

# A Cylindrical Weir for the Application of Surfactants to Coating Processes

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Presented at the 16<sup>th</sup> International Coating Science and Technology Symposium  
September 9-12, 2012, Atlanta, Georgia

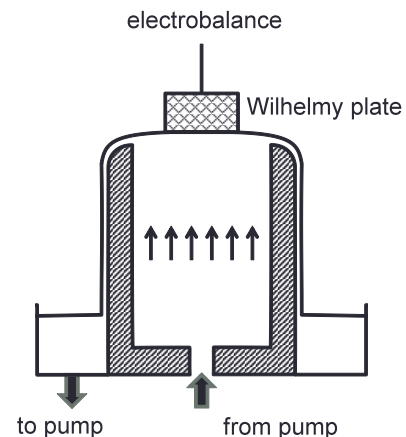
## ABSTRACT

Coating processes involve the rapid creation of interfacial area between liquid and air. Surfactants are employed to reduce surface tension values and the gradients that may arise and cause unwanted flow. A simple, inexpensive and useful laboratory apparatus for guiding surfactant deployment is a vertical, cylindrical weir supplied with a steady flow of coating liquid that after overflowing is collected and recycled. As in a coating process, surface area is created. Surface tension is measured with a Wilhelmy plate. A protocol for use of the weir in screening and deploying surfactants is demonstrated. For a surfactant to keep up with a high rate of surface area creation, it must diffuse rapidly and have fast adsorption kinetics. A model of low computational load that considers surfactant diffusion and adsorption explains why the method works. The data can be used to calibrate the model so that it may be applied to coating processes with different rates of area creation.

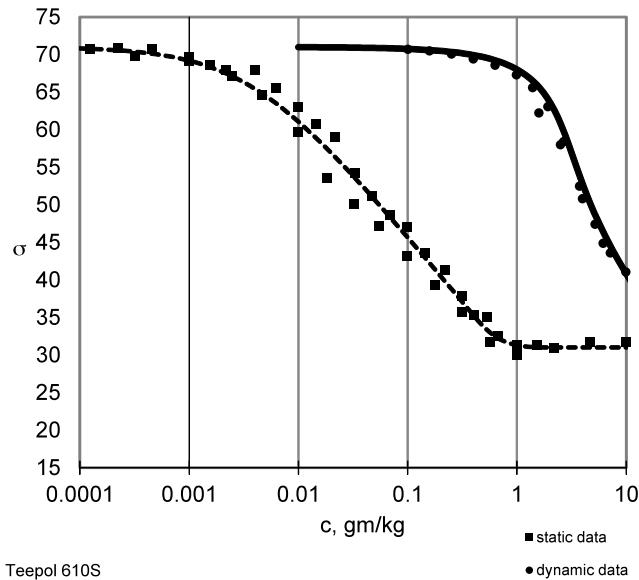
## INTRODUCTION

Surfactants are components of many product formulas that are coated, but they are also added as coating aids to control the level of surface tension (Y.-M. Tricot, Ch.4 in *Liquid Film Coating*, Chapman & Hall, New York, 1997). Coating is a process of creating surface area. Two uses of coating-aid surfactants are preventing repellency spots, craters caused by surface-active components or contaminants, and the spreading of the external layers over the internal layers that are stacked for simultaneous coating. Surface expansion may take place suddenly, as at the point of application to a moving substrate, or gradually, as in a liquid curtain. Static surface tension measurements are not predictive of dynamic surface tensions, and measurements under dynamic conditions are required.

A practical and inexpensive method of proven utility uses a cylindrical weir to create surface area continuously. The weir used in this study has a radius of 1.91 cm and a rounded lip of radius 0.64 cm. The purpose of the rounded lip is to minimize any dependence of the central flow on surface tension levels or gradients. The flow rate was fixed at 500 cc/min. Surface tension is measured with a centrally positioned Wilhelmy plate that is a glass microscope slide cover 2.2 cm wide and that was



etched in a strip about 3 mm wide along its lower edge to promote wetting. The weir is used by increasing surfactant concentration in increments until the dynamic surface tension approaches the minimum static surface tension. That concentration is then taken as that required in moderate and slow speed coating operations (<100 cm/sec) and is usually a few times that required to minimize static surface tension. This work shows the use of the method and how the method might be used to calibrate a model for dynamic surface tension for detailed application to coating processes.



The figure shows dynamic and static surface tension measurements for Teepol® 610S in distilled water. Note that even at a concentration ten times higher than that minimizing static surface tension, the dynamic surface tension remains high. Such a disparity is undesirable for coating aid surfactants. It is common that surfactants present for product reasons are inadequate as coating aid surfactants.

Static surface tension can be difficult to measure in the weir apparatus because of contamination. Therefore, we recommend that static surface tension be measured in a beaker to which surfactant is

incrementally added and mixed with a magnetic stir bar.

### MODEL FOR DYNAMIC SURFACE TENSION

The Szyszkowski equation  $\sigma = \sigma_0 - b \ln(1 + c/a)$  is used to relate surface tension  $\sigma$  to bulk surfactant concentration  $c$  at equilibrium. The constants  $a$  and  $b$  are determined by fitting data, and  $\sigma_0$  is the surface tension value without surfactant. The equation is truncated at the minimum value of surface tension.

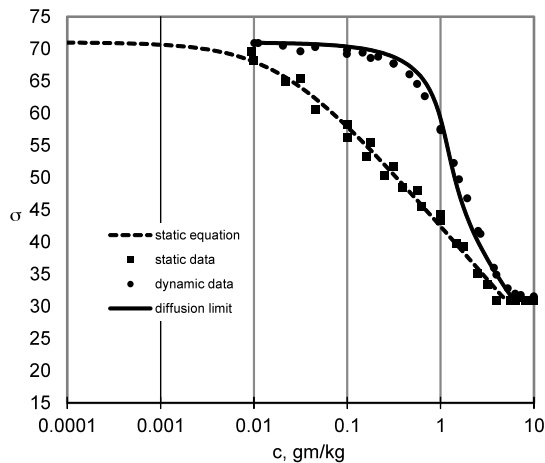
Langmuir-Hinshelwood adsorption kinetics are used, for which the flux of surfactant to the surface  $J$  is given by  $J = [k_f c(1 - \gamma) - k_r \Gamma] e^{-N\gamma^n}$  where  $k_f$  and  $k_r$  are rate constants,  $\Gamma$  is surface concentration,  $\gamma$  is fractional surface adsorption  $\Gamma/\Gamma_\infty$  where  $\Gamma_\infty$  is maximum surface concentration, and  $N$  and  $n$  are parameters. This rate expression yields the Langmuir isotherm  $\gamma = (c_e/a)/(1 + c_e/a)$  where  $c_e$  is the bulk concentration in equilibrium and  $a = k_r \Gamma_\infty / k_f$  corresponds to the Szyszkowski equation. The convective-diffusion equation in axial coordinates is standard.

The hydrodynamics of the lip region are computed as a thin-film flow with a critical point (K. J. Ruschak and S. J. Weinstein, *J. of Fluids Engng*, **125**, 10-17, 2003). This analysis determines the surface velocity  $V$  and the position of the air interface at the start of the lip, which depend upon flow rate and viscosity.

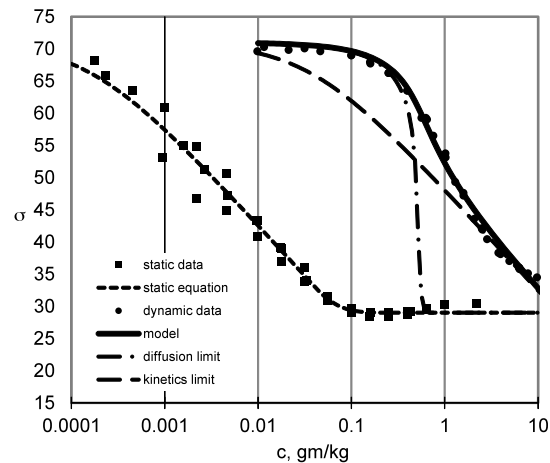
The modeling strategy is to construct a solution for which surface tension is constant on the surface of the weir. Observations supporting this strategy are that the measurement is not sensitive to plate position, and surface mapping using a narrow Wilhemy plate shows little variation. Another observation is that surfactant transfer to the surface is local, occurring within a few microns of the surface, and so only the velocity field adjacent to the surface matters. The local velocity field is proposed to be  $v_r = Vr/R$  and  $v_z = -2Vz/R$  where  $v$  is velocity,  $r$  is radial coordinate,  $z$  is the vertical coordinate measured upward from the surface, and  $R$  is weir radius. From the  $z$ -component of velocity, surfactant is convected to the expanding surface. We have shown that this velocity field is consistent with the inviscid flow expected and it furthermore satisfies the Navier-Stokes equation. According to this velocity field, if  $A$  is the area of a material surface element, then  $\frac{1}{A} \frac{dA}{dt} = \frac{2V}{R}$ , which means that the rate of surface area creation is constant over the surface of the weir. With this velocity field, the convective-diffusion equation is readily solved in terms of the error function, and surfactant concentration  $c$  depends only on the vertical coordinate  $z$ . The solution is completed by solving algebraic equations. The surfactant concentration and the dynamic surface tension are the same everywhere on the weir surface. The limiting solutions for diffusion controlling and adsorption controlling were also obtained.

## RESULTS

Modeling is not required to use the method. However, the proposed model can be fit to the static and dynamic data to aid interpretation of results. When the model seems appropriate, it can also be applied in detail to coating processes.



Alkanol XC



10G

Results for Alkanol<sup>®</sup> XC surfactant in distilled water were fitted to the diffusion-controlled model. The diffusion coefficient was thereby determined to be  $3.9 \times 10^{-6} \text{ cm}^2/\text{sec}$ . For this surfactant, the bulk concentration required to produce a dynamic surface tension near the minimum static tension is not much above that giving the minimum static tension. Therefore Alkanol<sup>®</sup> XC is an example of an efficient coating-aid surfactant.

Results for surfactant 10G in distilled water were fitted to the diffusion-adsorption model. The diffusion coefficient was thereby determined to be  $4.6 \times 10^{-6} \text{ cm}^2/\text{sec}$ , and the adsorption rate constant  $k_f$  0.071 cm/sec. The chart shows that at low concentrations, dynamic surface tension is diffusion controlled, but at high concentrations it is adsorption controlled. Consequently, 10G is not an efficient coating-aid surfactant.

## **CONCLUSIONS**

The cylindrical weir method makes differences in the effectiveness of surfactants as coating aids readily apparent. It accesses conditions where a constant rate of surface expansion leads to a constant rate of surfactant adsorption. The convection of surfactant towards the surface is an important element of surfactant dynamics that is not present without an expanding surface. Adsorption kinetics can slow surfactant action, and coating aid surfactants are preferably diffusion limited.