Reduced Capillary Length Scale in the Application of Ostwald Ripening Theory to the Precipitation of Charged Colloidal Particles in Electrolyte Solutions

J.D. Rowe and J.K. Baird[C, S]
Department of Chemistry, University of Alabama in Huntsville, Huntsville, AL, U.S.A.
jkbaird@matsci.uah.edu

Under the usual conditions of precipitation of colloidal particles from an electrolyte solution, the particles will exchange ions with the electrolyte. Any net charge built up on a particle will cause the ions in the solution to organize themselves into a space charge surrounding the particle. The electrostatic energy, as well as the entropy, associated with the formation of this space charge will contribute to the interfacial free energy. The effect will be to renormalize the capillary length scale that governs the particle size dimension in the theory of Ostwald ripening.

In the ordinary theory of Ostwald ripening, the capillary length scale depends upon the temperature, the molecular volume of the precipitate, and the particle/solution surface tension. The introduction of space charge into the theory extends this list to include the particle surface charge density, the stoichiometric coefficients of the adsorbed ions, the solution ionic strength, and the dielectric constant of the solvent.

The space charge makes a negative contribution to the capillary length, which is independent of the sign of the surface charge density on the colloidal particle. The effect on the theory of Ostwald ripening is to increase the number density of the precipitate particles, decrease their average radius, and accelerate the rate of decay of the solute supersaturation that drives the precipitation.