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Electrokinetics over liquid/liquid interfaces[1]

TODD M. SQUIRES, Chemical Engineering Department, University of California, Santa Barbara

Since liquid-liquid interfaces flow in response to an applied stress, one might expect electrokinetic flows at liquid-liquid interfaces to be significantly higher than over liquid-solid interfaces. The earliest predictions for the electrophoretic mobility of charged mercury drops – distinct approaches by Frumkin and Levich (1946), and Booth (1951) – differed by $\mathcal{O}(a/\lambda_D)$, where a is the radius of the drop and λ_D is the Debye screening length. Seeking to reconcile this rather striking discrepancy, Levine (1973) showed double-layer polarization to be the key ingredient. Without a physical mechanism by which electrokinetic effects are enhanced, however, it is difficult to know how general the enhancement is – whether it holds only for liquid metal surfaces, or more generally, for all liquid/liquid surfaces. By considering a series of systems in which a planar metal strip is coated with either a liquid metal or liquid dielectric, we show that the central physical mechanism behind the enhancement predicted by Frumkin and Levich (1946) is the presence of an unmatched electrical stress upon the electrolyte-liquid interface, which establishes a Marangoni stress on the droplet surface and drives it into motion. The source of the unbalanced electrokinetic stress on a liquid metal surface is clear – metals represent equipotential surfaces, so no field exists to drive an equal and opposite force on the surface charge. This might suggest that liquid metals represent a unique system, since dielectric liquids can support finite electric fields, which might be expected to exert an electrical stress on the surface charge that balances the electric stress. We demonstrate, however, that electrical and osmotic stresses on relaxed double-layers internal to dielectric liquids precisely cancel, so that internal electrokinetic stresses generally vanish in closed, ideally polarizable liquids. The enhancement for liquid mercury drops can thus be expected quite generally over clean, ideally polarizable liquid drops. More broadly, the ability to reliably engineer liquid interfaces in microfluidic systems, then, may provide a path to significantly enhanced electrokinetic flows.

[1]Research done in collaboration with A. J. Pascall