

ITC XXII – Surfactant-polymer interactions

Bai G., Catita J. A., Nichifor M. and Bastos M. (2007) Microcalorimetric evidence of hydrophobic interactions between hydrophobically modified cationic polysaccharides and surfactants of the same charge. *J Phys. Chem B* **111**, 11453-11462.

Abstract: We synthesized and characterized a series of new polymers-hydrophobically modified cationic polysaccharides-based on dextran having pendant N-(2-hydroxypropyl)-N,N-dimethyl-N-alkylammonium chloride groups randomly distributed along the polymer backbone. These polymers are good candidates for studying the hydrophobic effect on polymer/surfactant association. In previous papers we reported their interactions with oppositely charged surfactants. For further insight into the relative importance of the hydrophobic interaction in the association process now we studied the thermodynamics of the interaction of these hydrophobically modified polymers with surfactants of the same charge (DMRX/CnTAC) by isothermal titration calorimetry (ITC). In order to try to discriminate the solution behavior of these polymer/surfactant systems, we analyzed separately the interaction of unmodified dextran with ionic surfactants and the interactions between the corresponding cationic surfactants. The interaction enthalpies for DMRX/CnTAC systems were derived from a proposed thermodynamic model with equations that describe the polymer-surfactant interactions. The thermodynamic parameters for the DMRX/CnTAC aggregation process as well as surfactant micellization in the presence of the polymer were also calculated. From all the results we were able to ascertain the effect on the interactions of changing the alkyl chain length of the polyelectrolyte pendant groups or the surfactant. The importance of the polymer aggregation state on the mechanism of interaction was also addressed.

Barbosa S., Taboada P., Castro E., and Mosquera V. (2006) Influence of SDS and two anionic hydrotropes on the micellized state of the triblock copolymer E71G7E71. *J Colloid Interface Sci* **296**, 677-684.

Abstract: Complex formation between the triblock copolymer E71G7E71, where E denotes ethylene oxide, the central hydrophobic block, phenyl glycidyl ether, is denoted as G, and the subscripts denote the block length, the surfactant sodium dodecyl sulfate (SDS), and the penicillins cloxacillin and dicloxacillin, which can be considered as hydrotropes has been investigated by dynamic light scattering (DLS) and isothermal titration calorimetry (ITC). The different copolymer/amphiphile systems have been studied at a constant copolymer concentration of 10 g dm⁻³ and at different amphiphile concentrations. For all systems, the relaxation time distributions show a well-defined single mode with a shift toward slightly faster times, which indicates that the electrostatic interactions between the complexes is minimum, and so it is possible to estimate a size in terms of the apparent hydrodynamic radii. For ITC the amphiphile solutions were titrated in two different forms: as monomers (below the cmc) and as aggregates. The data indicate that the interaction between the surfactant and the hydrotropes with the copolymer occurs even at the lowest SDS concentration measured.

Barbosa M. E., Bouteiller L., Cammas-Marion S., Montembault V., Fontaine L. and Ponchel G. (2008) Synthesis and ITC characterization of novel nanoparticles constituted by poly(γ -benzyl L-glutamate)- β -cyclodextrin. *J Mol Recognit* **21**, 169-178.

Abstract: Imparting desired technological characteristics to polymeric nanoparticles requires the development of original polymers. In the present work, the synthesis and characterization of a novel PBLG-derivative, the poly(γ -benzyl L-glutamate)- β -cyclodextrin (PBLG- β -CD-50), have been carried out. Nanoparticles from either PBLG- β -CD-50 polymer or from mixtures with PBLG have been prepared using a modified nanoprecipitation method. Spherically shaped nanoparticles with diameter in the range of 50-70 nm were obtained, as determined by dynamic laser light scattering and transmission electron microscopy. The presence of a surfactant in the suspension medium had almost no influence on these parameters and was not necessary to the shelf-stability of the suspension. Further, isothermal titration microcalorimetry (ITC) experiments have been used to show unambiguously that about 20% of the cyclodextrins remain functional within the particles. Consequently, this system may be of interest when association of large amounts of hydrophobic drugs to nanoparticles is required

Chakraborty T., Chakraborty I., and Ghosh S. (2006) Sodium carboxymethylcellulose-CTAB interaction: a detailed thermodynamic study of polymer-surfactant interaction with opposite charges. *Langmuir* **22**, 9905-9913.

Abstract: Interaction between polymer and surfactant bearing opposite charges is much more complex from a physicochemical point of view as compared to interaction between ionic surfactant and nonionic polymer. Electrostatic and hydrophobic interactions interplay in the former, whereas the hydrophobic effect is the prevailing factor in the latter. We have studied the interaction between a water-soluble polyanion, sodium salt of carboxymethylcellulose (NaCMC), with a cationic amphiphile, CTAB, in aqueous medium. There were manifold discrepancies with the reported works in NaCMC-alkyltrimethylammonium bromide, which is assumed to be an effect of difference in degree of substitution, which in turn affects the charge density of the polymer chain. We have noticed that the bulk complexation and interfacial interaction driven by electrostatic forces operate side by side. Thereafter, there is a wrapping process by the polyanion to the polymer-induced smaller surfactant aggregates driven by increase in entropy of the solution as a result of expulsion of the counterions from the ionic atmosphere around the surfactant aggregate. Because of the electrostatic interaction, hydrophobicity of the polymer-surfactant complex increases, leading to coacervation, and again solubilization in the hydrophobic core of the self-aggregated structure provided by the added excess CTAB. The tensiometric, conductometric, microcalorimetric, and turbidimetric techniques have been applied to address these problems.

Chakraborty T., Chakraborty I., Moulik S. P. and Ghosh S. (2007) Physicochemical studies on pepsin-CTAB interaction: energetics and structural changes. *J Phys. Chem B* **111**, 2736-2746.

Abstract: The interaction between pepsin and CTAB has been elaborately studied with a number of techniques. The enzyme-induced interaction produced complexes, aggregates, and micelles of CTAB with distinct physicochemical features. It was found that at very low surfactant concentration (much below the critical micellar concentration (cmc) of pure CTAB), the surfactant got adsorbed both in monomeric and lower aggregated forms to the high-energy sites of the native biopolymer, leading to enhanced hydrophobicity of the combine, and hence, lowering of the interfacial (air/solution) tension. This was followed by the formation of a faintly turbid solution of the polymer-surfactant coacervate. The CTAB interacted unfolded pepsin along with the surfactant monomer remained adsorbed at the interface to decrease the interfacial tension (γ) to a low level to produce a break in the γ vs \log [CTAB] plot prior to the normally observed extended cmc (cmce) in presence of polymers. The cac-like aggregation (as observed in tensiometry and viscometry) was not found in conductometry and microcalorimetry, whereas microcalorimetry evidenced the formation of the cmce of CTAB in the presence of the biopolymer. The CTAB influenced structural features of the pepsin were assessed from spectral, viscometric, and circular dichroism measurements.

Couderc-Azouani S., Sidhu J., Georgiou T. K., Charalambous D. C., Vamvakaki M., Patrickios C. S., Bloor D. M., Penfold J., Holzwarth J. F., and Wyn-Jones E. (2004) Binding of sodium dodecyl sulfate to linear and star homopolymers of the nonionic poly(methoxyhexa(ethylene glycol) methacrylate) and the polycation poly(2-(dimethylamino)ethyl methacrylate): electromotive force, isothermal titration calorimetry, surface tension, and small-angle neutron scattering measurements. *Langmuir* **20**, 6458-6469.

Abstract: We investigated the binding of sodium dodecyl sulfate (SDS) to various linear and star polymers of the nonionic methoxyhexa(ethylene glycol) methacrylate (PMHEGMA) and the ionic 2-(dimethylamino)ethyl methacrylate (PDMAEMA), the latter being a polycation at low pH. The dodecyl sulfate ion selective electrode (EMF), isothermal titration calorimetry (ITC), and surface tension (ST) were applied to gain detailed information about interactions. In all cases there is evidence of significant binding of SDS over an extensive SDS concentration range spanning from ca. 10^{-6} to 0.1 mol dm^{-3} . At pH 3, the polymer PDMAEMA is a strong polycation and here the binding is dominated by electrostatic 1:1 charge neutralization with the anionic surfactant. At their natural pH of 8.6, PMHEGMA and PDMAEMA polymers are essentially nonionic and bind SDS in the form of polymer-bound aggregates in the concentration range of ca. 1×10^{-3} to $3 \times 10^{-2} \text{ mol dm}^{-3}$. All the polymers also bind SDS to a lesser extent at concentrations below $1 \times 10^{-3} \text{ mol dm}^{-3}$ reaching as low as $10^{-7} \text{ mol dm}^{-3}$. This low concentration binding process involves the polymer and nonassociated SDS monomers. As far as we are aware, this is the first example that such a low concentration noncooperative binding process could be observed in SDS/neutral polymer systems by EMF and ST. We also showed that the nonionic surfactant hexa(ethylene glycol) mono-n-dodecyl ether (C12EO6) and the cationic cetyltrimethylammonium bromide (C16TAB) interact with star PDMAEMA. We believe that the interaction of C12EO6 and CTAB is of similar noncooperative type as the first SDS binding process in the range from ca. 10^{-5} to $0.3 \times 10^{-3} \text{ mol dm}^{-3}$. At the high concentration binding limit C_{sat} of SDS, the above polymers become fully saturated with bound SDS

micelles. We applied small angle neutron scattering (SANS) to determine the structure and aggregation numbers of the star polymer/bound SDS micelles and calculated the stoichiometry of such supramolecular complexes. The SANS data on PDMAEMA star polymers in the presence of C12EO6 showed only a limited monomer binding in contrast to linear PDMAEMA, which showed monomer C12EO6 binding at low concentrations but micellar aggregates at $6 \times 10^{-3} \text{ mol dm}^{-3}$.

Castro E., Taboada P., Barbosa S., and Mosquera V. (2005) Size control of styrene oxide-ethylene oxide diblock copolymer aggregates with classical surfactants: DLS, TEM, and ITC study. *Biomacromolecules* **6**, 1438-1447.

Abstract: The interactions between the diblock copolymer S(15)E(63) and the surfactants sodium dodecyl sulfate (SDS), sodium decyl sulfate (SDeS), and sodium octyl sulfate (SOS) have been investigated by dynamic light scattering (DLS), transmission electron microscopy (TEM), and isothermal titration calorimetry (ITC). The surfactants with the same headgroup differentiate in their chain length. At 20 degrees C, the block copolymer is associated into micelles with a hydrodynamic radius of 11.6 nm, which is composed of a hydrophobic styrene oxide (S) core and a water-swollen oxypolyethylene (PEO or E) corona. The different copolymer/surfactant systems have been studied at a constant copolymer concentration of 2.5 g dm^{-3} and in a vast range of surfactant concentrations, from 7.5×10^{-6} up to 0.75 M. When SDS and SDeS are added to the block copolymer solution, different regions are observed in the DLS data: at low surfactant concentrations ($c < 1.0 \times 10^{-4} \text{ M}$), single surfactant molecules associate with the copolymer micelle, probably the former being solubilized in the micelle core, leading to a certain disruption of the mixed micelle due to repulsive electrostatic interactions between surfactant headgroups followed by a stabilization of the mixed micelle. At higher concentrations ($1.0 \times 10^{-4} < c < 0.1 \text{ M}$), two types of copolymer-surfactant complexes coexist: one large copolymer-rich/surfactant complex and one small complex consisting of one or a few copolymer chains and rich in surfactants. At higher SDS and SDeS concentrations, complete disintegration of mixed micelles takes place. In contrast, SOS-S(15)E(63) interactions are less important up to surfactant concentrations of 0.05 M due to its higher hydrophilicity, reducing the hydrophobic interactions between surfactant alkyl chains and copolymer micelles. At concentration larger than the critical aggregation concentration (cac) of the system, 0.05 M, disruption of copolymer micelles occurs. These regions have been confirmed by transmission electron microscopy. On the other hand, the titration calorimetric data for SDS and SDeS present an endothermic increase indicating the formation of mixed copolymer-rich-surfactant micelles. From that point, important differences in the ITC plot for both surfactants are present. However, the ITC curve obtained after titration of a SOS solution in the copolymer solution is quite similar to that of its titration in water.

Chen Y., Wang F. and Benson H. A. (2008) Effect of formulation factors on incorporation of the hydrophilic peptide dalargin into PLGA and mPEG-PLGA nanoparticles. *Biopolymers* **90**, 644-650.

Abstract: The objective of this study was to examine formulation factors that influence the incorporation of the hydrophilic peptide dalargin into poly(D, L-lactic-co-glycolic acid) (PLGA) and methoxy-polyethylene glycol (mPEG)-PLGA nanoparticles. In particular, the effect of ionic additives and nanoparticle method of preparation on the incorporation of dalargin and resultant nanoparticle properties was investigated. Biodegradable nanoparticles were prepared from mPEG-PLGA and PLGA by both solvent evaporation and solvent diffusion methods with inclusion of ionic additives of dextran sulphate (DS), sulfobutyl ether-beta-cyclodextrin (SB-CD), or sodium dodecyl sulfate (SDS). The resultant nanoparticles were analyzed for their mean particle size and size distribution, zeta-potential, peptide loading, yield, and morphology. The inclusion of ionic additives in the nanoparticle formulation significantly influenced dalargin entrapment efficiency (EE). For example, with the PLGA/SDS formulation EE increased from 13.3% to 91.2% and from 4.1% to 68.6% with the solvent diffusion and evaporation methods, respectively. The inclusion of ionic surfactant SDS has also lead to the formation of smaller size of nanoparticles. Isothermal titration microcalorimetry revealed a strong interaction between dalargin and DS, medium level interaction with SDS, and weak interaction with SB-CD. The results of this study suggest that a strong ionic interaction between peptides and additives may lead to enhanced peptide incorporation but also increased particle size. Intermediate ionic interaction, especially when it is associated with the formation of reversed micelles in a hydrophobic polymer solution, could be used to enhance the incorporation of hydrophilic peptides in PLGA and mPEG-PLGA nanoparticles

Couderc-Azouani S., Sidhu J., Thurn T., Xu R., Bloor D. M., Penfold J., Holzwarth J. F., and Wyn-Jones E. (2005) Binding of sodium dodecyl sulfate and hexaethylene glycol mono-n-dodecyl ether to the block copolymer L64: electromotive force, microcalorimetry, surface tension, and small angle neutron scattering investigations of mixed micelles and polymer/micellar surfactant complexes. *Langmuir* **21**, 10197-10208. **Abstract:** The interactions of sodium dodecyl sulfate (SDS) with the triblock copolymer L64 (EO13-PO30-EO13) and hexaethylene glycol mono-n-dodecyl ether (C12EO6) were studied using electromotive force, isothermal titration microcalorimetry, differential scanning microcalorimetry, and surface tension measurements. In certain regions of binding, mixed micelles are formed, and here we could evaluate an interaction parameter using regular solution theory. The mixed micelles of L64 with both SDS and C12EO6 exhibit synergy. When L64 is present in its nonassociated state, it forms polymer/micellar SDS complexes at SDS concentrations above the critical aggregation concentration (cac). The cac is well below the critical micellar concentration (cmc) of pure SDS, and a model suggesting how bound micelles are formed at the cac in the presence of a polymer is described. The interaction of nonassociated L64 with C12EO6 is a very rare example of strong binding between a nonionic surfactant and a nonionic polymer, and C12EO6/L64 mixed micelles are formed. We also carried out small angle neutron scattering measurement to determine the structure of the monomeric polymer/micellar SDS complex, as well as the mixed L64/C12EO6 aggregates. In these experiments, contrast matching was achieved by using the h and d forms of SDS, as well as C12EO6. During the early stages of the formation of polymer-bound SDS micelles, SDS aggregates with aggregation numbers of approximately 20 were found and such complexes contain 4-6 bound L64 monomers. The L64/C12EO6 data confirmed the existence of mixed micelles, and structural information involving the composition of the mixed micelle and the aggregation numbers were evaluated.

daDilva R.C., Loh W. and Olofsson G. (2004) Calorimetric investigation of temperature effect on the interaction between poly(ethylene oxide) and sodium dodecylsulfate in water. *Thermochim Acta* **417**, 295-300.

D'Errico G., Ciccarelli D., Ortona O., Paduano L., and Sartorio R. (2004) Interaction between pentaethylene glycol n-octyl ether and low-molecular-weight poly(acrylic acid). *J Colloid Interface Sci* **270**, 490-495.

Abstract: The interaction between pentaethylene glycol n-octyl ether (C8E5) and low-molecular-weight poly(acrylic acid) (PAA, $M(w)=2000$) in aqueous solution has been investigated by various experimental techniques at constant polymer concentration (0.1% w/w) with varying surfactant molality. Spectrofluorimetry, using pyrene as molecular probe, shows (i) the formation of surfactant-polymer aggregates at a surfactant molality (T(1)) lower than the critical micelle concentration (cmc) of C8E5 in water and (ii) the formation of free micelles at a surfactant molality (T(2)) slightly higher than the cmc. Fluorescence quenching measurements indicate that the presence of PAA induces a lowering of the C8E5 aggregation number. Calorimetry confirms spectrofluorimetric evidence; in addition, it shows the presence of weak interactions below T(1) between monomeric surfactant molecules and the polymer chains. Tensiometry shows that, above T(1), only a low fraction of surfactant molecules interact with the polymer and that free micelle formation occurs before polymer saturation. The peculiarities of the interaction between surfactants and low-molecular-weight polymers have been discussed.

D'Errico G., Ciccarelli D., Ortona O., Paduano L. and Sartorio R. (2007) Interaction between pentaethylene glycol n-octyl ether and poly(acrylic acid): effect of the polymer molecular weight. *J Colloid Interface Sci* **314**, 242-250.

Abstract: The effect of the polymer molecular weight on the interaction between pentaethylene glycol n-octyl ether (C(8)E(5)) and poly(acrylic acid) (PAA) has been investigated by a combined experimental strategy including tensiometry, potentiometry, calorimetry, fluorescence quenching and intradiffusion (pulsed gradient spin echo-NMR) measurements. PAA samples with an average molecular weight varying in a wide range ($M(w)=2000, 100,000, 250,000, \text{ and } 450,000$) have been considered. The measurements have been performed at constant polymer concentration (0.1% w/w) with varying surfactant molality. In all the considered systems, at low surfactant concentration, adsorption of surfactant monomers onto the polymer chain has been detected. At a C(8)E(5) molality (T(1)) independent of the PAA $M(w)$, surfactant molecules start to aggregate, forming clusters to which the polymer co-participates. Above this concentration, the behavior of the system depends on $M(w)$. In fact, if polymer samples with high

molecular weight (M_w)100,000) are employed, all the added surfactant aggregates onto the polymer leading to the polymer saturation and, subsequently, to free micelles formation. Both saturation and free micellization occur at surfactant concentrations which are independent of the polymer molecular weight. C(8)E(5) aqueous mixtures containing PAA with low molecular weight (M_w)=2000) behaves differently, in that, above $T(1)$, only a fraction (approximately 20%) of the added surfactant molecules interact with the polymer, forming aggregates to which more than one PAA chain participate. In this case, C(8)E(5) free micellization occurs before polymer saturation. The experimental evidences have been interpreted in terms of the subtle balance between the various molecular interactions driving the surfactant-polymer aggregation.

Diab C., Winnik F. M. and Tribet C. (2007) Enthalpy of interaction and binding isotherms of non-ionic surfactants onto micellar amphiphilic polymers (amphipols). *Langmuir* **23**, 3025-3035.

Abstract: The interactions in water between short amphiphilic macromolecules, known as amphipols, and three neutral surfactants (detergents), dodecylmaltoside (DM), n-octylthioglucoside (OTG), and n-octyltetraethyleneoxide (C8E4), have been assessed by static and dynamic light-scattering (SLS and DLS), capillary electrophoresis (CE), and isothermal titration calorimetry (ITC). The amphipols selected are random copolymers of the hydrophobic n-octylacrylamide (25-30 mol %), a charged hydrophilic monomer, either acrylic acid (approximately 35 mol %) or a phosphorylcholine-modified acrylamide (40-70 mol %), and, optionally, N-isopropylacrylamide (30-40 mol %). In water, the copolymers form micelles of small size (hydrodynamic radius: approximately 5 nm). Neutral surfactants, below their critical micellar concentration (cmc), form mixed micelles with the amphipols irrespective of the chemical structure of the detergent or the polymer. The fraction of detergent in the surfactant/polymer complexes increases significantly (cooperatively) as the surfactant concentration nears the cmc. The ITC data, together with data gathered by CE, were fitted via a regular mixing model, which allowed us to predict the detergent concentration in equilibrium with complexes and the heat evolved upon transfer of detergent from water into a mixed surfactant/polymer complex. The enthalpy of transfer was found to be almost equal to the enthalpy of micellization, and the regular mixing model points to a near-ideal mixing behavior for all systems. Amphipols are promising tools in biochemistry where they are used, together with neutral surfactants, for the stabilization and handling of proteins. This study provides guidelines for the optimization of current protein purification protocols and for the formulations of surfactant/polymer systems used in pharmaceuticals, cosmetics, and foodstuffs.

Diab C., Tribet C., Gohon Y., Popot J. L. and Winnik F. M. (2007) Complexation of integral membrane proteins by phosphorylcholine-based amphipols. *Biochim Biophys Acta* **1768**, 2737-2747.

Abstract: Amphiphilic macromolecules, known as amphipols, have emerged as promising candidates to replace conventional detergents for handling integral membrane proteins in water due to the enhanced stability of protein/amphipol complexes as compared to protein/detergent complexes. The limited portfolio of amphipols currently available prompted us to develop amphipols bearing phosphorylcholine-based units (PC). Unlike carboxylated polymers, PC-amphipols remain soluble in aqueous media under conditions of low pH, high salt concentration, or in the presence of divalent ions. The solubilizing properties of four PC-amphipols were assessed in the case of two membrane proteins, cytochrome b(6)f and bacteriorhodopsin. The protein/PC-amphipol complexes had a low dispersity in size, as determined by rate zonal ultracentrifugation. Short PC-amphipols (M_w approximately 22 kDa) of low dispersity in length, containing approximately 30 mol% octyl side groups, approximately 35 mol% PC-groups, and approximately 35 mol% isopropyl side groups, appeared best suited to form stable complexes, preserving the native state of BR over periods of several days. BR/PC-amphipol complexes remained soluble in aqueous media at $pH \geq 5$, as well as in the presence of 1 M NaCl or 12 mM calcium ions. Results from isothermal titration calorimetry indicated that the energetics of the conversion of BR/detergent complexes into BR/amphipol complexes are similar for PC-amphipols and carboxylated amphiphils.

Franke D., Egger C. C., Smarsly B., Faul C. F., and Tiddy G. J. (2005) Synthesis and phase characterization of a double-tailed pyrrole-containing surfactant: a novel tecton for the production of functional nanostructured materials. *Langmuir* **21**, 2704-2712.

Abstract: A double-tailed polymerizable (pyrrolylalkyl) ammonium amphiphile has been synthesized, and its interfacial properties and aqueous phase behavior have been studied by polarized optical microscopy and X-ray diffraction. The Krafft temperature is about 27 degrees C, and the critical micelle concentration

at 40 degrees C is about 1 mM, as obtained from surface tension measurements, potentiometry, and isothermal titration calorimetry. The lyotropic behavior of the surfactant is found to be of a complex nature. At concentrations higher than the micellar (L(1)) region, two mesophases have been identified: a second isotropic (L(2)) phase, which is probably micellar but not fully miscible with water, and a lamellar (L(alpha)) phase, showing interesting alignment properties. Small-angle X-ray scattering analysis of the mesophases has been evaluated in terms of a model of spherical micelles, which describes a mutual arrangement by a structure factor derived from a hard-sphere potential (Percus-Yevick, "PY", approach). Interest in the comprehensive phase behavior of the polymerizable surfactant is based on the desire to integrate the system into a composite material to obtain potentially conducting self-assembled hybrid mesostructures.

Ge L., Guo R. and Zhang X. (2008) Formation and Microstructure Transition of F127/TX-100 Complex. *J Phys. Chem B* **112**, 14566-14577.

Abstract: Formation and structure transition of the complex composed of triblock copolymer F127 and nonionic surfactant TX-100 have been investigated by (1)H NMR spectroscopy, dynamic light scattering (DLS), and isothermal titration calorimetry (ITC). Three TX-100 concentration regions are identified, within which TX-100/20 mg/mL F127 complex undergoes different temperature-induced structure transitions. In low concentration region (<9.42 mM), F127 single molecular species (unimers) wrap around TX-100 micelles forming F127/TX-100 complex with TX-100 micelle as the skeleton at a lower temperature (5 degrees C), and the skeleton transfers to F127 micelle at higher temperature (40 degrees C); in intermediate TX-100 concentration region (9.42-94.85 mM), the skeleton of F127/TX-100 complex transfers from TX-100 micelle successively into F127 micelle and TX-100 micelle again upon heating. The interaction of F127 with TX-100 is saturated in high TX-100 concentration region (>157.57 mM), and free TX-100 micelles coexist with larger clusters of F127/TX-100 complexes. In addition, TX-100-induced F127/TX-100 complex formation and structure transition are also investigated at constant temperatures. The results show that within 5-10 degrees C, F127 unimers mainly adsorb on the surface of TX-100 micelles just like normal water soluble polymers; in the temperature region of 15-25 degrees C, TX-100 micelles prompts F127 micelle formation. Within 30-40 degrees C, TX-100 inserts into F127 micelles leading to the breakdown of F127 aggregates at higher TX-100 concentrations, and the obtained unimers thread through TX-100 micelles forming complex with TX-100 micelle as skeleton

Gianni P., Bernazzani L., Carosi R. and Mollica V. (2007) Micellization of lithium perfluoroheptanoate and its aggregation on poly(ethylene glycol) oligomers in water. *Langmuir* **23**, 8752-8759.

Abstract: The interaction of lithium perfluoroheptanoate (LiPFHep) with poly(ethylene glycol) (PEG) of different molecular weights (300 < MW < 20 000 Da) was investigated in water at 298.15 and 308.15 K by the isothermal titration calorimetry (ITC). Density and sound velocity measurements were also performed at 288.15, 298.15, and 308.15 K, while viscosity and conductivity data were only collected at 298.15 K. The aggregation process of this surfactant on the PEG polymeric chain was found to be very similar to the process exhibited by the two homologous perfluorooctanoate and perfluorononanoate. Viscosity and ITC data indicated that the formation of polymer-surfactant complexes between PEG and LiPFHep also leads to a conformational change in the polymer. The aggregation of micelles of the lithium perfluoro surfactants on the PEG polymeric chain is characterized by a comparable thermodynamic stability, which results from a balance of enthalpy and entropy contributions, which both increase with the length of the surfactant hydrophobic chain.

Haldar B., Chakrabarty A., Mallick A., Mandal M. C., Das P., and Chattopadhyay N. (2006) Fluorometric and isothermal titration calorimetric studies on binding interaction of a telechelic polymer with sodium alkyl sulfates of varying chain length. *Langmuir* **22**, 3514-3520.

Abstract: Steady-state fluorescence measurements and isothermal titration calorimetric experiments have been performed to study the interaction between a telechelic polymer, pyrene-end-capped poly(ethylene oxide) (PYPY), and sodium alkyl sulfate surfactants having decyl, dodecyl, and tetradecyl hydrocarbon tails. Fluorometric results suggest polymer-surfactant interaction in the very low range of polymer concentrations. The relative variation in the excimer to monomer pyrene emission intensities with varying surfactant concentration reveals that initial addition of surfactant favors intramolecular preassociation until the surfactant molecules start binding with the ethylene oxide (EO) chain. With the growing number of surfactant aggregates along the EO chain, the association becomes hindered due to the polyelectrolyte

effect. The results from microcalorimetric titrations in the low concentration range of PYPY solution (approximately 10^{-6} M) with alkyl sulfates suggest two kinds of surfactant-polymer interactions, one with the polymer hydrophobic end groups and the other with the ethylene oxide backbone. The overall polymer-surfactant interaction starts at a much lower surfactant concentration for the hydrophobically modified polymers compared to that in the case of unsubstituted poly(ethylene oxide) homopolymer. From the experiments critical aggregation concentration values and the second critical concentration where free micelles start forming have been determined. An endeavor has been made to unveil the mechanism underlying the corresponding associations of the surfactants with the polymer.

Lapitsky Y., Parikh M. and Kaler E. W. (2007) Calorimetric determination of surfactant/polyelectrolyte binding isotherms. *J Phys. Chem B* **111**, 8379-8387.

Abstract: Mixing of oppositely charged surfactants and polyelectrolytes in aqueous solutions leads to cooperative surfactant adsorption onto the polyelectrolyte chains. Experimental determination of surfactant/polyelectrolyte binding isotherms is usually done using custom-built surfactant-ion-specific electrodes. As an alternative, we present an indirect isotherm approximation method that uses conventional isothermal titration calorimetry (ITC). The calorimetric data is fitted to the two-binding-state Satake-Yang adsorption model, which quantifies the extent of binding in terms of the binding constant (K_u) and the cooperativity parameter (u). This approach is investigated using two surfactant/polyelectrolyte mixtures: sodium perfluorooctanoate (FC7) and N,N,N-trimethylammonium derivatized hydroxyethyl cellulose (UCARE Polymer JR-400), whose binding behavior follows the Satake-Yang model, and dodecyltrimethylammonium bromide (DTAB) and poly(styrenesulfonate) (NaPSS), whose behavior deviates dramatically from the Satake-Yang model. These studies demonstrate that, in order to apply the indirect ITC method of binding isotherm determination, the surfactant/polyelectrolyte adsorption process must have no more than two dominant binding states. Thus, the technique works well for the FC7/JR-400 mixture. It fails in the case of the DTAB/NaPSS adsorption, but its mode of failure offers insight into the multiple-binding-state adsorption mechanism.

Li L., Liu E. and Lim C. H. (2007) Micro-DSC and rheological studies of interactions between methylcellulose and surfactants. *J Phys. Chem B* **111**, 6410-6416.

Abstract: The effects of a cationic surfactant, cetyltrimethylammonium bromide (CTAB), on the gelation of methylcellulose (MC) in aqueous solutions have been investigated by micro differential scanning calorimetry (micro DSC) and rheology. Methylcellulose had a weight average molecular weight of 310,000 and a degree of substitution of 1.8. The concentration of MC was kept at 0.5 wt % (0.016 mM) and 1 wt % (0.032 mM), and the concentration of CTAB in the MC solutions was varied from 0 to 0.6 wt % (16.5 mM). Upon heating, a single endothermic peak, which is due to the hydrophobic association and gelation of MC, shifts to lower temperatures with increasing CTAB for $CTAB \leq CMC$ (0.93 mM or 0.034 wt %), and then it shifts to higher temperatures linearly with CTAB for $CTAB > CMC$. At the same time, the endothermic enthalpy decreases with increasing CTAB concentration. Even though CTAB shows a significant "salt-in" effect on the gelation of MC, it does not affect the pattern of the sol-gel transition as well as the gel strength of MC. At the highest concentration of CTAB, 0.60 wt %, MC is still able to form a gel. At a given ratio of CTAB/MC, the effect of CTAB on MC becomes stronger when the MC concentration is lower. The results for the MC-CTAB system are compared with an ionic surfactant, SDS and the significant differences in affecting the gelation of MC between two surfactants are recognized.

Li X., Wettig S. D., and Verrall R. E. (2005) Isothermal titration calorimetry and dynamic light scattering studies of interactions between gemini surfactants of different structure and Pluronic block copolymers. *J Colloid Interface Sci* **282**, 466-477.

Abstract: The interactions between triblock copolymers of poly(ethylene oxide) and poly(propylene oxide), P103 and F108, EO(n)PO(m)EO(n), $m=56$ and $n=17$ and 132 , respectively, and m-s-m type gemini surfactants, $m=8, 10, 12$, and 18 , and $s=3, 6, 12$, and 16 , have been studied in aqueous solution using isothermal titration calorimetry and dynamic light scattering techniques. The enthalpograms of F108 as a function of surfactant concentration show one broad peak at polymer concentrations $C(p) \leq 0.50$ wt%, below the cmc of the copolymer at 25 degrees C. It is attributed to interactions between the surfactant and the triblock copolymer monomer. DLS results show hydrodynamic radii ($R(h)$) initially consistent with copolymer monomers that change to values consistent with gemini surfactant micelles as the surfactant concentration is increased. In P103 solutions at $C(p) \geq 0.05$ wt%, two peaks appear in the

enthalpograms, and they are attributed to the interactions between the gemini surfactant and the micelle or monomer forms of the copolymer. An origin-based nonlinear fitting program was employed to deconvolute the two peaks and to obtain estimates of peak properties. An estimate of the fraction of copolymer in aggregated form was also obtained. The enthalpy change due to interactions between the surfactants and P103 aggregates is very large compared to values obtained for traditional surfactants. This suggests that extensive reorganization of copolymer aggregates and surrounding solvent occurs during the interaction. DLS results for the P103 systems containing C(p) > or = 0.05% show evidence of very large aggregates in solution, likely P103 micelle clusters. The transitions observed in the hydrodynamic radii are consistent with a breakdown of micelle clusters with addition of gemini surfactant, followed by mixed micelle formation and/or deaggregation into monomer P103. This is followed by interactions similar to those typically observed in surfactant-nonionic polymer systems. Mechanisms for the interaction and the observed structural changes are discussed.

Liu Y. and Guo R. (2007) Interaction between casein and the oppositely charged surfactant. *Biomacromolecules*. **8**, 2902-2908.

Abstract: The interactions between the classical cationic surfactant dodecyltrimethylammonium bromide (DTAB) and 2.0 mg/mL casein were investigated using isothermal titration calorimetry (ITC), turbidity, dynamic light scattering (DLS), and fluorescence spectra measurements. The results suggest that the cationic headgroup of the surfactant individually binds to the negatively charged amino acid sites on the casein chains because of the electrostatic attraction upon the addition of DTAB. When the surfactant concentration reaches a critical value c_1 , DTAB forms micelle-like aggregates on the casein chain, resulting in the formation of insoluble casein/DTAB complexes. Further addition of DTAB leads to the redissolution of casein/DTAB complexes because of the net positive charge on casein/DTAB complexes and the formation of DTAB free micelles. The addition of salt screens the repulsion between the surfactant headgroups and the attraction between casein and surfactant molecules, which weakens the binding of surfactant onto the casein chain, favoring the formation of free surfactant micelles.

Liu Y. and Guo R. (2007) Interaction between casein and sodium dodecyl sulfate. *J Colloid Interface Sci* **315**, 685-692.

Abstract: The interaction of the anionic surfactant sodium dodecyl sulfate (SDS) with 2.0 mg/ml casein was first investigated using isothermal titration calorimetry (ITC), dynamic light scattering (DLS), and fluorescence spectra. ITC results show that individual SDS molecules first bind to casein micelles by the hydrophobic interaction. The micelle-like SDS aggregate is formed on the casein chains when SDS concentration reaches the critical aggregation concentration (c_1), which is far below the critical micellar concentration (cmc) of SDS in the absence of casein. With the further increase of SDS concentration to the saturate binding concentration c_2 , SDS molecules no longer bind to the casein chains, and free SDS micelles coexist with casein micelles bound with SDS aggregates in the system. DLS results show that the addition of SDS leads to an increase in the hydrodynamic radius of casein micelles with bound surfactant at SDS concentration higher than 4 mM, and also an increase in the casein monomer molecule (or submicelles) at SDS concentration higher than 10 mM. Fluorometric results suggest the addition of SDS leads to some changes in the binding process of hydrophobic probes to casein micelles.

Lof D., Niemiec A., Schillen K., Loh W. and Olofsson G. (2007) A calorimetry and light scattering study of the formation and shape transition of mixed micelles of EO20PO68EO20 triblock copolymer (P123) and nonionic surfactant (C12EO6). *J Phys. Chem B* **111**, 5911-5920.

Abstract: The interaction between the nonionic surfactant C12EO6 and the poly(ethylene oxide)-poly(propylene oxide)-poly(ethylene oxide) triblock copolymer EO20PO68EO20 (P123) has been investigated by means of isothermal titration and differential scanning calorimetry (DSC) as well as static and dynamic light scattering (SLS and DLS). P123 self-assembles in water into spherical micelles at ambient temperatures. At raised temperatures, the DSC data revealed a sphere-to-rod transition of the P123 micelles around 60 degrees C. C12EO6 interacts strongly with P123 micelles in aqueous solution to give mixed micelles with a critical micelle concentration (cmc) well below the cmc for pure C12EO6. The presence of C12EO6 also lowers the critical micelle temperature of P123 so aggregation starts at significantly lower temperatures. A new phenomenon was observed in the P123-C12EO6 system, namely, a well-defined sphere-to-rod transition of the mixed micelles. A visual phase study of mixtures containing 1.00 wt % P123 showed that in a narrow concentration range of C12EO6 both the sphere-to-rod transition

and the liquid-liquid phase separation temperature are strongly depressed compared to the pure P123-water system. The hydrodynamic radius of spherical mixed micelles at a C12EO6/P123 molar ratio of 2.2 was estimated from DLS to be 9.1 nm, whereas it is 24.1 nm for the rodlike micelles. Furthermore, the hydrodynamic length of the rods at a molar ratio of 2.2 is in the range of 100 nm. The retarded kinetics of the shape transition was detected in titration calorimetric experiments at 40 degrees C and further studied by using time-resolved DLS and SLS. The rate of growth, which was slow (>2000 s), was found to increase with the total concentration.

Majhi P. R., Moulik S. P., Burke S. E., Rodgers M., and Palepu R. (2001) Physicochemical Investigations on the Interaction of Surfactants and Salts with Polyvinylpyrrolidone in Aqueous Medium. *J Colloid Interface Sci* **235**, 227-234.

Abstract: Microcalorimetric investigations have been carried out on the interaction of the surfactants sodium cholate, sodium deoxycholate, tetradecyltrimethylammonium bromide, cetyl(hexadecyl)trimethylammonium bromide, and p-tert-octylphenoxy polyoxy-ethylene ether (Triton X-100) and the salts potassium iodide, sodium benzoate, sodium bromide, and sodium salicylate with the neutral polymer polyvinylpyrrolidone (PVP). The enthalpy of dilution of the surfactants has been measured in the absence and presence of the polymer and the results are compared to determine the effect of PVP on the micellization of the surfactants and the energetics of the process. As well, the micellization activity of the surfactants in the presence of the polymer has been studied by conductometric and fluorimetric methods. The enthalpy of dilution of the salts has been measured to provide an understanding of the nature and magnitude of their interaction with PVP. Copyright 2001 Academic Press.

Muzzalupo R., Infante M. R., Perez L., Pinazo A., Marques E. F., Antonelli M. L., Strinati C. and La M. C. (2007) Interactions between gemini surfactants and polymers: thermodynamic studies. *Langmuir* **23**, 5963-5970.

Abstract: Aqueous mixtures containing a homopolymer, poly(vinylpyrrolidone) (PVP), or a hydrophobically modified graft copolymer, HM-pullulan, (PULAU9, where 9 stands for the nominal substitution degree), and different Gemini surfactants have been investigated at 25.0 degrees C. A wide variety of experimental conditions were addressed by changing the amount of polymer and of surfactant. The Gemini surfactants were synthesized, purified, and characterized by routine methods. They differ from each other in polar head groups (two sulfonate-, two quaternary ammonium-, or two arginine-based groups), in alkyl chain length (11 or 12 carbon atoms), and in the distance between the polar head groups. The spacers consist of 2, 3, and 6 methylene units or 3 oxyethylene units. Surface activity and solution calorimetry measurements yield some physicochemical features inherent to micelle formation and polymer-surfactant interactions. The data are supported by ionic conductivity, detecting the critical thresholds and quantifying the modifications in binding associated with critical association (CAC) and micelle formation (CMC*). The Gibbs energy of transfer from the micelles to a polymer-binding site, ΔG_{trans} , was evaluated from the CAC/CMC* ratios versus the amount of added polymer. A similar procedure determined the enthalpy of transfer, ΔH_{trans} . ΔG_{trans} decreases with added polymer, whereas ΔH_{trans} becomes more negative on increasing the amount of polymer in the medium. According to the selected data presented here, cationic Geminis do not interact with PVP, while significant interactions have been observed in other surfactants. In mixtures with PULAU9, the interaction is significant for all Geminis. This effect is due to interactions between the surfactants and the hydrophobic alkyl groups on the main polymer chain. The pendent groups facing away from the polysaccharide chain act as binding sites for aggregates onto such polymers.

Nichifor M., Bastos M., Lopes S. and Lopes A. (2008) Characterization of Aggregates formed by Hydrophobically Modified Cationic Dextran and Sodium Alkyl Sulfates in Salt-Free Aqueous Solutions. *J Phys. Chem B*.(epublication)

Abstract: The interaction between polyelectrolytes based on dextran with pendant N-alkyl- N, N-dimethyl-N-(2-hydroxypropyl) ammonium chloride groups, where $n = 2, 4, 8, 12, \text{ or } 16$, and sodium alkyl sulfates, SC n S, with $n = 8, 10, 12, 14, \text{ and } 16$, has been studied by conductometry and fluorescence techniques. Comparison of cumulative specific conductivities of the mixtures of polymer-surfactant over a large surfactant concentration range, with those of pure surfactant and NaCl, has clearly shown that the surfactants start to bind to polymer at very low concentrations (10^{-6} M), forming mixed aggregates. The steady-state emission fluorescence measured in the presence of pyrene, 1,3,6-diphenylhexatriene (DPH),

and 1-pyrenylbutyric acid sodium salt demonstrated the existence of a critical surfactant concentration (CAC S) at which the previously formed mixed aggregates are interconnected due to self-association of surfactant molecules included in different mixed polymer/surfactant aggregates. Above CAC S, the mixed aggregates change dramatically their properties (hydrophobicity, size, DPH solubilization) which depend on both polymer and surfactant hydrophobicities and concentrations. The characterization of the new formed aggregates at different surfactant concentration ranges is derived mainly from their ability to solubilize hydrophobic compounds. The variety of fluorescence techniques used, combined with conductometric measurements and previous calorimetric information allowed us to provide here a comprehensive study and new interpretation of the solution behavior of these polymer-surfactant systems

Niemiec A. and Loh W. (2008) Interaction of ethylene oxide-propylene oxide copolymers with ionic surfactants studied by calorimetry: random versus block copolymers. *J Phys. Chem B* **112**, 727-733.

Abstract: The present study used calorimetric techniques to follow the interaction of random and block ethylene oxide (EO)-propylene oxide (PO) copolymers with ionic surfactants. Features such as the intensity of the interaction (evaluated through their critical aggregation concentrations) and the profile of the isothermal titration calorimetry (ITC) curves were comparatively analyzed for random and block copolymers with similar composition (number of EO and PO units). Random copolymers displayed an interaction similar to that observed with other hydrophilic homopolymers with the additional characteristic that the intensity of the interaction increased with the increase in the copolymer hydrophobicity (as determined by its PO content), revealing that these copolymers display an intermediate behavior between PEO and PPO. For nonaggregated block copolymers (unimers) with large enough EO blocks (molar mass above 2000 g mol⁻¹), ITC curves revealed that the anionic surfactant sodium dodecylsulfate (SDS) interacts with the PO and EO blocks almost independently, being more favorable with the PO block, which controls the critical aggregation concentration (cac) value. Effects of temperature and of the nature of the ionic surfactants on their interaction with these copolymers were found to agree with the previously reported trends

Nizri G., Lagerge S., Kamyshny A., Major D. T. and Magdassi S. (2008) Polymer-surfactant interactions: binding mechanism of sodium dodecyl sulfate to poly(diallyldimethylammonium chloride). *J Colloid Interface Sci* **320**, 74-81.

Abstract: The binding mechanism of poly(diallyldimethylammonium chloride), PDAC, and sodium dodecyl sulfate, SDS, has been comprehensively studied by combining binding isotherms data with microcalorimetry, zeta potential, and conductivity measurements, as well as ab initio quantum mechanical calculations. The obtained results demonstrate that surfactant-polymer interaction is governed by both electrostatic and hydrophobic interactions, and is cooperative in the presence of salt. This binding results in the formation of nanoparticles, which are positively or negatively charged depending on the molar ratio of surfactant to PDAC monomeric units. From microcalorimetry data it was concluded that the exothermic character of the interaction diminishes with the increase in the surfactant/polymer ratio as well as with an increase in electrolyte concentration

Olofsson G., and Wang G. (1998) Isothermal Titration and Temperature Scanning Calorimetric Studies of Polymer-Surfactant Systems in Polymer-Surfactant Systems. Kwak J.C.T. ed., Marcel Dekker Inc. New York, pp. 317-356.

Ortona O., D'Errico G., Paduano L., and Vitagliano V. (2006) Interaction between cationic, anionic, and non-ionic surfactants with ABA block copolymer Pluronic PE6200 and with BAB reverse block copolymer Pluronic 25R4. *J Colloid Interface Sci* **301**, 63-77.

Abstract: The interaction in aqueous solution between either the normal block copolymer poly(ethylene oxide)-poly(propylene oxide)-poly(ethylene oxide): Pluronic PE6200 [(EO)(11)-(PO)(28)-(EO)(11)], or the reverse block copolymer poly(propylene oxide)-poly(ethylene oxide)-poly(propylene oxide): Pluronic 25R4 [(PO)(19)-(EO)(33)-(PO)(19)] and the surfactants sodium decylsulfate, C(10)OS, decyltrimethyl ammonium bromide, C(10)TAB, and pentaethylene glycol monodecyl ether, C(10)E(5), was investigated and the aggregation behavior of these surfactants with Pluronic was compared. Surface tension measurements show that Pluronic in their non-aggregated state better interact with the anionic surfactant C(10)OS than with cationic and non-ionic ones. The presence of the two Pluronic induces the same lowering of the aggregation number of C(10)OS as shown by fluorescence quenching measurements. The

number of polymer chains necessary to bind each C(10)OS aggregate has been estimated to be approximately 6 for PE6200 and approximately 2 for 25R4. Furthermore, this surfactant also induces the same increment in the gyration radius of the polymers as revealed by viscosimetry. Calorimetric results have been reasonably reproduced by applying a simple equilibrium model to the aggregation processes. Santonicola M. G., Yocum M. A., Lenhoff A. M. and Kaler E. W. (2007) Self-assembly of medium-chain alkyl monoglucosides in ammonium sulfate solutions with poly(ethylene glycol). *Langmuir* **23**, 5358-5366.

Abstract: We study the phase behavior and microstructure of alkyl-beta-monoglucosides with intermediate chain lengths (octyl- and nonyl-beta-glucoside) in aqueous solutions containing ammonium sulfate and poly(ethylene glycol) (PEG). When the glucoside surfactants are mixed with PEG of molecular weight 3350 or larger, two different phase transitions are observed in the temperature range 0-100 degrees C, with lower and upper miscibility gaps separated by a one-phase isotropic region. Isothermal titration calorimetry is used to quantify the effect of PEG on the micellization properties of the alkyl monoglucosides, whereas small-angle neutron scattering gives insight into the microstructure of the surfactant/polymer mixtures near the liquid-liquid phase boundary. Results show that the range and the strength of the interactions in these solutions are highly affected by the presence of PEG. Solutions with nonyl-beta-glucoside contain larger micelles than those with octyl-beta-glucoside, and the intermicellar interactions are much stronger and longer ranged. The relevance of these findings for membrane protein crystallization is discussed.

Semenova M. G., Belyakova L. E., Polikarpov Y. N., Il'in M. M., Istarova T. A., Anokhina M. S., and Tsapkina E. N. (2006) Thermodynamic analysis of the impact of the surfactant-protein interactions on the molecular parameters and surface behavior of food proteins. *Biomacromolecules* **7**, 101-113.

Abstract: This paper reports on the thermodynamics of the interactions between surfactants (anionic, CITREM, SSL; nonionic, PGE; zwitterionic, phospholipids) and food proteins (sodium caseinate, legumin) depending on the chemical structure and molecular state (individual molecules, micelles) of the surfactants and the molecular parameters (conformation, molar mass, charge) of the proteins under changes of pH in the range from 7.2 to 5.0 and temperature from 293 to 323 K. The marked effect of the protein-surfactant interactions on the molecular parameters (the weight-average molar mass, the gyration and hydrodynamic radii) and the thermodynamic affinity of the proteins for an aqueous medium were determined by a combination of static and dynamic laser light scattering. Thermodynamically justified schematic sketches of the molecular mechanisms of the complex formation between like-charged proteins and surfactants have been proposed. In response to the complex formation between the proteins and the surfactants, the more stable and fine foams have been detected generally.

Seng, W.P., Tam, K.C., Jenkins, R.D., and Bassett, D.R. (2000) Calorimetric studies of model hydrophobically modified alkali-soluble emulsion polymers with varying spacer chain length in ionic surfactant solutions. *Macromolecules* **33**, 1727-1733.

Abstract: The binding behavior of SDS onto several model hydrophobically modified alkali-soluble emulsion (HASE) polymers with different spacer chain length was studied using the isothermal titration calorimetric technique. The titration was performed by injection 0.1 M SDS into 0.1 wt% HASE polymer solution, which yielded a negative enthalpy and a positive entropy, thus confirming that the interactions between SDS and HASE polymer is entropy-driven. At low degree of ethoxylation (0-5 mol), HASE polymers with short spacer chains form a type I structure consisting of hydrophobic cross-links and hydrophobe-EA junctions. As the length of the spacer chain increases to 10 mol of ethoxylation, the hydrophobes are more accessible to form interchain junctions, yielding a type II cluster. Associative junctions in type II clusters are more accessible to surfactant than those of type I. With increasing spacer chain length, the critical aggregation concentration (cac) and the deltaG of aggregation decrease, while deltaH remains unchanged. A physical model describing the interaction mechanisms between the polymer and the surfactant is proposed.

Sidhu J., Bloor T. L., Couderc-Azouani S., Penfold J., Holzwarth J. F., and Wyn-Jones E. (2004) Interactions of poly(amidoamine) dendrimers with the surfactants SDS, DTAB, and C12EO6: an equilibrium and structural study using a SDS selective electrode, isothermal titration calorimetry, and small angle neutron scattering. *Langmuir* **20**, 9320-9328.

Abstract: Interactions in aqueous solutions of different generations of poly(amidoamine) (PAMAM) dendrimers containing amine, hydroxyl, or delta-glucolactone functional groups at the periphery with the anionic surfactant sodium dodecyl sulfate (SDS) were investigated. We used a SDS-specific electrode

(EMF) for SDS monomer concentration monitoring, isothermal titration calorimetry (ITC) for binding information, and small angle neutron scattering (SANS) for structural studies. ITC experiments monitoring the interaction of the dendrimers with cationic dodecyltrimethylammonium bromide (DTAB) and nonionic hexaethylene glycol mono-n-dodecyl ether (C12EO6) showed no significant binding effects. In contrast, SDS binds to all of the above dendrimers. EMF and ITC data demonstrated a regular trend for both the onset of binding and binding saturation as the generation in each family of dendrimers increased. In addition, generation G6 exhibited a noncooperative binding process at very low SDS concentrations. Furthermore, the onset of cooperative binding in the EMF experiments started at lower concentrations as the weight % (w/v), the size, and the numbers of the internal or surface groups increased. On the other hand, the binding capacity of the dendrimers showed only a small dependence on the above parameters. At SDS concentrations approaching the binding limit and also at selective concentrations within the binding range, SANS measurements indicated that in all cases the bound surfactant is in the micellar form. From the electromotive force (EMF) measurements, ITC data, and SANS data, the stoichiometry of the supramolecular complexes was determined.

Singh S. K. and Nilsson S. (1999) Thermodynamics of Interaction between Some Cellulose Ethers and SDS by Titration Microcalorimetry. *J Colloid Interface Sci* **213**, 133-151.

Abstract: The interaction between certain nonionic cellulose ethers (ethyl hydroxyethyl cellulose and hydroxypropyl methyl cellulose) and sodium dodecyl sulphate (SDS) has been investigated using isothermal titration microcalorimetry at temperatures between 25-50 degrees C. The observed heat flow curves have been interpreted in terms of a plausible mechanism of the interaction of the substituent groups with SDS monomers and clusters. The data have been related to changes occurring in the system at the macro- and microscopic levels with the addition of surfactants and with temperature. The process consists predominantly of polymer-surfactant interactions initially and surfactant-surfactant interactions at the later stages. A phenomenological model of the cooperative interaction (adsorption) process has been derived, and earlier published equilibrium binding data have been used to recover binding constants and Gibbs energy changes for this process. The adsorption enthalpies and entropies have been recovered along with the heat capacity change. The enthalpic cost of confining the nonpolar regions of the polymers in surfactant clusters is high, but the entropy gain from release of hydration shell water molecules as well as increased freedom of movement of these nonpolar regions in the clusters gives the process a strong entropic driving force. The process is entropy-driven initially and converts to being both enthalpy and entropy-driven at high SDS concentrations. An enthalpy-entropy compensation behavior is seen. Strongly negative heat capacity changes have been obtained resulting from the transfer of nonpolar groups from aqueous into nonpolar environments, as well as a reduction of conformational domains that the chains can populate. Changes in these two components cause the heat capacity change to become less negative at the higher binding levels. The system can be classified as exhibiting nonclassical hydrophobic binding at the later stages of binding. Copyright 1999 Academic Press.

Singh S. K. and Nilsson S. (1999) Thermodynamics of Interaction between Some Cellulose Ethers and SDS by Titration Microcalorimetry. *J Colloid Interface Sci* **213**, 152-159.

Abstract: A titration calorimetric study of the interaction between nonionic cellulose ethers and ionic surfactant (SDS) has been extended to a larger number of polymers to explore the effect of variation of polymer hydrophobicity on the energetics of the process. "Hydrophobicity" as used here is an overall effect of the nature, degree, and number of substituents and is characterized by the cloud point and (aqueous) surface tension lowering abilities of the polymer. A direct correlation is found between the extent of "hydrophobicity" and the endo-enthalpic peak in the initial SDS concentration region of interaction. However, the overall mechanism of interaction is similar for all the polymers, being dominated by polymer-surfactant interactions initially and converting into a surfactant-surfactant interaction process at higher SDS concentrations. The importance of polymer characteristics thus becomes weaker at the later stages of the process. Differences between the polymers is also reduced by an increase of temperature, leading to a near overlap of observed enthalpy curves at 40 degrees C. The energetics of interaction are also mirrored by the isothermal surfactant binding curves and the changes in macroscopic and microviscosity of the system. Copyright 1999 Academic Press.

South C. R., Higley M. N., Leung K. C., Lanari D., Nelson A., Grubbs R. H., Stoddart J. F., and Weck M. (2006) Self-assembly with block copolymers through metal coordination of SCS-Pd(II) pincer complexes

and pseudorotaxane formation. *Chemistry* **12**, 3789-3797.

Abstract: Poly(norbornene)-based block copolymers containing side chains of palladated pincer complexes/dibenzo[24]crown-8 or palladated pincer complexes/dibenzylammonium salts were synthesized. Noncovalent functionalization was accomplished with their corresponding recognition units through simple 1:1 addition with association constants (K_a) greater than 10^5 m^{-1} . The self-assembly processes were monitored by using both ^1H NMR spectroscopy and isothermal titration calorimetry. In all cases, we found that the self-assembly of the recognition units along each polymer block does not preclude the self-assembly processes along the other block.

Tam K.C., and Wyn-Jones E. (2006) Insights on polymer-surfactant complex structures during the binding of surfactants to polymers as measured by equilibrium and structural techniques. *Chem Soc Rev* **35**, 693-709.

Thongngam M. and McClements D. J. (2005) Influence of pH, ionic strength, and temperature on self-association and interactions of sodium dodecyl sulfate in the absence and presence of chitosan. *Langmuir* **21**, 79-86.

Abstract: Chitosan is a cationic biopolymer that has many potential applications in the food industry because of its unique nutritional and physicochemical properties. Many of these properties depend on its ability to interact with anionic surface-active molecules, such as surfactants, phospholipids, and bile acids. The purpose of this study was to examine the influence of pH (3 and 7), ionic strength (0-200 mM NaCl), and temperature (10-50 degrees C) on the interactions between a model anionic surfactant (sodium dodecyl sulfate, SDS) and chitosan using isothermal titration calorimetry, selective surfactant electrode, and turbidity measurements. At pH 3 and 30 degrees C, SDS bound strongly to chitosan to form an insoluble complex that contained about 4-5 mmol of SDS/1 g of chitosan at saturation. When SDS and chitosan were mixed at pH 7 they did not interact strongly, presumably because the biopolymer had lost most of its positive charge at this pH. However, when SDS and chitosan were mixed at pH 3 and then the solution was adjusted to pH 7, the SDS remained bound to the chitosan. The presence of NaCl (0-200 mM) in the solutions decreased the critical micelle concentration (cmc) of SDS (in both the absence and the presence of chitosan) but had little influence on the amount of SDS bound to chitosan at saturation. The cmc of SDS and the amount of SDS bound to the chitosan at saturation were largely independent of the holding temperature (10-40 degrees C). Nevertheless, the enthalpy changes associated with micelle dissociation were highly temperature-dependent, indicating the importance of hydrophobic interactions, whereas the enthalpy changes associated with SDS-chitosan binding were almost temperature-independent, indicating the dominant contribution of electrostatic interactions. This study provides information that may lead to the rational design of chitosan-based ingredients or products with specific nutritional and functional characteristics, for example, cholesterol lowering.

Thongngam M. and McClements D. J. (2004) Characterization of interactions between chitosan and an anionic surfactant. *J Agric Food Chem* **52**, 987-991.

Abstract: Chitosan is a cationic biopolymer that has many potential applications in the food industry because of its unique nutritional and physicochemical properties. Many of these properties depend on its ability to interact with anionic surface-active molecules, such as phospholipids, surfactants, and bile acids. The purpose of this study was to characterize the interaction between chitosan and a model anionic surfactant (sodium dodecyl sulfate, SDS) using isothermal titration calorimetry (ITC), surfactant-selective electrode (SSE), and turbidity measurements. ITC and SSE indicated that SDS bound strongly to chitosan via a highly exothermic interaction. The turbidity measurements indicated that chitosan formed insoluble complexes with SDS that strongly scattered light. The chitosan bound approximately 4 mM of SDS per 0.1 wt % chitosan before becoming saturated with surfactant. The SDS-chitosan interaction was weakened appreciably by the presence of 100 mM NaCl, which suggested that it was electrostatic in origin. This study provides information about the origin and characteristics of molecular interactions between chitosan and anionic surface-active lipids that may be useful for the rational design of chitosan-based food ingredients with specific nutritional and functional characteristics, e.g., cholesterol lowering or fat replacement.

Thongngam M., and McClements D.J. (2005) Isothermal titration calorimetry study of the interactions between chitosan and a bile salt (sodium taurocholate). *FOOD HYDROCOLLOIDS* **19**, 813-819.

Tjandra W., Yao J., and Tam K. C. (2006) Interaction between silicates and ionic surfactants in dilute solution. *Langmuir* **22**, 1493-1499.

Abstract: Understanding the interaction between silicate ions and surfactants is critical for the design and development of mesoporous siliceous materials. We examined the interaction between sodium silicate ions and three different cationic surfactants [namely, cetyltrimethylammonium bromide (CTAB), tetradecyltrimethylammonium bromide (TTAB), and dodecyltrimethylammonium bromide (DTAB)] and an anionic surfactant [sodium dodecyl sulfate (SDS)] in dilute solution at room temperature. From the combination of several techniques, such as conductometric and potentiometric titrations, dynamic light scattering, and isothermal titration calorimetry, the phase behavior of the sodium silicate and CTAB system was determined. We observed that the aggregation behavior of the silicate-CTAB system is similar to that of a polymer-surfactant system. The formation of the silicate-CTAB complex is induced by the adsorption of SiOH and SiO- groups, aided by CTAB unimers. The electrostatic attraction and hydrophobic interaction are the dominant forces controlling the formation of silicate-CTAB complexes. When these complexes are saturated with CTAB unimers, free CTAB micelles are then produced. TEM micrographs revealed that a stable Si-O-Si network is absent within the silicate-CTAB complexes, and surprisingly, stable silicate-CTAB complexes with ordered structure were observed. The present finding is important for understanding the interaction between silicate and surfactant in the synthesis of mesoporous structure in the dilute solution regime.

Wang C., Tam K. C., and Tan C. B. (2004) Binding of dodecyltrimethylammonium bromide to pH-responsive nanocolloids containing cross-linked methacrylic acid-ethyl acrylate copolymers. *Langmuir* **20**, 7933-7939.

Abstract: The binding of dodecyltrimethylammonium bromide (DoTab) to cross-linked methacrylic acid-ethyl acrylate (MAA-EA) copolymers with various MAA/EA molar ratios at different degrees of neutralization (α) was quantitatively studied using isothermal titration calorimetry, dynamic light scattering, surfactant selective electrode, and electrophoresis techniques. The surfactant binds to the polymers at all degrees of neutralization, but via different mechanisms. When α is sufficiently high, the binding is primarily electrostatic interaction between the surfactant and ionized polymer chains, which is reinforced by the micellization of electrostatically bound surfactant molecules. The saturation takes place at charge ratio ($[DoTa(+)]/[approximately\ COO(-)]$) close to 1, indicating that the binding is a one-to-one charge neutralization between the cationic surfactant headgroups and anionic carboxylate sites of the polymers. When α is low, the binding of DoTab to the unneutralized polymers is driven by the hydrophobic interaction. The onset of hydrophobic binding takes place at DoTab concentration as low as 0.01 mM in 0.05 wt % polymer solution, where the saturation occurs at $C(DoTab)$ approximately 0.19 mM and the amount of bound surfactant is approximately 0.09 mmol of DoTab/(g of polymer) at saturation concentration. The binding results in the formation of the polymer-surfactant complex. For the polymer with low MAA/EA molar ratio, the complex coagulates at a higher DoTab concentration that leads to phase separation; however, for polymers with high MAA/EA molar ratio, the complex remains dispersed and the mixture is stable even at high DoTab concentration.

Wang C., Ravi P., and Tam K. C. (2006) Morphological transformation of [60]fullerene-containing poly(acrylic Acid) induced by the binding of surfactant. *Langmuir* **22**, 2927-2930.

Abstract: Water-soluble pH-responsive [60]fullerene end-capped poly(acrylic acid) (PAA85-b-C60) was synthesized using atom-transfer radical polymerization (ATRP) technique. The unusual morphological transformation of the polymer induced by the binding of nonionic surfactant Triton X-100 (TX100) at different degrees of neutralization (α) was investigated using isothermal titration calorimetry (ITC), UV-vis spectroscopy, dynamic light scattering (DLS), and transmission electron microscopy (TEM). For the 5 mM (monomer concentration) polymer solution at $pH < 4$, approximately 1.3 mM TX100 binds specifically to C60 domains of the polymeric micelles driven by hydrophobic interaction, which induces a structural transformation of the polymer from a large compound micelle with a radius of 110 nm to a dense precipitated spherical polymer/surfactant complex (PSC) with a radius of 500 nm. The precipitates are resolubilized by a wetting layer of TX100 in excess surfactant (> 1.7 mM in the polymer solution). The binding is significantly weakened and the complexation is disrupted with increasing pH, where the interaction completely ceased at $pH > 6$.

Wang C., Wyn-Jones E., Sidhu J. and Tam K. C. (2007) Supramolecular complex induced by the binding of sodium dodecyl sulfate to PAMAM dendrimers. *Langmuir* **23**, 1635-1639.

Abstract: Isothermal titration calorimetry (ITC) and dynamic light scattering (DLS) were employed to study the spontaneous supramolecular complexation of amine terminated PAMAM dendrimer (G3[EDA] PAMAM-NH₂) induced by the binding of an anionic surfactant, sodium dodecyl sulfate (SDS). At pH ≤ 2 , SDS molecules bound to protonated amines on the outer rims of G3[EDA] PAMAM-NH₂ driven by electrostatic interaction, which induced the formation of PAMAM/SDS supramolecular complex via hydrophobic association between bound SDS molecules. The complex with radius of approximately 37 nm was observed at SDS concentration as low as 0.02 mM (in 0.2 mM PAMAM). The size of the complex increased progressively with increasing SDS concentration and precipitated when the SDS concentration exceeded 15 mM. At pH of approximately 7.4, the formation of PAMAM/SDS complex was observed at higher SDS concentration (0.1 mM in 0.2 mM PAMAM), and it resolubilized with further increase of SDS concentration to approximately 18 mM due to weaker electrostatic interaction at higher pH. At pH ≥ 10 , the electrostatic binding ceased because the deprotonated PAMAM dendrimer was uncharged, and hence the surfactant-induced supramolecular assembly could not be formed.

Wang C., Ravi P. and Tam K. C. (2007) Supramolecular complex of [60]fullerene-grafted polyelectrolyte and surfactant: mechanism and nanostructures. *Langmuir* **23**, 8798-8805.

Abstract: Water-soluble, pH-responsive mono- and di-[60]fullerene end-capped poly(acrylic acid)s (PAA-C60 and C60-PAA-C60) were synthesized using the atom transfer radical polymerization technique. Isothermal titration calorimetry, dynamic light scattering, UV-vis spectroscopy, and transmission electron microscopy were employed to study the supramolecular complexation between fullerene end-capped PAAs and nonionic surfactant, polyethylene glycol (9-10) tert-octylphenyl ether, also known as Triton X100 (TX100) at different pH values. At pH < 4 , TX100 bound specifically to C60 domains driven by hydrophobic and pi-pi interactions between TX100 and fullerene molecules. The binding was exothermic, and the magnitude of the interaction decreased gradually with increasing pH. The amount of polymer-bound TX100 was proportional to the fullerene content, which was approximately 1.3 and approximately 2.5 mM for 5 mM (concentration of carboxylic groups) PAA-C60 and C60-PAA-C60, respectively. Morphological transformations resulting in the formation of polymer/surfactant complex (PSC) precipitates in the course of binding were observed for both polymers. The PSC of PAA-C60 possessed a dense spherical structure, whereas the PSC of C60-PAA-C60 possessed a lamellar stacking structure. The PSC precipitates resolubilized in excess amounts of TX100 to form stable aggregates.

Wang C., Wettig S. D., Foldvari M. and Verrall R. E. (2007) Synthesis, characterization, and use of asymmetric pyrenyl-gemini surfactants as emissive components in DNA-lipoplex systems. *Langmuir* **23**, 8995-9001.

Abstract: Gemini surfactants are potential candidates as synthetic vectors for the delivery of genes into cells to induce protein expression. With the ultimate objective of obtaining a better understanding of the mechanism of DNA transfection, two new asymmetric gemini surfactants (py-3-12 and py-6-12) have been synthesized as fluorescence probes. The physicochemical properties and morphologies of the self-assembled aggregates formed in aqueous solution have been studied using surface tension, specific conductance, dynamic light scattering (DLS), isothermal titration calorimetry (ITC), and fluorescence techniques. The interaction between pyrene-based gemini surfactants and DNA was investigated by using UV-vis and fluorescence spectroscopy. Binding constants for the DNA (salmon sperm)-gemini lipoplexes were measured. Fluorescence studies show that excimer emission occurs upon complexation with DNA.

Wang C., Li X., Wettig S. D., Badea I., Foldvari M. and Verrall R. E. (2007) Investigation of complexes formed by interaction of cationic gemini surfactants with deoxyribonucleic acid. *Phys. Chem Chem Phys.* **9**, 1616-1628.

Abstract: Cationic gemini surfactants, N,N-bis(dimethylalkyl)-alpha,omega-alkanediammonium dibromide [C(m)H(2m+1)(CH₃)₂N⁺(CH₂)_sN⁺(CH₃)₂C(m)H(2m+1) x 2 Br⁻], or m-s-m, have proven to be effective synthetic vectors for gene delivery (transfection). Complexes (lipoplexes) of gemini compounds, where m = 12, s = 3, 12 and m = 18 : 1(oleyl), s = 2, 3, 6, with DNA have been investigated using isothermal titration calorimetry (ITC), dynamic light scattering (DLS), zeta potential, atomic force microscopy (AFM) and circular dichroism (CD) techniques. The results show that lipoplex properties depend on the structural properties of the gemini surfactants, the presence of the helper lipid

dioleoylphosphatidylethanolamine (DOPE), and the titration sequence. ITC data show that the interaction between DNA and gemini surfactants is endothermic and the observed enthalpy vs. charge ratio profile depends upon the titration sequence. Isoelectric points (IP) of lipoplex formation were estimated from the zeta potential measurements and show good agreement with the reaction endpoints (RP) obtained from ITC. DLS data indicate that DNA is condensed in the lipoplex. AFM images suggest that the lipoplex morphology changes from isolated globular-like aggregated particles to larger-size aggregates with great diversity in morphology. This change is further accentuated by the presence of DOPE in the lipoplexes. The results are interpreted in terms of some current models of lipoplex formation.

Wang H., Wang Y., Yan H., Zhang J., and Thomas R. K. (2006) Binding of sodium dodecyl sulfate with linear and branched polyethyleneimines in aqueous solution at different pH values. *Langmuir* **22**, 1526-1533.

Abstract: Isothermal titration microcalorimetry (ITC), conductivity, and turbidity measurements have been carried out to study the interaction of sodium dodecyl sulfate (SDS) with polyethyleneimines (PEI) including linear PEI and branched PEI at different pH values of 3, 7, and 10. In all cases, the polymers show a remarkable affinity toward SDS. At pH 3, the polymer PEI is a strong polycation, and the binding is dominated by electrostatic 1:1 charge neutralization with the anionic surfactant. At pH 7, the electrostatic attraction between SDS and PEI is weak, and the hydrophobic interaction becomes stronger. At the natural pH of 10, PEI is essentially nonionic and binds SDS in the form of polymer-bound surfactant aggregates. The charge neutralization concentration (C1) of SDS for the PEI-SDS complex can be derived from the curves of variation of the enthalpy, conductivity, and turbidity with SDS concentration. There is good agreement between the results from the three methods and all show a decrease with increasing pH. The total interaction enthalpies ($\Delta H(\text{total})$) of PEI with SDS are obtained from the observed enthalpy curves and the difference enthalpy (ΔH^*) between the total enthalpy of branched PEI with SDS, and the total enthalpy of linear PEI with SDS can be derived from the obtained $\Delta H(\text{total})$. The difference ΔH^* increases dramatically as pH increases, which indicates that the interactions are different for linear PEI and branched PEI at high pH values. A schematic map of the different states of aggregation is presented.

Xiang J., Fan J. B., Chen N., Chen J., and Liang Y. (2006) Interaction of cellulase with sodium dodecyl sulfate at critical micelle concentration level. *Colloids Surf B Biointerfaces* **49**, 175-180.

Abstract: The interactions between *Trichoderma reesei* cellulase and an anionic surfactant, sodium dodecyl sulfate (SDS), at critical micelle concentration level have been investigated using isothermal titration calorimetry, fluorescence spectroscopy, and circular dichroism. SDS micelles have dual interactions with cellulase: electrostatic at first and then hydrophobic interactions. When the concentration of SDS is smaller than 45.0mM, SDS micelles cause a partial loss in the hydrolytic activity together with a steep decrease in the alpha-helical content of cellulase. With further increasing the concentration of SDS, however, a re-formation of the alpha-helical structure and a partial recovery of the hydrolytic activity of cellulase induced by SDS micelles are observed. Taken together, these results indicate that SDS micelles exert dual effects on cellulase through binding as both a denaturant and a recovery reagent.

Yan H., Kawamitsu H., Kushi Y., Kuwajima T., Ishii K. and Toshima N. (2007) Calorimetric study on interaction of water-soluble copolymers with ionic surfactant. *J Colloid Interface Sci* **315**, 94-98.

Abstract: Using isothermal titration microcalorimetry (ITC), we examined the aggregation behavior of water-soluble copolymers, poly(methoxypolyethylene glycol methacrylate-co-ethyl acrylate)s (PME-EA)s, with ionic surfactant, sodium dodecyl sulfate (SDS). From ITC measurements the values of critical aggregation concentration (cac) and saturation concentration (C(2)), the concentration at which the aggregation of the copolymers starts to form and reaches saturation, respectively, were determined. Thermodynamic parameters such as $\Delta G(0)(\text{agg})$, $\Delta H(\text{agg})$, and $T\Delta S(0)(\text{agg})$ of the aggregation were deduced. Results indicate that cac of the PME-EA remained constant with increase in the concentration of the copolymers, while C(2) increased linearly. On the other hand, the effect of the weight ratio of the EA unit in the copolymer was such that cac of the PME400-EA decreased, while C(2) increased with increase in the weight ratio. The results suggested that the EA units are the main binding sites of the copolymer with SDS.

Yang J., Zhao J. and Fang Y. (2008) Calorimetric studies of the interaction between sodium alginate and sodium dodecyl sulfate in dilute solutions at different pH values. *Carbohydr. Res* **343**, 719-725.

Abstract: Interactions between the polyelectrolyte sodium alginate (NaAlg) and the anionic surfactant sodium dodecyl sulfate (SDS) have been investigated by microcalorimetric techniques. The polymer-surfactant interactions were observed between NaAlg and SDS at different pH values in dilute solution. The thermodynamic parameters for their interaction process are evaluated from the results of the observed dilution enthalpy curves. As the pH value of the solution decreases from 7 to 6, NaAlg polymers have an obvious effect on the cmc of SDS as a simple salt, which indicates no association between SDS and NaAlg owing to electrostatic repulsion. With the progressive decrease of pH value from 5 to 3, the hydrophobic segments in the alginate chains are increasing and the hydrophilic segments decreasing, and the aggregation between SDS and alginate due to hydrophobic interactions is observed