

NUMERICAL SOLUTION OF THE DIP COATING PROCESS WITH INSOLUBLE SURFACTANTS: LANGMUIR OR A LINEAR APPROXIMATION FOR SURFACE TENSION?

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Abstract— In this work the dip coating process when an insoluble surfactant is adsorbed at the interface is numerically studied. The work centers in the applicability of the linear approximation usually employed to model the relationship between surface tension and the concentration of the surface active agent. Reported solutions show that film thicknesses predicted with a linear model can differ significantly from those computed with a more reliable equation of state.

Keywords— dip coating, insoluble surfactant, surface equation, finite elements.

I. INTRODUCTION

When a flat plate is vertically pulled out of a liquid bath with a constant speed, a uniform liquid film is deposited on the solid. The first theoretical analysis of this process—known as dip coating—was carried out by Landau and Levich (1942), and Derjaguin (1943) who reported an approximate expression for the film thickness valid at low coating speeds. Thenceforth, a large number of works have been published to incorporate the effects of gravity, inertia and Marangoni stresses.

Experiments as well as numerical and approximate analysis of the process usually report that the film thickness in the presence of a surfactant. The particular situation in which the surface active agent can be regarded as insoluble was considered by Park (1991) and more recently by Campana *et al.* (2011).

Park studied the problem in the limit of very small capillary number (i.e. very low coating velocities) using the method of matched asymptotic expansions. He considered two cases, one in which the interfacial distribution of surfactant has small gradients and the other one in which the concentration itself is small. The former may be associated with the deposition of Langmuir Blodgett films (Petty, 1996) and the latter with surface contamination. Results of this asymptotic analysis show that the film thickness is affected by the surfactant within a range of capillary number that depends on the magnitude of the elasticity parameter (see the definition below Eq. 6). Within that range, the thickening factor (i.e. the ratio between the thickness of the contaminated system and the Landau-Levich one for a uniformly distributed surfactant) is a non monotonic function of that parameter: at the lower and upper ends it is equal to one and in between it is equal to $4^{2/3}$.

Campana *et al.* (2011) numerically solved the full hydrodynamic problem. This study not only corroborates the predictions of Park's asymptotic analysis but also extends those results by incorporating the influence of inertia and gravity forces. An interesting finding is the non monotonic behavior exhibited by the film thickness as the substrate speed increases, a behavior that is not detected when inertia is not considered. The authors also describe the evolution of the flow patterns when the coating speed is increased and the Landau-Levich result is recovered.

One of the hypotheses proposed in the above works assumes a linear equation of state to model the dependence of surface tension on the concentration of adsorbed surfactant, an assumption that is reasonable only if the interfacial concentration of surfactant and/or its variation along the free surface are small.

In this paper we numerically study the influence of the equation of state used to model surface tension on the dip coating process. To this end we compute solutions when the adsorption of the surfactant corresponds to a Langmuir isotherm and compare them with the predictions of the corresponding linear model to determine the conditions under which the film thickness predictions of the linear model are reasonable. In order to explore the influence on the results of the concentration of surfactant about which the linearization process is carried out, we selected two values: one corresponds to the concentration of solute far away from the substrate and the other one is the concentration of solute carried out by the film.

II. MODEL FORMULATION

A. Governing equations and boundary conditions

A flat plate is vertically pulled out of a pool of liquid with constant speed U . The bath has infinite depth and semi-infinite horizontal dimensions; we assume that the liquid is Newtonian and incompressible with viscosity (μ) and density (ρ). The air in contact with the liquid is regarded as inviscid and its pressure is arbitrarily set equal to zero. An insoluble surfactant is adsorbed at the gas/liquid interface whose concentration is kept constant and equal to $\hat{\Gamma}(s=0)$; since the solute distribution depends on surface convection and surface diffusion the concentration of surfactant may present spatial variations which in turn give rise to gradients of the surface