Application Report

Characterization of cationic surfactants

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Force Tensiometer – K12

Method:	
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Measuring Surface Tension and Critical Micelle Concentration on Cationic Surfactant Solutions

Background

Most solid surfaces are negatively charged, so cations will adsorb onto them. Cationic surfactants (such as quaternary ammonium salts and amine or imidazoline salts) have a positive charge at low pH values. These surfactants are readily adsorbed onto a wide variety of surfaces such as cellulosics (paper and cotton), fibers (wool, acrylic, and polyamide), silicates, metals and pigments. Depending on chemical structure of the cationic surfactant, it is possible to make a hydrophilic solid behave as if it were hydrophobic. Thus, surface properties of solids can be modified by using cationic surfactants.

Applications

Examples of cationic surfactant applications are:

Softeners and anti-static treatments for textiles

Cationics adsorb onto the fiber surfaces with the hydrophobic groups oriented away from the fiber. This imparts a soft, fluffy feel to the textile surface. Character of the hydrophobic group can be modified to reduce buildup of static charge.

Hair care

Mechanism for cationic surfactants adsorbing on to hair is the same as that for fibers. The surfactants also have similar structures to those used for textiles. Silicone hydrophobes have been widely used in this application of late.

Emulsifiers for asphalt (bitumen)

Asphalt emulsions are used as a primer on crushed stone (gravel) to bond hot mix asphalt to the gravel base. Rock surfaces are often damp, providing a surface difficult to adhere with petroleum materials. Cationic surfactants in the asphalt emulsion bond to the rock surfaces and yield a hydrophobic surface ideal for asphalt wetting.

Pigment and clay treatment

Normally hydrophilic materials such as bentonite clay can be treated with quaternary ammonium salts to give their surfaces hydrophobic properties. Treated clay can be used as a thickener in grease.

Pigments used in organic coatings need to be quite dry. Water soluble fatty amine salts will displace adsorbed water and produce a water repellent effect. Pigments treated in this manner will disperse readily in an organic medium.

Lubricants and metal working

Cationic surfactants adsorb onto metal surfaces and act as corrosion inhibitors for fuels and lubricants. They also improve lubricity.

Mining

Amine salts will adsorb onto potash and zinc ore. In flotation processing the ore is finely ground and mixed with water containing the cationic surfactant. The surfactant adsorbs onto the mineral surface and renders it hydrophobic. Mixing fuel oil into such an ore suspension agglomerates the particles which can then be separated by froth flotation.

Measurement Technique

Cationic surfactants adsorb on solid surfaces rendering them hydrophobic. This can pose problems for surface tension measurement. Some cationic surfactants adsorb so strongly on metals such as platinum that the Wilhelmy plate and Du Noüy ring method of measurement cannot be used to determine surface tension.

In the equations for surface tension measurement, contact angle between the ring or plate and the liquid is assumed to be zero.

$$\sigma = \frac{F_T - F_b}{L \cdot \cos\theta} \qquad \text{Wilhelmy plate} \qquad (1)$$

$$\sigma = \frac{F_{max} - F_r}{L \cdot \cos\theta} \qquad \text{Du Noüy ring} \qquad (2)$$

σ	=	surface tension
F_T	=	total force measured
F_{max}	=	maximum pull in the ring as a function of distance the ring is above the surface
F_b	=	buoyancy correction for the plate
F_r	=	ring correction
L	=	wetted length for the plate, L = 2(a+b) where a is thickness of the plate and b is its width; for the ring, L = 4πR where R is major radius of the ring (from its center to the center of the wire)

For cationic surfactants, θ may not be zero so these equations cannot be certain to give a correct surface tension even if the measurement can be made.

When using the ring method on cationic surfactant solutions, the ring sometimes breaks free from the surface well below the correct maximum pull. For the plate method, the force is sometimes too low for a correct reading. During critical micelle concentration (CMC) measurements on cationic surfactants, the problem is more severe. At low concentrations, the cationic surfactant may not adsorb thoroughly onto the ring or plate. This will allow correct measurements. However, as surfactant concentration increases, the ring or plate becomes coated with a hydrophobic layer. Unless the ring or plate is cleaned before each measurement, surface tension values have no hope of being correct. In automatic measurement mode, a Dosimat is used to increase surfactant concentration while the Processor Tensiometer K12 measures surface tension of each successive concentration. Having to stop the measurement to clean the ring or plate for every single measurement means the determination is no longer automatic. For some cationic surfactants, it is simply impossible to measure a CMC using the standard ring or plate method.

It is possible to measure surface tension and CMC on cationic surfactants by borrowing a well-established technique used with Langmuir-Blodgett troughs. These devices are designed to monitor surface pressure (surface tension of pure water less surface tension of water containing surfactant) as a solid is dipped into or withdrawn from a solution. Langmuir-Blodgett troughs work best with insoluble materials such as stearic acid (octadecanoic acid) or stearamine (octadecyl amine). These materials often cause wetting problems on metals. Their surface pressure cannot be routinely monitored using a platinum plate positioned at the film surface. However, a plate made of filter paper works fine. Chromatography paper (Whatman Chr 1) is the recommended type to use. Although cationic surfactants adsorb onto the paper, they do not render it hydrophobic. Wetting is maintained due to porosity of the paper. As long as contact angle between the liquid and paper is less than 90°, we know from the Washburn equation that only the wetting speed (m^2/t) will vary.

$$\cos\theta = \frac{m^2}{t} \cdot \frac{\eta}{\rho^2 \sigma c} \qquad (3)$$

θ = contact angle between the surfactant solution and chromatography paper
m^2/t = wetting speed
η = viscosity of surfactant solution
ρ^2 = density of surfactant solution squared
σ = surface tension of surfactant solution
c = a constant based on porosity of the chromatography paper

A correct surface tension value can still be obtained if we wait for the porous plate to wet completely. This occurs during the first measurement. If we retare after the porous plate is wetted the first time, we will get correct values for surface tension. Wetted length is width and thickness of the dry plate. Chromatography paper is chosen because it does not swell when wetted.

Experimental

A Processor Tensiometer K12 with Dosimat was used for all CMC measurements. Plate was made from Whatman Chr 1 chromatography paper. It is supplied in rolls that are 20 mm wide. Plates were cut to be this width and 10 mm tall. Paper plates were held using a contact angle sample holder CLMP10. Plate was oriented so that bottom edge of the paper was parallel to the surface. Before measurement, the plate was allowed to wet completely in water and the instrument was then tared. Width and thickness of the paper plate (20.0 - 0.19 mm) yielded a wetted length of 40.38 mm. Variations in height of the plate (10 ± 1 mm) had no effect on the data.

Surfactants used were nonylphenol ethoxylate (9.5 moles EO, Gradonic N-95 from Graden Chemical, Havertown PA), dodecyl, tetradecyl, and hexadecyl trimethyl-ammonium bromide (Sigma Chemical) and unknown cationic surfactant (Westvaco, South Charleston, SC). Distilled water was used as a solvent in all experiments. All measurements were made at room temperature, 23 ± 1°C.

Results

Nonylphenol ethoxylate is a non-ionic surfactant. It is easy to measure CMC on this material using the standard ring or the plate method. Data comparing the platinum plate to filter paper plate are shown in figures 1 and 2. The same CMC value was obtained in each case. CMC measurements on cationic surfactants are shown in figures 3-5. Each compares data obtained using the platinum plate to data measured using the paper plate. Again results are identical for both techniques. CMC data are summarized in Table 1.

A sample of unknown cationic surfactant was sent to Krüss USA for CMC measurement. Unlike the previous four samples, it was not possible to obtain surface tension measurements using the plate method for this surfactant. Even at low concentrations, the plate became hydrophobic upon contact with the liquid. Apparent surface tension values were 9 mN/m! This same sample gives an acceptable CMC measurement using the paper plate as shown in figure 6.

Conclusion

Use of a paper Wilhelmy plate allows surface tension and CMC measurements on cationic surfactant solutions. Results are comparable to those obtained with the standard platinum plate or ring.

Surfactant	Platinum Plate (mg/L)	Filter Paper Plate (mg/L)	Difference (%)
Nonylphenol ethoxylate (9.5 moles EO)	39	36	7.7
Dodecyltrimethyl-ammonium bromide	4948	4948	0.0
Tetradecyltrimethyl-ammonium bromide	1196	1169	2.2
Hexadecyltrimethyl-ammonium bromide	331	303	8.4
Unknown cationic	...	453	...

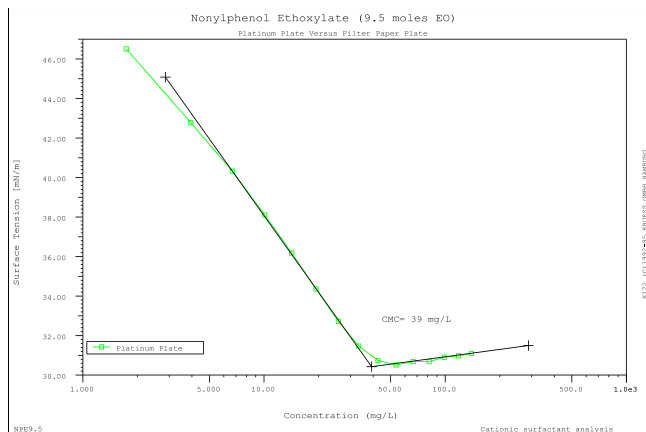Table 1: Comparison of Critical Micelle Concentration Data
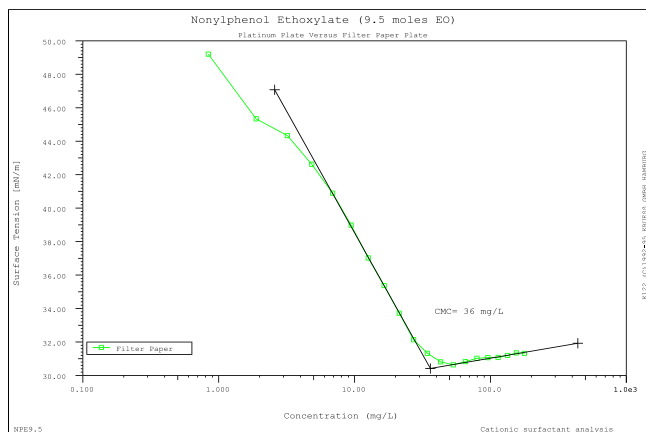
Figure 1: Nonylphenol ethoxylate (9.5 moles EO)

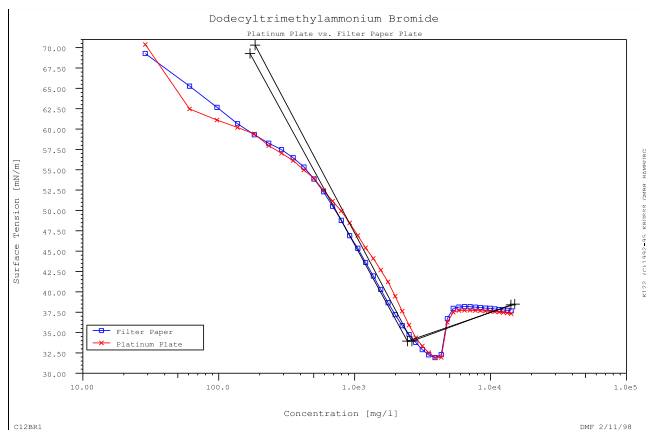Figure 2: Nonylphenol ethoxylate (9.5 moles EO)

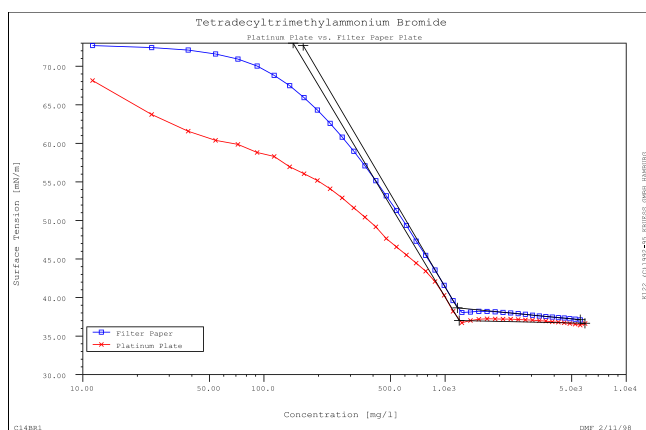Figure 3: Dodecyltrimethylammonium bromide

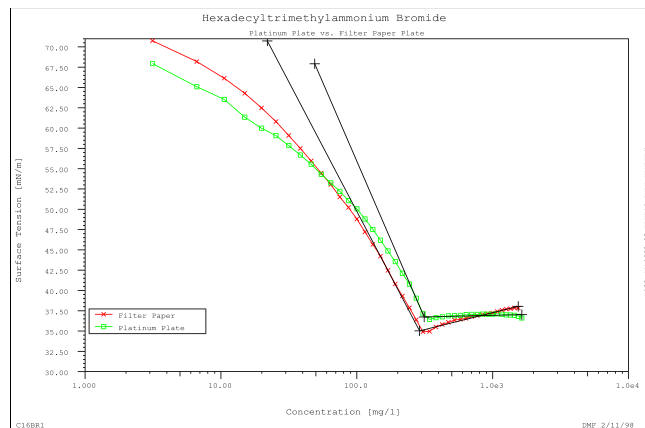Figure 4: Tetradecyltrimethylammonium bromide

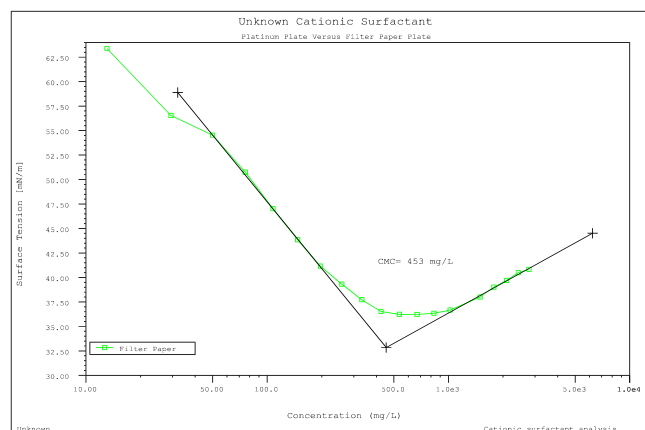Figure 5: Hexadecyltrimethylammonium bromide

Figure 6: Unknown cationic surfactant

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