124h Effect of Insoluble Surfactant on the Selective Dip-Coating of Chemically Micropatterned Surfaces

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Free-surface microfluidic flow on chemically heterogeneous surfaces is used extensively in such fields as nanotechnology, sol-gel processing, patterned colloidal deposition, microfluidic devices and sensors, microelectronics, and tissue engineering, with applications ranging from selective material deposition to controlling the self-assembly of hierarchically organized nanostructures. One of the most useful ways to coat these patterned surfaces with fluid is the dip-coating process, which has been extensively investigated for chemically homogeneous plates, rods, and fibers Microscopic surface heterogeneity can selectively confine liquids to particular regions on the substrate. Such confinement induces a significant lateral curvature of the liquid free surface, which can cause significant quantitative and qualitative deviations from fluidic behavior on homogeneous surfaces. The recent theoretical analysis by Davis [1] of the dip coating of a pure fluid onto vertical, wetting stripes surrounded by non-wetting regions quantified the experimentally observed deviations from the classical Landau-Levich result. The thickness of the entrained film along the centerline of the stripe was predicted to be $h = 0.35\ W\,\mathrm{Ca}^{1/3}$, where W is the stripe width and Ca is the capillary number. The significant lateral curvature of the free surface near the liquid bath and the streamwise change in this lateral curvature along the stripe were shown responsible for the strong deviations from behavior observed on homogeneous surfaces. The predicted film thickness was in excellent agreement with experimental measurements [2]. Emerging applications of microfluidic flow on micropatterned surfaces often include the presence of surfactants, either as integral parts of the process or as trace contaminants. Gradients in the surfactant concentration can induce Marangoni stresses at the liquid-vapor interface, which can significantly modify the coating dynamics and thickness of the entrained liquid film. While these effects have been quantified for the dip-coating of homogeneous plates and the related problem of bubble motion in capillary tubes, they have not been previously analyzed for chemically heterogeneous substrates. In this present work, the dip coating of wetting microstripes is examined for a liquid containing an insoluble surfactant. Matched asymptotic expansions are used to determine the thickness of the entrained liquid film and the surfactant concentration in the entrained monolayer for a wide range of material and process parameters. The increase in the entrained film thickness from the prediction of Davis [1] for a pure liquid is shown analytically to be limited by a multiplicative factor of $4^{1/3}$, and the numerical results demonstrate that the thickening (*i.e*., increase in numerical prefactor) due to Marangoni stresses is non-monotonic in the Capillary number. These numerical and theoretical results are explained on physical grounds.

References: [1] J. M. Davis, "Asymptotic analysis of liquid films dip-coated onto chemically micropatterned surfaces," *Phys. Fluids* **17**, 038101 (2005). [2] A. A Darhuber, S. M. Troian, J. M. Davis, S. M. Miller, and S. Wagner, "Selective dip-coating of chemically micropatterned surfaces," *J. Appl. Phys*. **88**, 5119 (2000).