587c Calorimetric Determination of Surfactant/Polyelectrolyte Binding Isotherms

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Mixing of oppositely charged surfactants and polyelectrolytes in aqueous solutions leads to surfactant adsorption onto the polyelectrolyte chain. Experimental determination of the binding isotherm is normally achieved by ion-selective electrode methods, which require time consuming experiments with sensitive, custom-built equipment. Here we present a simple method for approximating binding isotherms from isothermal titration calorimetry (ITC) data. The Satake-Yang model is used to fit the binding constant (Ku), cooperativity parameter (u), and specific heats of cooperative and non-cooperative surfactant adsorption to the total measured heat of adsorption. The fitted binding parameters, Ku and u, are then used to estimate the model polyelectrolyte coverage (β) as a function of free surfactant concentration. This approach is applied to two surfactant/polyelectrolyte mixtures: dodecyltrimethylammonium bromide (DTAB) and poly(styrene sulfonate) (PSS), and sodium perfluorooctanoate (FC_7) and N,N,N-trimethylammonium derivatized hydroxyethyl cellulose (JR-400^{TM}). The results suggest that while both systems exhibit cooperative surfactant binding, the interactions in DTAB/PSS mixtures favor the formation of intrapolymer surfactant aggregates, while the FC_7/JR-400 mixtures form interpolymer surfactant/polyelectrolyte networks.