is not enough time for the aqueous system to reach an equilibrium.

## Applications

The AL-20 is an ideal solution for regular batch sampling of process liquids. The sample preparation is simple, and the measurement takes less than 2 minutes. The analysis can for example be done once per day, batch or hour. If the process liquid is heated, the sample can first be allowed to cool down to room temperature before measurement. The AL-20 is a very easily operated instrument that can also be used for research and process development to optimize conditions for the actual industrial process. Since the AL-20 is capable of measuring water based solutions in a very large pH scale, it is an ideal solution for industrial applications where strong acids and bases are often utilized.

## INDUSTRIAL CLEANING

Monitoring of surface tension of cleaning liquids used in various industrial processes is of high importance for the effectiveness of the whole manufacturing process. To maintain cleaning efficiency, fresh detergent needs to be added when the cleaning agent's concentration is reduced to a certain defined level. To ensure clean enough surface and hence proper finishing of the surface treatment process, the concentration of cleaning agents must be constantly monitored.

Alkaline cleaning is the dominant process for cleaning metal surfaces in the industry today. Cleaning of metals after metal working processes of cast metals is one of the main applications of cleaning in automotive production. Cleaning is also the first step of surface treatment processes like coating or painting of tubes, aluminium cans, engines, gearboxes etc.

Sodium dodecyl sulfate (SDS) is an anionic surfactant found in many industrial degreasers. Figure 1 shows the concentration dependence of the surface tension of SDS solutions measured at room temperature with the AL-20. Surface tension decreases with increasing surfactant concentration until the critical micelle concentration,  $8,3 \cdot 10^{-3}$  M.

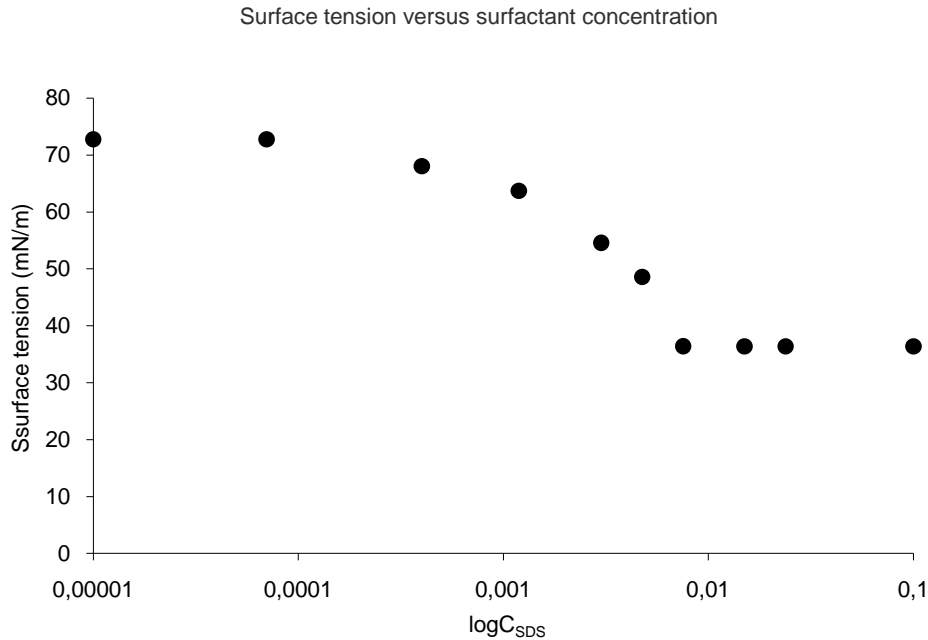


Figure 1. Surface tension of SDS solution as a function of concentration.

## SURFACE MODIFICATION

In aluminium can manufacturing processes the cans are transported from the washing stage to other remote operations in the facility along a conveyor or trackwork. In order to decrease the coefficient of static friction on the outside of the container without adversely affecting subsequently applied can coatings, the cans are treated with surfactant and wax including mobility enhancer solutions. In addition to improved mobility, mobility enhancer solutions provide a substantially clean surface after the application.

## NICKEL PLATING

Nickel coatings are widely used in applications where good resistance to corrosion, oxidation and wear is needed. One of the products of the combination of several types of chemical reactions involved in the electroless nickel plating system is hydrogen gas, which is removed from the surface as tiny bubbles. Reducing the surface tension of the bath by surfactants can enhance the removal of the hydrogen gas bubbles from the surface and thus increase the deposition rate of nickel. In principle, the surfactants lower the surface tension of the plating solution at H<sub>2</sub>-liquid interface and thus assist the detachment of the bubbles from the surface. The addition of surfactants can further hence the formation of pit-free and uniform nickel deposits. By measuring the surface tension of the plating bath with AL-20, the operator gets a quick check of the concentration of the surfactant and may optimise the process conditions in order to get a nonporous and bright nickel deposit.

## EMULSIFICATION

Highly porous monolithic chromatographic supports are often used as protein separation medias. One method for the preparation of such highly porous material is polymerization of the continuous phase of an emulsion. The internal phase of an emulsion is trapped inside the continuous phase and the continuous phase is polymerized. An open cellular structure with interconnects is obtained by extracting the inner phase after polymerization. The addition of a surfactant is necessary for stabilization of an emulsion against heating needed for the initiation of polymerization. Monitoring the surface tension of such surfactant solution used in emulsification is thus of great importance in the manufacturing of large-scale separation media.

## COSMETICS

The primary function of a conditioner is to give hair a soft and smooth feel, and hence increase combing ease. Conditioner also prevents flyaway hair due to static electricity and protects the hair from further damage by forming a thin layer over the fibers. The primary ingredient in most conditioner formulations is a long chain cationic surfactant, which attracts to the more or less negatively charged hair surface. This binding results in a reduction of static electricity on the hair surface, and consequently a reduction in the flyaway behavior. Silicone surfactants, important also in various other pharmaceutical and cosmetic applications, are one of the main sources of lubrication in the conditioner formulations. Although, the deposition of these hydrophobic silicone molecules on the hair surface is quite limited, cationic polymers may promote this deposition by making the surface of the hair less hydrophilic. Since surface tension depends on not just the concentration of the surfactants but also their chemical nature, it is important to investigate the concentration dependence of surface tension, when there is a combination of surfactants present.

## DEINKING

One way to decrease the plastic waste generation is to recycle plastic packages as effectively as possible. However, since for commercial use sufficient clearness in color and physical properties are required from recycled plastic material, printing ink on plastic packaging films must be well removed before recycling as inks on the film are mixed with the film when the plastic is melted for extrusion. Amphiphilic surfactants can be used to remove the ink from the films so that the plastic can be recycled into high quality film for reuse. The removal of various colors and layers of ink from the plastic film is aided by adsorption of surfactants onto the polymer and ink surfaces. If the reduction of interfacial tension is so strong that the sum of the interfacial tensions of polymer-water and ink-water is equal to less than the ink-polymer interfacial tension, the ink will detach from the polymer surface.

## REFERENCES

1. Baquerizo, I., Ruiz, M. A., Holgado, J. A., Cabreziso, M. A., Gallardo, V., Measurement of dynamic surface tension to determine critical micellar concentration in lipophilic silicone surfactants, // *Farmaco* **55** (2000) 583-589.
2. Bhushan, B., Nanoscale characterization of human hair and hair conditioners, *Prog. Mater. Sci.* **53** (2008) 585-710.

3. Chen, B.-H., Hong, L., Ma, Y. and Ko, T.-M., Effects of surfactants in an electroless nickel-plating bath on the properties of Ni-P alloy deposits, *Ind. Eng. Chem. Res.* **41** (2002) 2668-2678.
4. Gecol, H., Scamehorn, J. F., Christian, S. D., Grady, B. P. and Riddell, F. E., Deinking of water-based ink printing from plastic film using nonionic surfactants, *J. Surfac. Deterg.* **5** (2002) 363-374.
5. Gecol, H., Scamehorn, J. F., Christian, S. D., Riddell, F. E., Use of surfactants to remove solvent based inks from plastic films, *Colloid. Polym. Sci* **281** (2003) 1172-1177.
6. Kranjnc, P., Leber, N., Stefanec, D., Kontrec, S. and Podgornik, A., Preparation and characterisation of poly(high internal phase emulsion) methacrylate monoliths and their application as separation media, *J. Chromatogr A.* **1065** (2005) 69-73.
7. Pugh, R. J., Dynamic surface tension measurements in mineral flotation and de-inking flotation systems and the development of the on line dynamic surface tension detector (DSTD), *Minerals Engineering* **14** (2001) 1019-1031.
8. Songsiri, D, Min, S. S., Scamehorn, J. F., Osuwan, S. and Ellis, J. W., Use of cationic surfactant to remove solvent-based ink from rigid high density polyethylene surfaces, *Coll. Surf.* **204** (2002) 261-269.
9. *Surfactants in cosmetics*, 2nd ed., rev. and expanded / edited by Martin M. Rieger and Linda D. Rhein, Marcel Dekker, Inc., 1997.
10. US Patent 4529586 – Hair conditioning composition and process.