Thermodynamic stability of nanoparticle dispersions

Ramanathan Nagarajan
Molecular Sciences and Engineering Team
Natick Soldier Research, Development and Engineering Center
Natick MA 01760

Emeritus Professor of Chemical Engineering
The Pennsylvania State University

Nanoparticles need to retain their identity as single particles and not be vulnerable to aggregation if one has to take advantage of their nanoscale properties. However, given the large specific surface area characteristic of nanoparticles, even small magnitudes of van der Waals attractions are adequate to cause the nanoparticles to aggregate. Classical approaches to stabilization of colloidal particle dispersions have focused on attaining kinetic stability, usually by creating an electrostatic and/or steric potential barrier between the particles. We examine whether a thermodynamically stable dispersion of nanoparticles can be generated as a results of spontaneous molecular assembly in nanoparticle-block copolymer systems in selective solvents. The block copolymer can form micelles excluding the nanoparticles or it can form micelles in which the nanoparticles are solubilized. The nanoparticle size, inter-particle attractions, particle-polymer interactions and the molecular weight and composition of the copolymer blocks, all control whether thermodynamically stable micelles solubilizing nanoparticles will form or not. We investigate the solubilization of spherical nanoparticles and also of carbon nanotubes in block copolymer micelles, using a simple phenomenological theory of solubilization. We also examine how the solubilization of nanoparticles by the block copolymer micelle can be further tuned by the addition of small hydrophobic molecules.

Biographical Information

Prof. Nagarajan is currently a research scientist in the Molecular Sciences and Engineering Team at the Natick Soldier Research, Development and Engineering Center (NSRDEC) at Natick, MA. Nagarajan received his Ph.D. in chemical engineering from the State University of New York at Buffalo. He was a member of the chemical engineering faculty at The Pennsylvania State University from 1979 until 2005 when he retired as Emeritus Professor. His research interests span the fundamentals and applications of soft colloidal systems where self-assembly plays a critical role. He received the Outstanding Research Award from the Pennsylvania State Engineering Society and the Collaborative Teaching Award from the Penn State University. Prof. Nagarajan is a Fellow of the American Institute of Chemical Engineers and the American Institute of Chemists. He was Elf-Aquitaine Fellow at the École Normale Supérieure in Paris, France (1988-89); Directeur de Recherche at Université Paul Sabatier in Toulouse, France (1997-98); Senior Scientist at Cabot Corporation, MA (2002-03); and National Research Council Senior Research Associate at NSRDEC, MA (2005-06). He has been the Program Chair of the ACS Division of Colloid and Surface Chemistry during 1999-2006 and 2010-present. He has been on the editorial board of the Journal of Colloid and Interface Science, Encyclopedia of Surface and Colloid Science, Journal of Macromolecular Science Part A. Pure and Applied Chemistry and served as editor of special issues for Advances in Colloid and Interface Science and Colloids and Surfaces. He was the Chair of the National Colloid and Surface Science Symposia held in 1988 and 1998 at Penn State and in 2002 at the University of Michigan. Prof. Nagarajan has edited the ACS Symposium Series Books, Nanoparticles: Synthesis, Stabilization, Passivation and Functionalization (2008), Nanoscience and Nanotechnology for Chemical and Biological Defense (2009), Amphiphiles: Molecular Assembly and Applications (2012) and Nanomaterials for Biomedicine (in press).

A. Thermodynamic Stability Near Equilibrium. Consider a system containing a chemical species A at uniform concentration c, which is thermodynamically un-stable to concentration uctuations. Here, we show that thermodynamic stability of reac-tive mixtures is determined by the competition of auto-catalysis and chemical diusion. In driven open systems, such as electrochemical interfaces, this competition can be controlled by applied potentials and currents. The image shows a two-phase lithium iron phosphate nanoparticle driven far from equilibrium by an ap-plied Faradaic current [15] from Fig. 7 below. for an arbitrary set of conjugate forces $F\hat{I}\pm$ and uxes $J\hat{I}\pm$. Thermodynamic stability prevents any possibility of scale deposition, while kinetic stability results in an extended period of time before deposition will occur. From: Geothermal Power Generation, 2016. Related terms The thermodynamic stability of hydrates, with respect to temperature and pressure, may be represented by the hydrate curve. The hydrate curve represents the thermodynamic boundary between hydrate stability and dissociation. Conditions to the left of the curve represent situations in which hydrates are stable and "can" form. Keywords: thermodynamic instability, critical state, phase explosion, metal dispersion, nanoparticles, oxides, electrical explosion of conductors, supercritical fluid. Contents. 1. Introduction. 4.2. Phenomenological modeling of critical phenomena and thermodynamic stability of one- and two-phase systems in the mean-field approximation. If the linear dimensions of phases are large enough, one can neglect the curvature of their interface. In this case, thermodynamic equilibrium sets in when their temperatures, pressures and chemical potentials are equal [67,69]