

## 588c Physical Basis for the Formation and Stability of Silica Nanoparticles in Basic Solutions of Monovalent Cations

*Jeffrey D. Rimer, Raul F. Lobo, and Dionisios G. Vlachos*

Aqueous silica chemistry remains an important, yet not fully understood topic in the synthesis of mesostructured materials, catalysts and adsorbents, low-dielectric coatings, biomineralization, etc., to name a few. The classical view of silica polymerization is that it is a rather uncontrolled process leading to poorly defined structures with broad distributions of molecular weights and connectivity, as it is typically the case in sol-gel processes [1]. Recent experiments conducted in our laboratories reveal a rather different view of silica polymerization [2, 3]. We observe that at well-defined concentrations of silica in basic solutions of monovalent cations, further addition of silica leads suddenly to the formation of silica nanoparticles with a size that is fairly uniform, nearly independent of the cation identity (from Na<sup>+</sup> to organic cations such as tetrabutylammonium, TBA<sup>+</sup>), and with a structure formed of a silica core and a cation shell. Moreover, the formation and dissolution of these nanoparticles appears to be a reversible process at room temperature over typical observation times [3].

Here we present studies of the colloidal stability and phase behavior of silica nanoparticles (<10 nm) using a combination of electrostatic and chemical equilibrium models. By accounting for the deprotonation and condensation of silica species we have been able to develop a model that predicts the phase diagram and critical aggregation concentration for silica nanoparticles in basic solutions [4]. Inclusion of a complexation model allows for the first determination of the equilibrium constant for nanoparticle silanol deprotonation along with the charge of the particle surface – from which we are able to explain the colloidal stability of these small, 3-5 nm nanoparticles in solution. In addition, we show that the charging of the surface plays a significant role in the free energy of condensation and can explain why the formation of small particles is energetically favorable.

1. Iler, R. K. The chemistry of silica: solubility, polymerization, colloid and surface properties, and biochemistry. 1979, New York: Wiley.
2. Fedeyko, J. M.; Rimer, J. D.; Lobo, R. F.; Vlachos, D. G. J. Phys. Chem. B 2004, 108, 12271.
3. Fedeyko, J. M.; Vlachos, D. G.; Lobo, R. F. Langmuir 2005, 21, 5197.
4. Rimer, J. D.; Vlachos, D. G.; Lobo, R. F. J. Phys. Chem. B, Accepted 2005.