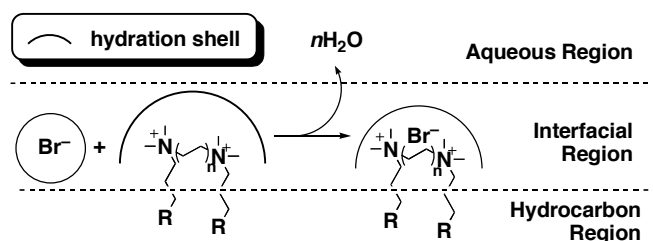


A New View on the Balance of Forces Controlling Micellar Morphologies of Ionic Surfactants

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The sphere-to-rod transitions of ionic micelles in aqueous solution are exquisitely sensitive to the nature and concentrations of surfactants and counterions. The dependence of these transitions on the nature of the surfactant headgroups and counterions, often expressed in terms of the Hofmeister series, are not understood. In the specific ion pair-hydration model proposed here, the free energies of hydration of headgroups and counterions and specific headgroup-counterion pairs in the interfacial region of the aggregates balance the hydrophobic effect.

Morphological transitions occur when headgroups and counterions in the interfacial region form ion pairs, with lower demand for hydration than the free ions, and release excess water of hydration into the surrounding aqueous phase, i.e., both surfactant aggregation and morphological transitions are driven by an increase in entropy of the system.



We have developed a chemical trapping method for estimating the interfacial concentrations of a wide variety of weakly basic nucleophiles, including water, that are commonly found in biological and surfactant based systems over wide ranges of solution composition. The method is based on the unique characteristics of heterolytic dediazonium reactions of arenediazonium ions, which are trapped by weakly basic nucleophiles to give stable products whose yields are measured by HPLC. The interfacial concentration of a nucleophile within the interfacial region of the micelles is obtained when the yield reaction of a nucleophile with the amphiphilic, micellar bound, arenediazonium ion is the same as the yield from reaction of a water soluble arenediazonium ion analog in an aqueous reference solution of known concentration in the absence of surfactant, i.e., *when the yields are the same, the concentrations are the same.*

This talk will include an overview of the chemical trapping method and experimental evidence that demonstrates that the specific ion pair-hydration model provides a sensible interpretation of the dependence of the sphere-to-rod transition for cationic surfactants with Cl⁻, Br⁻, 2,6-dichlorobenzoate and 3,5-dichlorobenzoate counterions, and gemini surfactants with variable spacer lengths. Other applications of chemical trapping such as probing interfacial compositions of microemulsions, hydration numbers of nonionic micelles and emulsions, interfacial urea concentrations and other applications will be covered briefly.

Lead Reference. Geng, Y.; Romsted, L. S.; Menger, F. M., Specific Ion-Pairing and Interfacial Hydration as Controlling Factors in Gemini Micelle Morphology. *Chemical Trapping Studies. J. Am. Chem. Soc.* **2006**, *128*, 492-501.