

ITC XXI – Colloids, Surfactant Studies (critical micelle concentrations)

Aranda F. J., Espuny M. J., Marques A., Teruel J. A., Manresa A. and Ortiz A. (2007) Thermodynamics of the interaction of a dirhamnolipid biosurfactant secreted by *Pseudomonas aeruginosa* with phospholipid membranes. *Langmuir* **23**, 2700-2705.

Abstract: Rhamnolipids are bacterial biosurfactants produced by *Pseudomonas* spp. These compounds have been shown to present several interesting biological activities, restricting the growth of *Bacillus subtilis* and showing zoosporicidal activity on zoosporic phytopathogens. It has been suggested that the interaction with the membrane could ultimately be responsible for these actions. Therefore, it is of great interest to gain insight into the molecular mechanism of the interaction of purified rhamnolipids with the various phospholipid components of biological membranes. In this work, the critical micelle concentration (cmc) of a purified dirhamnolipid produced by *Pseudomonas aeruginosa* has been determined both by isothermal titration calorimetry and surface tension measurements. The partition coefficients from water to membranes of different compositions, as well as the corresponding thermodynamic parameters, have been determined by isothermal titration calorimetry measurements. The results indicate that dirhamnolipid membrane partitioning is an entropically driven process. The presence of cholesterol in the membrane decreases the partition of dirhamnolipid. On the other hand, phosphatidylethanolamine stimulates dirhamnolipid binding, whereas lysophosphatidylcholine opposes binding, suggesting that the biosurfactant behaves as an inverted-cone-shaped molecule. The values obtained for the cmc and the partition constant are considered in relation to the surfactant potency of dirhamnolipids.

Arnulphi C., Sot J., Garcia-Pacios M., Arrondo J. L., Alonso A. and Goni F. M. (2007) Triton X-100 partitioning into sphingomyelin bilayers at subsolubilizing detergent concentrations: effect of lipid phase and a comparison with dipalmitoylphosphatidylcholine. *Biophys J* **93**, 3504-3514.

Abstract: We examined the partitioning of the nonionic detergent Triton X-100 at subsolubilizing concentrations into bilayers of either egg sphingomyelin (SM), palmitoyl SM, or dipalmitoylphosphatidylcholine. SM is known to require less detergent than phosphatidylcholine to achieve the same extent of solubilization, and for all three phospholipids solubilization is temperature dependent. In addition, the three lipids exhibit a gel-fluid phase transition in the 38-41 degrees C temperature range. Experiments have been performed at Triton X-100 concentrations well below the critical micellar concentration, so that only detergent monomers have to be considered. Lipid/detergent mol ratios were never <10:1, thus ensuring that the solubilization stage was never reached. Isothermal titration calorimetry, DSC, and infrared, fluorescence, and ³¹P-NMR spectroscopies were applied in the 5-55 degrees C temperature range. The results show that, irrespective of the chemical nature of the lipid, DeltaG degrees of partitioning remained in the range of -27 kJ/mol lipid in the gel phase and of -30 kJ/mol lipid in the fluid phase. This small difference cannot account for the observed phase-dependent differences in solubilization. Such virtually constant DeltaG degrees occurred as a result of the compensation of enthalpic and entropic components, which varied with both temperature and lipid composition. Consequently, the observed different susceptibilities to solubilization cannot be attributed to differential binding but to further events in the solubilization process, e.g., bilayer saturability by detergent or propensity to form lipid-detergent mixed micelles. The data here shed light on the relatively unexplored early stages of membrane solubilization and open new ways to understand the phenomenon of membrane resistance toward detergent solubilization.

Bai G., Wang Y., Yan H., and Thomas R. K. (2001) Enthalpies of Micellization of Double Chain and Gemini Cationic Surfactants. *J Colloid Interface Sci* **240**, 375-377.

Abstract: Microcalorimetric measurements have been made on double chain cationic surfactants with the formula [C(N)H(2N+1)C(M)H(2M+1)N(CH₃)(2)]Br, referred to as C(N)C(M)DAB, and a cationic gemini surfactant with the formula [C(12)H(25)(CH₃)(2)N(CH₂)(12)N(CH₃)(2)C(12)H(25)]Br(2), referred to as C(12)C(12)C(12)Br(2). The CMCs and enthalpies of micellization for the compounds C(12)C(6)DAB, C(14)C(4)DAB, C(16)C(2)DAB, and C(12)C(12)C(12)Br(2) are obtained from experiments. The effect of the ratio (N/M) of the two alkyl chain lengths for the C(N)C(M)DABs on the micellization process has been investigated. The contribution of ΔH_{mic} to ΔG_{mic} is about 3.4% at N/M=2, about 11% at N/M=3.5 and about 39% at N/M=8, suggesting that when the total carbon atoms (N+M) remain constant, the micellization process will be driven by entropy or entropy and enthalpy jointly with increasing ratio (N/M). In addition, the comparison between C(12)C(12)C(12)Br(2) and its corresponding monomer (C(12)C(6)DAB) is interesting. The micellization process for C(12)C(12)C(12)Br(2) is driven

jointly by enthalpy and entropy, whereas the micellization process for C(12)C(6)DAB is driven mainly by entropy. Copyright 2001 Academic Press.

Basu R. G., Chakraborty I., and Moulik S. P. (2006) Pyrene absorption can be a convenient method for probing critical micellar concentration (cmc) and indexing micellar polarity. *J Colloid Interface Sci* **294**, 248-254.

Abstract: The critical micellar concentration (cmc) of both ionic and non-ionic surfactants can be conveniently determined from the measurements of UV absorption of pyrene in surfactant solution. The results on a number of surfactants have agreed with that realized from pyrene fluorescence measurements as well as that obtained following conductometric, tensiometric and calorimetric methods. The absorbance vs [surfactant] profiles for all the major UV spectral peaks of pyrene have been found to be sigmoidal in nature which were analyzed according to Sigmoidal-Boltzmann equation (SBE) to evaluate the cmcs of the studied surfactants. The difference between the initial and the final asymptotes ($a(i)$ and $a(f)$, respectively) of the sigmoidal profile, $\Delta a = (a(f) - a(i))$ and the slope of the sigmoid, $S(\text{sig})$ have been observed to depend on the type of the surfactant. The Δa has shown a linear correlation with the ratio of the fluorescence intensities of the first and the third vibronic peaks, $I(1)/I(3)$ of pyrene which is considered as a measure of the environmental polarity (herein micellar interior) of the probe (pyrene). Thus, Δa values have the prospect for use as another index for the estimation of polarity of micellar interior.

Beyer K., Leine D., and Blume A. (2006) The demicellization of alkyltrimethylammonium bromides in 0.1 M sodium chloride solution studied by isothermal titration calorimetry. *Colloids Surf B Biointerfaces* **49**, 31-39.

Abstract: The demicellization of the cationic detergents dodecyltrimethylammonium bromide, tetradecyltrimethylammonium bromide, and cetyltrimethylammonium bromide was studied at temperatures between 20 and 60 degrees C in 0.1 M NaCl (pH 6.4) using isothermal titration calorimetry (ITC). We determined the critical micellization concentration (cmc) of the cationic detergents which show a minimum at temperatures between 20 and 34 degrees C. In accordance with the lengthening of the hydrophobic tail of the detergents the cmc decreases with increasing alkyl chain length. The thermodynamic parameters describing the changes of enthalpy ($\Delta H(\text{demic})$), the changes of entropy ($\Delta S(\text{demic})$) and the Gibbs free energy change ($\Delta G(\text{demic})$) for demicellization were first obtained using the pseudophase-separation model. The aggregation number n at the cmc as well as the demicellization enthalpy, entropy and Gibbs free energy change were also calculated using a simulation based on the mass-action model. Furthermore, we investigated the demicellization of CTAB in deionized water in comparison to demicellization in sodium chloride solution to determine the influence of counter ion binding on the demicellization.

Bhattacharya S. and Haldar J. (2004) Thermodynamics of micellization of multiheaded single-chain cationic surfactants. *Langmuir* **20**, 7940-7947.

Abstract: The energetics of micelle formation of three single-chain cationic surfactants bearing single ($h = 1$), double ($h = 2$), and triple ($h = 3$) trimethylammonium $[(+)\text{N}(\text{CH}_3)(3)]$ headgroups have been investigated by microcalorimetry. The results were compared with the microcalorimetric data obtained from well-known cationic surfactant, cetyl trimethylammonium bromide (CTAB), bearing a single chain and single headgroup. The critical micellar concentrations (cmc's) and the degrees of counterion dissociation (α) of micelles of these surfactants were also determined by conductometry. The cmc and the α values increased with the increase in the number of headgroups of the surfactant. The relationship between the cmc of the surfactant in solution and its free energy of micellization (ΔG_m) was derived for each surfactant. Exothermic enthalpies of micellization (ΔH_m) and positive entropies of micellization (ΔS_m) were observed for all the surfactants. Negative ΔH_m values increased from CTAB to $h = 1$ to $h = 2$ and decreased for $h = 3$ whereas ΔS_m values decreased with increase in the number of headgroups. The ΔG_m values progressively became less negative with the increase in the number of headgroups. This implies that micelle formation becomes progressively less favorable as more headgroups are incorporated in the surfactant. From the steady-state fluorescence measurements using pyrene as a probe, the micropolarities sensed by the probe inside various micelles were determined. These studies suggest that the micelles are more hydrated with multiheaded surfactants and the micropolarity of micelles increases with the increase in the number of headgroups.

Bhattacharya S. and Haldar J. (2005) Microcalorimetric and conductivity studies with micelles prepared from multi-headed pyridinium surfactants. *Langmuir* **21**, 5747-5751.

Abstract: A set of novel single-chain surfactants bearing one (P1), two (P2), and three (P3) pyridinium headgroups have been synthesized in an attempt to achieve control over the aggregate properties. The critical micellar concentrations (cmc's) and the degrees of counterion dissociation (α) of micelles of these surfactants were determined by conductometry. The cmc and the α values increased with increase in the number of headgroups of the surfactant. The thermodynamics of micellization of these surfactants were investigated by microcalorimetry, and the results were compared with that of well-known single-chain/single-headgroup surfactant, cetylpyridinium bromide (CPB). The relationship between the cmc of surfactant in solution and its free energy of micellization ($\Delta G(o)m$) was derived for each surfactant. Exothermic enthalpies of micellization ($\Delta H(o)m$) and positive entropies of micellization ($\Delta S(o)m$) were observed for all the surfactants. $\Delta H(o)m$ values were found to be more negative for CPB than P1, and it increased with a negative sign from P1 to P2 and decreased for P3. In contrast the $\Delta S(o)m$ values decreased with increase in the number of headgroups. The $\Delta G(o)m$ values progressively became less negative with increase in the number of headgroups. This implies that micelle formation becomes less favorable as more headgroups are incorporated in the surfactant.

Cao M., Deng M., Wang X. L. and Wang Y. (2008) Decomposition of cationic gemini surfactant-induced DNA condensates by beta-cyclodextrin or anionic surfactant. *J Phys. Chem B* **112**, 13648-13654.

Abstract: Compaction of DNA by cationic gemini surfactant hexamethylene-1,6-bis-(dodecyltrimethylammoniumbromide) (C12C6C12Br₂) and the subsequent decomposition of the DNA-C12C6C12Br₂ complexes by beta-cyclodextrin (beta-CD) or sodium dodecyl sulfate (SDS) have been studied by using zeta potential and particle size measurements, atomic force microscopy (AFM), isothermal titration microcalorimetry (ITC), and circular dichroism. The results show that C12C6C12Br₂ can induce the collapse of DNA into densely packed bead-like structures with smaller size in an all-or-none manner, accompanied by the increase of zeta potential from highly negative values to highly positive values. In the decomposition of the DNA-C12C6C12Br₂ complexes, beta-CD and SDS exhibit different behaviors. For beta-CD, the experimental results suggest that it can remove the outlayer hydrophobically bound C12C6C12Br₂ molecules from the DNA-C12C6C12Br₂ complexes by inclusion interaction, and the excess beta-CD may attach on the complexes by forming inclusion complexes with the hydrocarbon chains of the electrostatically bound C12C6C12Br₂ that cannot be removed. The increase of steric hindrance due to the attachment of beta-CD molecules results in the decomposition of the DNA condensates though the true release of DNA cannot be attained. However, for SDS, the experimental results suggest that it can realize the decomposition and release of DNA from its complexes with C12C6C12Br₂ due to both ion-pairing and hydrophobic interaction between SDS and C12C6C12Br₂.

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 x 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 ($c < 1.0 \times 10^{-4}$ 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 ($1.0 \times 10^{-4} < c < 0.1$ 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.

Chaghi R., de Menorval L. C., Charnay C., Derrien G. and Zajac J. (2008) Interactions of phenol with cationic micelles of hexadecyltrimethylammonium bromide studied by titration calorimetry, conductimetry, and ¹H NMR in the range of low additive and surfactant concentrations. *J Colloid Interface Sci* **326**, 227-234.

Abstract: Interactions of phenol (PhOH) with micellar aggregates of hexadecyltrimethylammonium bromide (HTAB) in aqueous solutions at surfactant concentrations close to the CMC and phenol contents of 1, 5, or 10 mmol kg⁻¹ have been investigated at 303 K by means of titration calorimetry, solution conductimetry, and ¹H NMR spectroscopy. Estimates of the main thermodynamic parameters related to HTAB micellization were made for PhOH/HTAB/H₂O systems based on the specific conductivity measurements and calorimetric determination of the cumulative enthalpy of dilution as functions of the surfactant concentration at a fixed additive content. The combined analysis of the results obtained in H₂O solutions pointed to the preferential location of PhOH in the outer micelle parts by an enthalpy-driven mechanism. Additional PhOH molecules were located increasingly deeper within the micelle core. The ¹H NMR study of PhOH solubilization by 1.5 mmol kg⁻¹ HTAB solutions in D₂O indicated that the two categories of the solubilization site became saturated with the solubilize already at the lowest additive content. Dissimilar amounts of the solubilized material in H₂O and D₂O solutions were ascribed to the difference in the initial micelle structures formed in the two solvents, as inferred from calorimetry and ¹H NMR studies of the HTAB micellization in D₂O and H₂O

Chakraborty I. and Moulik S. P. (2007) Self-aggregation of ionic C₁₀ surfactants having different headgroups with special reference to the behavior of decyltrimethylammonium bromide in different salt environments: a calorimetric study with energetic analysis. *J Phys. Chem B* **111**, 3658-3664.

Abstract: Self-aggregation of C₁₀ ionic surfactants with different head groups, viz., decylpyridinium chloride, sodium decylsulfate, decylammonium bromide, decyldimethylammonium bromide, and decyltrimethylammonium bromide, was studied in the aqueous medium by microcalorimetric and conductometric methods. The effects of temperature and different salts (NaF, NaCl, NaBr, NaI, Na₂SO₄, Na₂S₂O₇, Na-benzoate, and Na-salicylate) were also studied on decyltrimethylammonium bromide representatives. The cmc, counterion binding, and energetics of micellization were evaluated and discussed. The energetic parameters, enthalpy, entropy, and specific heat of micellization obtained from direct calorimetry and the indirect van't Hoff method were compared and discussed.

Chatterjee A., Moulik S. P., Majhi P. R., and Sanyal S. K. (2002) Studies on surfactant-biopolymer interaction. I. Microcalorimetric investigation on the interaction of cetyltrimethylammonium bromide (CTAB) and sodium dodecylsulfate (SDS) with gelatin (Gn), lysozyme (Lz) and deoxyribonucleic acid (DNA). *Biophys Chem* **98**, 313-327.

Abstract: The interaction of the surfactants cetyltrimethyl ammonium bromide (CTAB) and sodium dodecyl sulfate (SDS) with the biopolymers gelatin (Gn), lysozyme (Lz) and deoxyribonucleic acid (DNA) was studied by isothermal titration microcalorimetry at varied biopolymer concentration, pH and temperature. The nature of interaction of the surfactants with the biopolymers was assessed from the observed enthalpy-[surfactant] profiles. The biopolymer-induced aggregation of the surfactants was observed. The enthalpies of aggregation of amphiphiles, binding of aggregates with macromolecules, organisational change of bound aggregates, and threshold concentrations for micelle formation of surfactants in the presence of biopolymers were estimated. The results collected on the three biopolymers were analysed and compared.

Chou D. K., Krishnamurthy R., Randolph T. W., Carpenter J. F., and Manning M. C. (2005) Effects of Tween 20(R) and Tween 80(R) on the stability of Albutropin during agitation. *J Pharm Sci* **94**, 1368-1381.

Abstract: The objectives of this work were to determine the effects of nonionic surfactants (Tween 20(R)

and Tween 80(R)) on agitation-induced aggregation of the recombinant fusion protein, Albutropintrade mark (human growth hormone genetically fused to human albumin), and to characterize the binding interactions between the surfactants and the protein. Knowing the binding stoichiometry would allow a rational choice of surfactant concentration to protect the protein from surface-induced aggregation. Fluorescence spectroscopy and isothermal titration calorimetry (ITC) were employed to study Albutropin surfactant binding. Albutropin was agitated at 25 +/- 2 degrees C to induce aggregation, and samples were taken during a 96-h incubation. Size-exclusion chromatography (SEC-HPLC) (HPLC, high-performance liquid chromatography) was used to detect and quantify the extent of protein aggregation. The effect of surfactants on the protein's free energy of unfolding was determined using guanidine HCl as a denaturant. Tween 20 and Tween 80 had saturable binding to Albutropin with a molar binding stoichiometry of 10:1 and 9:1 (surfactant:protein), respectively. Binding of the surfactants to Albutropin increased the free energy of unfolding by over 1 and 0.6 kcal/mol, respectively. In protein samples that were agitated in the absence of surfactant, soluble aggregates were detected within 24 h, and there was almost complete loss of monomer to soluble aggregates by the end of the 96-h experiment. At the molar binding stoichiometry, Tween 20 and Tween 80 prevented the formation of soluble aggregates, even though the concentrations of surfactants were well below their critical micelle concentrations (CMC). Tween 20 and Tween 80 protected Albutropin against agitation-induced aggregation, even at concentrations below the CMC. Equilibrium unfolding data indicate that Tween confer protection by increasing the free energy of unfolding of Albutropin. (c) 2005 Wiley-Liss, Inc. and the American Pharmacists Association J Pharm Sci 94:1368-1381, 2005.

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.

Custers J. P., Broeke L. J. and Keurentjes J. T. (2007) Phase behavior and micellar properties of carboxylic Acid end group modified pluronic surfactants. *Langmuir* **23**, 12857-12863.

Abstract: The micellar behavior of three different carboxylic acid end standing (CAE) surfactants has been characterized using conductometry, differential scanning calorimetry, isothermal titration calorimetry, and dynamic light scattering. The CAE surfactants are modified high molecular weight Pluronic (PEO-PPO-PEO triblock copolymer) surfactants. The influence of pH and salt additives on the critical micellization temperature (CMT) and the cloud point of the CAE surfactants have been studied. Both the CMT and the cloud points of the CAE surfactants increase as a function of pH and decrease as a function of ionic strength. For the CAE surfactants, the CMT varies by about 5 degrees C, and the cloud point shows a variation in the order of 20-30 degrees C, as compared to the unmodified Pluronics. From the different experimental techniques, it follows that at low pH values (pH < 3.5), the CAE surfactants show the same micellar behavior as the unmodified Pluronic, while at high pH values (pH > 6), the micellar properties of

the CAE surfactants are considerably different from those observed for the corresponding Pluronic. It has been demonstrated that the CAE micelles are capable of removing simultaneously divalent ions and phenanthrene. The CAE surfactants are the first known anionic surfactants that show cloud point behavior with the addition of low concentrations of simple salts, such as, for example, NaCl.

Dai S. and Tam K. C. (2005) Laser light scattering and isothermal titration calorimetric studies of poly(ethylene oxide) aqueous solution in presence of sodium dodecyl sulfate. *J Colloid Interface Sci* **292**, 79-85.

Abstract: The aqueous solution of poly(ethylene oxide) (PEO) in the presence of different concentrations of sodium dodecyl sulfate (SDS) was examined by laser light scattering and isothermal titration calorimetric techniques. A small fraction of PEO aggregates were found to coexist with unimeric PEO chains in dilute solution. The presence of monovalent salt does not alter the hydrodynamic properties of PEO in aqueous solution. Addition of a monovalent anionic surfactant, such as SDS, induces cooperative binding of surfactant monomers to PEO backbones at SDS concentrations ranging from 4.0 mM (critical aggregation concentration) to 16.5 mM (saturation concentration). The hydrodynamic radius of PEO unimers decreases initially and then increases with SDS concentration, resulting from the structural reorganization of the PEO/SDS complex. Beyond the saturation concentration, the hydrodynamic radii of PEO/SDS complex are independent of SDS concentration.

Dai S. and Tam K. C. (2006) Effect of cosolvents on the binding interaction between poly(ethylene oxide) and sodium dodecyl sulfate. *J Phys Chem B Condens Matter Mater Surf Interfaces Biophys* **110**, 20794-20800.

Abstract: The micellization of sodium dodecyl sulfate (SDS) in different glycol-water solvent mixtures was studied using the isothermal titration calorimetric (ITC) technique. At the same time, microcalorimetric titrations were also carried out to monitor the binding interaction of SDS and poly(ethylene oxide) (PEO) in the presence of different cosolvents. The demicellization of SDS in mixtures of water and cosolvents is different from that in water due to the reduction in solvent polarity and charge interaction of surfactants. The critical micelle concentration (cmc) first decreases with the addition of a small amount of cosolvents and then increases at higher cosolvent concentrations. The thermodynamics of surfactant micellization can be analyzed using the solubility parameters of solvent mixtures. For the binding interaction between SDS and PEO in different solvent mixtures, the dehydration process at low SDS concentrations is replaced by the chain solubilization process with decreasing solvent polarity. With further reduction in the solvent polarity, the binding interaction between SDS and PEO becomes weak and no aggregates can be formed beyond a certain glycol concentration. The binding interaction between SDS and PEO in different solvent mixtures was analyzed and ascribed to the effects of PEO solubility and hydrophobicity of SDS.

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.

Dan A., Chakraborty I., Ghosh S. and Moulik S. P. (2007) Interfacial and bulk behavior of sodium dodecyl sulfate in isopropanol-water and in isopropanol-poly(vinylpyrrolidone)-water media. *Langmuir* **23**, 7531-7538.

Abstract: The surface activity of isopropanol (IP) and poly(vinylpyrrolidone) (PVP) at the air/water interface has been studied. The self-aggregation of sodium dodecyl sulfate (SDS) in IP-water as well as in IP-PVP-water media has been investigated using physical methods, viz., tensiometry, conductometry, calorimetry, and viscometry. The interaction of SDS with PVP in IP-water medium as well as its self-aggregation (or micellization) in the presence of PVP has been assessed. The results reveal a fair degree of surface activity of IP in aqueous medium, which is only moderate for PVP. The critical micellar concentration (CMC) of SDS passes through a minimum at (v/v) % IP = 6.62. SDS interacts with PVP, yielding a critical aggregation concentration (CAC) at a low [SDS], independent of IP content in the medium. At a higher [SDS], free micelle formation takes place in solution, which is lower in mixed solvent than in water and is independent of solvent composition by tensiometry, but not by conductometry and calorimetry. The viscosity of micelle-interacted PVP in solution takes a long time to stabilize, whereas, for non-interacting additives, such as NaCl and cetyltrimethylammonium bromide (CTAB), it is time independent.

Dignam J. D., Qu X., Ren J. and Chaires J. B. (2007) Daunomycin binding to detergent micelles: a model system for evaluating the hydrophobic contribution to drug-DNA interactions. *J Phys. Chem B* **111**, 11576-11584.

Abstract: The interaction of daunomycin with sodium dodecyl sulfate and Triton X-100 micelles was investigated as a model for the hydrophobic contribution to the free energy of DNA intercalation reactions. Measurements of visible absorbance, fluorescence lifetime, steady-state fluorescence emission intensity, and fluorescence anisotropy indicate that the anthraquinone ring partitions into the hydrophobic micelle interior. Fluorescence quenching experiments using both steady-state and lifetime measurements demonstrate reduced accessibility of daunomycin in sodium dodecyl sulfate micelles to the anionic quencher iodide and to the neutral quencher acrylamide. Quenching of daunomycin fluorescence by iodide in Triton X-100 micelles was similar to that seen with free daunomycin. Studies of the energetics of the interaction of daunomycin with micelles by fluorescence and absorbance titration methods and by isothermal titration calorimetry in the presence of excess micelles revealed that association with sodium dodecyl sulfate and Triton X-100 micelles is driven by a large negative enthalpy. Association of the drug with both types of micelles also has a favorable entropic contribution, which is larger in magnitude for Triton X-100 micelles than for sodium dodecyl sulfate micelles. The thermodynamic profile for the interaction of daunomycin with both types of micelles is characteristic of the "nonclassical" hydrophobic effect. The enthalpy for the interaction of daunomycin with sodium dodecyl sulfate micelles increases nonlinearly with temperature, indicating a positive (and temperature dependent) heat capacity change. The binding isotherm for daunomycin association with sodium dodecyl sulfate micelles was cooperative, with a Hill coefficient of 1.6. The cooperative behavior and the positive heat capacity change suggest that the drug alters micelle size or imposes order on the hydrocarbon interior of the micelle.

Fan Y., Li Y., Yuan G., Wang Y., Wang J., Han C. C., Yan H., Li Z., and Thomas R. K. (2005) Comparative studies on the micellization of sodium bis(4-phenylbutyl) sulfosuccinate and sodium bis(2-ethylhexyl) sulfosuccinate and their interaction with hydrophobically modified poly(acrylamide). *Langmuir* **21**, 3814-3820.

Abstract: The micellization process of sodium bis(4-phenylbutyl) sulfosuccinate (SBPBS) has been studied compared to that of sodium bis(2-ethylhexyl) sulfosuccinate (AOT) by surface tension, steady-state fluorescence, microcalorimetry, dynamic light scattering (DLS), and transmission electron microscopy (TEM) measurements. Meanwhile, the interaction of these two surfactants with hydrophobically modified poly(acrylamide) (HMPAM) was investigated. The results show that the surface tension at the critical micelle concentration (cmc) of SBPBS and the micropolarity probed by pyrene in SBPBS aggregates are both larger than those of AOT. The enthalpy change of micellization ($\Delta H(\text{mic})$) of AOT is endothermic, while it is exothermic for SBPBS. Strong pi-pi interaction among the adjacent phenyl groups of SBPBS molecules is likely the cause for the above properties of SBPBS. Moreover, vesicles are observed for AOT and SBPBS by DLS and TEM, especially for AOT, whose micelle-vesicle transition has been first confirmed by its calorimetric curve. In the surfactant-HMPAM systems, the critical aggregation concentration (cac), the saturation concentration of aggregation ($C(2)$), and the thermodynamic parameters of binding have also been determined. The conclusion may be drawn that the binding strength of SBPBS onto HMPAM is stronger than that of AOT.

Fan Y., Li Y., Cao M., Wang J., Wang Y. and Thomas R. K. (2007) Micellization of dissymmetric cationic gemini surfactants and their interaction with dimyristoylphosphatidylcholine vesicles. *Langmuir* **23**, 11458-11464.

Abstract: The micellization process of a series of dissymmetric cationic gemini surfactants [C_mH_{2m+1}(CH₃)₂N(CH₂)₆N(CH₃)₂C₆H₁₃]Br₂ (designated as m-6-6 with m = 12, 14, and 16) and their interaction with dimyristoylphosphatidylcholine (DMPC) vesicles have been investigated. In the micellization process of these gemini surfactants themselves, critical micelle concentration (cmc), micelle ionization degree, and enthalpies of micellization (ΔH_{mic}) were determined, from which Gibbs free energies of micellization (ΔG_{mic}) and entropy of micellization (ΔS_{mic}) were derived. These properties were found to be influenced significantly by the dissymmetry in the surfactant structures. The phase diagrams for the solubilization of DMPC vesicles by the gemini surfactants were constructed from calorimetric results combining with the results of turbidity and dynamic light scattering. The effective surfactant to lipid ratios in the mixed aggregates at saturation (Resat) and solubilization (Resol) were derived. For the solubilization of DMPC vesicles, symmetric 12-6-12 is more effective than corresponding single-chain surfactant DTAB, whereas the dissymmetric m-6-6 series are more effective than symmetric 12-6-12, and 16-6-6 is the most effective. The chain length mismatch between DMPC and the gemini surfactants may be responsible for the different Re values. The transfer enthalpy per mole of surfactant within the coexistence range may be associated with the total hydrophobicity of the alkyl chains of gemini surfactants. The transfer enthalpies of surfactant from micelles to bilayers are always endothermic due to the dehydration of headgroups and the disordering of lipid acyl chain packing during the vesicle solubilization.

Feitosa E., Brazolin M. R., Naal R. M., Del Lama M. P., Lopes J. R., Loh W., and Vasilescu M. (2006) Structural organization of cetyltrimethylammonium sulfate in aqueous solution: The effect of Na₂SO₄. *J Colloid Interface Sci* **299**, 883-889.

Abstract: We used dynamic light scattering (DLS), steady-state fluorescence, time resolved fluorescence quenching (TRFQ), tensiometry, conductimetry, and isothermal titration calorimetry (ITC) to investigate the self-assembly of the cationic surfactant cetyltrimethylammonium sulfate (CTAS) in aqueous solution, which has SO₄²⁻ as divalent counterion. We obtained the critical micelle concentration (cmc), aggregation number (N_{agg}), area per monomer (a₀), hydrodynamic radius (R(H)), and degree of counterion dissociation (alpha) of CTAS micelles in the absence and presence of up to 1 M Na₂SO₄ and at temperatures of 25 and 40 degrees C. Between 0.01 and 0.3 M salt the hydrodynamic radius of CTAS micelle R(H) approximately 16 Å is roughly independent on Na₂SO₄ concentration; below and above this concentration range R(H) increases steeply with the salt concentration, indicating micelle structure transition, from spherical to rod-like structures. R(H) increases only slightly as temperature increases from 25 to 40 degrees C, and the cmc decreases initially very steeply with Na₂SO₄ concentration up to about 10 mM, and thereafter it is constant. The area per surfactant at the water/air interface, a₀, initially increases steeply with Na₂SO₄ concentration, and then decreases above ca. 10 mM. Conductimetry gives alpha = 0.18 for the degree of counterion dissociation, and N_{agg} obtained by fluorescence methods increases with surfactant concentration but it is roughly independent of up to 80 mM salt. The ITC data yield cmc of 0.22 mM in water, and the calculated enthalpy change of micelle formation, $\Delta H_{mic} = 3.8 \text{ kJ mol}^{-1}$, Gibbs free energy of micellization of surfactant molecules, $\Delta G_{mic} = -38.0 \text{ kJ mol}^{-1}$ and entropy $T\Delta S_{mic} = 41.7 \text{ kJ mol}^{-1}$ indicate that the formation of CTAS micelles is entropy-driven.

Fiscaro E., Compari C., Biemmi M., Duce E., Peroni M., Donofrio G., Sansone F., Rozycka-Rozsak B., Pruchnik H., Barbero N., Viscardi G. and Quagliotto P. (2008) Thermodynamics and biological properties of the aqueous solutions of new glucocationic surfactants. *J Phys. Chem B* **112**, 9360-9370.

Abstract: Thermodynamic properties of aqueous solutions of newly synthesized compounds, namely, N-[2-(beta-D-glucopyranosyl)ethyl]-N,N-dimethyl-N-alkylammonium bromides with hydrophobic tails of 12 (C12DGCB) and 16 (C16DGCB) carbon atoms, determined as a function of concentration by means of direct methods, are reported here. Dilution enthalpies, densities, and sound velocities were measured at 298 K, allowing for the determination of apparent and partial molar enthalpies, volumes, and compressibilities. Changes in thermodynamic quantities upon micellization were derived using a pseudophase-transition approach. From a comparison with the corresponding acetylated compounds N-[2-(2,3,4,6-tetra-O-acetyl-beta-D-glucopyranosyl)ethyl]-N,N-dimethyl-N-dodecylammonium bromide (C12AGCB) and N-[2-(2,3,4,6-tetra-O-acetyl-beta-D-glucopyranosyl)ethyl]-N,N-dimethyl-N-hexadecylammonium bromide

(C16AGCB), the role played in the micellization process by the acetylated glycosyl moiety was inferred: it enhances the hydrophobic character of the molecule and lowers the change in enthalpy of micelle formation by about 1.5 kJ mol⁻¹. By comparing the volume of C12DGCB with those of DEDAB and DTAB, the volumes taken up by the (beta- d-glucopyranosyl)ethyl and beta- d-glucopyranosyl groups were found to be 133 and 99 cm³ mol⁻¹, respectively. Regarding the interaction with DPPC membranes, it seems that the sugar moiety of the hexadecyl deacetylated compound gives rise to hydrogen bonds with the oxygen atoms of the lipid phosphates, shifting the phase transition of DPPC from a bilayer gel to a bilayer liquid crystal to lower temperatures. C16AGCB induces significantly greater changes than C16DGCB in the structure of liposomes, suggesting the formation of domains. The interaction is strongly enhanced by the presence of water. Neither compound interacts strongly with DNA or compacts it, as shown by EMSA assays and AFM images. Only C16AGCB is able to deliver little DNA inside cells when coformulated with DOPE, as shown by the transient transfection assay. This might be related to the ability of C16AGCB to form surfactant-rich domains in the lipid structure

Fisicaro E., Compari C., Biemmi M., Duce E., Peroni M., Barbero N., Viscardi G. and Quagliotto P. (2008) Unusual behavior of the aqueous solutions of gemini bispyridinium surfactants: apparent and partial molar enthalpies of the dimethanesulfonates. *J Phys. Chem B* **112**, 12312-12317.

Abstract: Apparent and partial molar enthalpies at 298 K of the aqueous solutions of cationic gemini surfactants 1,1'-didodecyl-2,2'-dimethylenebispyridinium dimethanesulfonate (12-Py(2)-2-(2)Py-12 MS); 1,1'-didodecyl-2,2'-trimethylenebispyridinium dimethanesulfonate (12-Py(2)-3-(2)Py-12 MS); 1,1'-didodecyl-2,2'-tetramethylenebispyridinium dimethanesulfonate (12-Py(2)-4-(2)Py-12 MS); 1,1'-didodecyl-2,2'-octamethylenebispyridinium dimethanesulfonate (12-Py(2)-8-(2)Py-12 MS); 1,1'-didodecyl-2,2'-dodecamethylenebispyridinium dimethanesulfonate (12-Py(2)-12-(2)Py-12 MS) were measured as a function of concentration and are here reported for the first time. They show a very peculiar behavior as a function of the spacer length, not allowing for the determination of a -

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.

Gao Y., Hilfert L., Voigt A. and Sundmacher K. (2008) Decrease of droplet size of the reverse microemulsion 1-butyl-3-methylimidazolium tetrafluoroborate/Triton X-100/cyclohexane by addition of water. *J Phys. Chem B* **112**, 3711-3719.

Abstract: In the present contribution, results concerning the role of small amounts of water in the 1-butyl-3-methylimidazolium tetrafluoroborate (bmimBF₄)-in-cyclohexane ionic liquid (IL) reverse microemulsions are reported. Dynamic light scattering (DLS) revealed that the size of microemulsion droplets decreased remarkably with increasing water content although water is often used as a polar component to swell reverse microemulsions. It was thus deduced that the number of microemulsion droplets was increased which was confirmed by conductivity measurements. The states of dissolved water were investigated by Fourier transform IR (FTIR) spectroscopic analysis showing that water molecules mainly act as bound water. ¹H NMR along with two-dimensional rotating frame nuclear Overhauser effect (NOE) experiments (ROESY) further revealed that water molecules were mainly located in the periphery of the polar core of the microemulsion droplets and behave like a chock being inserted in the palisade layer

of the droplet. This increased the curvature of the surfactant film at the IL/cyclohexane interface and thus led to the decrease of the microemulsion droplet size. The order of surfactant molecules arranged in the interface film was increased and thus induced a loss of entropy. Isothermal titration calorimetry (ITC) indicated that an enthalpy increase compensates for the loss of entropy during the process of microstructural transition

Gianni P., Barghini A., Bernazzani L., Mollica V., and Pizzolla P. (2006) Aggregation of cesium perfluorooctanoate on poly(ethylene glycol) oligomers in water. *J Phys Chem B Condens Matter Mater Surf Interfaces Biophys* **110**, 9112-9121.

Abstract: The interaction of cesium perfluorooctanoate (CsPFO) with poly(ethylene glycol) (PEG) of different molecular weight ($300 < \text{MW} < 20000$ Da) has been investigated at 298.15 K by isothermal titration calorimetry (ITC), density, viscosity, and conductivity measurements. Calorimetric titrations exhibited peculiar trends analogous to those already observed for sodium dodecyl sulfate (SDS). Micelles of the perfluorosurfactant, as compared to those of SDS, yield complexes with the polymer of similar thermodynamic stability but are able to interact with shorter PEG oligomers. The average number of surfactant molecules bonded per polymer chain at the saturation is about twice that observed for SDS. ITC data at 308.15 K indicate a larger thermodynamic stability of the aggregates but an almost constant stoichiometry. The peculiar thermal effects and the viscosity trend observed during the titration of an aqueous PEG solution with the surfactant appear consistent with a conformational change of the polymer. The PEG chain would evolve from a strained to an expanded conformation, induced by the growing of the surfactant micellar clusters bonded to the polymer, as suggested in a previous study of the PEG/SDS/H₂O system.

Gianni P., Barghini A., Bernazzani L., and Mollica V. (2006) Calorimetric investigation of the interaction between lithium perfluorononanoate and poly(ethylene glycol) oligomers in water. *Langmuir* **22**, 8001-8009.

Abstract: The interaction of lithium perfluorononanoate (LiPFN) with poly(ethylene glycol) (PEG) molecules of different molecular weights ($300 < \text{MW} < 20000$ Da) has been investigated in water at 298.15 and 308.15 K by isothermal titration calorimetry (ITC). Density, viscosity, and conductivity measurements were also performed at 298.15 K. The aggregation process of this surfactant on the PEG polymeric chain was found to be very similar to that exhibited by cesium perfluorooctanoate (CsPFO) and appears to be consistent with the necklace model. ITC titrations indicated that a fully formed LiPFN micellar cluster can be wrapped by a PEG chain having a molecular weight (MW) of approximately 3200 Da, longer than that required by the shorter perfluorooctanoate (MW approximately 2600 Da), and also suggested a stepwise mechanism for the aggregation of successive micelles. Viscosity data indicate that the formation of polymer-surfactant complexes between PEG and LiPFN involves a conformational change of the polymer. The aggregation of preformed micelles of LiPFN or CsPFO or SDS on the PEG polymeric chain always gives rise to further stabilization.

Goloub T. P. and Pugh R. J. (2005) The role of the surfactant head group in the emulsification process: Binary (nonionic-ionic) surfactant mixtures. *J Colloid Interface Sci* **291**, 256-262.

Abstract: Dilute emulsions of dodecane in water were prepared under constant flow rate conditions with binary surfactant systems. The droplet size distribution was measured as a function of the mixed surfactant composition in solution. The systems studied were (a) the mixture of anionic sodium dodecyl sulfate (SDS) with nonionic hexa(ethyleneglycol) mono n-dodecylether (C(12)E(6)) and (b) the mixture of cationic dodecyl pyridinium chloride (DPC) with C(12)E(6). At a constant concentration of SDS or DPC surfactant in solution (below the CMC) the mean emulsion droplet size decreases with the increase in the amount of C(12)E(6) added to the solution. However, a sharp break of this droplet size occurs at a critical concentration and beyond this point the mean droplet size did not significantly change upon further increase of the C(12)E(6). This point was found to corresponded to the CMC of the mixed surfactant systems (as previously determined from microcalorimetry measurements) and this result suggested the mixed adsorption layer on the emulsion droplet was similar to the surfactant composition on the mixed micelles. The emulsion droplet size as a function of composition at the interface was also studied. The mean emulsion droplet size in SDS-C(12)E(6) solution was found to be lower than that in DPC-C(12)E(6) system at the equivalent mole fraction of ionic surfactant at interface. This was explained by the stronger interactions between sulphate and polyoxyethylene head groups at the interface, which facilitate the droplet

break-up. Counterion binding parameter (β) was also determined from zeta-potential of dodecane droplets under the same conditions and it was found that (β) was independent of the type of the head group and the mole fraction of ionic surfactant at interface.

Jiang N., Li P., Wang Y., Wang J., Yan H., and Thomas R. K. (2005) Aggregation behavior of hexadecyltrimethylammonium surfactants with various counterions in aqueous solution. *J Colloid Interface Sci* **286**, 755-760.

Abstract: Both thermodynamic and microenvironmental properties of the micelles for a series of cationic surfactants hexadecyltrimethylammonium (C(16)TAX) with different counterions, F(-), Cl(-), Br(-), NO(-)(3), and (1/2)SO(2-)(4), have been studied. Critical micelle concentration (CMC), degree of micelle ionization (α), and enthalpy of micellization ($\Delta H(\text{mic})$) have been obtained by conductivity measurements and isothermal titration microcalorimetry. Both the CMC and the α increase in the order SO(2-)(4) < NO(-)(3) < Br(-) < Cl(-) < F(-), consistent with a decrease in binding of counterion, except for the divalent anion sulfate. $\Delta H(\text{mic})$ becomes less negative through the sequence NO(-)(3) < Br(-) < Cl(-) < F(-) < SO(2-)(4), and even becomes positive for the divalent sulfate. The special behavior of sulfate is associated with both its divalency and its degree of dehydration. Gibbs free energies of micellization ($\Delta G(\text{mic})$) and entropies of micellization ($\Delta S(\text{mic})$) have been calculated from the values of $\Delta H(\text{mic})$, CMC, and α and can be rationalized in terms of the Hofmeister series. The variations in $\Delta H(\text{mic})$ and $\Delta S(\text{mic})$ have been compared with those for the corresponding series of gemini surfactants. Electron spin resonance has been used to assess the micropolarity and the microviscosity of the micelles. The results show that the microenvironment of the spin probe in the C(16)TAX surfactant micelles depends strongly on the binding of the counterion.

Jiang N., Wang J., Wang Y., Yan H., and Thomas R. K. (2005) Microcalorimetric study on the interaction of dissymmetric gemini surfactants with DNA. *J Colloid Interface Sci* **284**, 759-764.

Abstract: The interaction of a series of dissymmetric gemini surfactants, $[C(m)H(2m+1)(CH_3)_2N(CH_2)_6N(CH_3)_2C(n)H(2n+1)]Br(2)$ (designated as C(m)C(6)C(n)Br(2), with constant $m+n=24$, and $m=12, 14, 16$, and 18) with DNA in 10 mM NaCl solution has been investigated by isothermal titration microcalorimetry (ITC). The curves for titration of the surfactants into DNA solution show noticeable differences from those into 10 mM NaCl solution without DNA. It is attributed to the interaction between DNA and surfactants. The critical aggregation concentration (CAC), the saturation concentration (C(2)), and the thermodynamic parameters for the aggregation and interaction processes were obtained from the calorimetric titration curves. The results show that the dissymmetry degree (m/n) has a marked effect on the interaction of the C(m)C(6)C(n)Br(2) surfactants with DNA. The CAC and C(2) tend to become smaller with increased m/n . The enthalpy change ($\Delta H(\text{agg})$) and the Gibbs free energy change ($\Delta G(\text{agg})$) for aggregation become more negative down the series, indicating that the hydrophobic interaction between the hydrophobic chains of the surfactant molecules increases and the aggregation process is more spontaneous with increased m/n . The entropy changes of aggregation ($\Delta S(\text{agg})$) are all positive and $T\Delta S(\text{agg})$ is much larger than $|\Delta H(\text{agg})|$, revealing that the aggregation process is mainly entropy-driven. However, the calculated Gibbs free energy ($\Delta G(\text{DS})$) for the interaction between the gemini surfactants and DNA becomes less negative with increased m/n , which reveals that the interaction between the gemini surfactants and DNA tends to be weaker with increased m/n . This is induced by the disruption of the chain-chain hydrophobic interaction between the surfactant molecules at higher m/n , where the entropy change $\Delta S(\text{DS})$ for the interaction process tends to be an unfavorable factor. In addition, the DNA concentration also has a remarkable influence on the interaction.

Heerklotz H. and Seelig J. (2000) Correlation of membrane/water partition coefficients of detergents with the critical micelle concentration. *Biophys J* **78**, 2435-2440.

Abstract: The membrane/water partition coefficients, K , of 15 electrically neutral (non-charged or zwitterionic) detergents were measured with phospholipid vesicles by using isothermal titration calorimetry, and were compared to the corresponding critical micellar concentrations, cmc . The detergents measured were oligo(ethylene oxide) alkyl ethers (C(m)EO(n) with $m = 10/n = 3, 7$ and $m = 12/n = 3.8$); alkylglucosides (octyl, decyl); alkylmaltosides (octyl, decyl, dodecyl); diheptanoylphosphatidylcholine; Tritons (X-100, X-114) and CHAPS. A linear relation between the free energies of partitioning into the membrane and micelle formation was found such that $K \cdot \text{CMC}$ approximately 1. The identity $K \cdot \text{CMC} = 1$ was used to classify detergents with respect to their membrane disruption potency. "Strong" detergents are

characterized by K . $CMC < 1$ and solubilize lipid membranes at detergent-to-lipid ratios $X(b) < 1$ (alkylmaltosides, tritons, heptaethylene glycol alkyl ethers). "Weak" detergents are characterized by K . $CMC > 1$ and accumulate in the membrane- to detergent-to-lipid ratios $X(b) > 1$ before the bilayer disintegrates (alkylglucosides, pentaethylene glycol dodecyl ether).

Heerklotz H. and Seelig J. (2000) Titration calorimetry of surfactant-membrane partitioning and membrane solubilization. *Biochim Biophys Acta* **1508**, 69-85.

Abstract: The interaction of surfactants with membranes has been difficult to monitor since most detergents are small organic molecules without spectroscopic markers. The development of high sensitivity isothermal titration calorimetry (ITC) has changed this situation distinctly. The insertion of a detergent into the bilayer membrane is generally accompanied by a consumption or release of heat which can be measured fast and reliably with modern titration calorimeters. It is possible to determine the full set of thermodynamic parameters, i.e., the partitioning enthalpy, the partitioning isotherm, the partition coefficient, the free energy, and the entropy of transfer. The application of ITC to the following problems is described: (i) measurement of the critical micellar concentration (CMC) of pure detergent solutions; (ii) analysis of surfactant-membrane partitioning equilibria, including asymmetric insertion; and (iii) membrane-surfactant phase diagrams. Finally, the thermodynamic parameters derived for non-ionic detergents are discussed and the affinity for micelle formation is compared with membrane incorporation.

Heerklotz H. and Seelig J. (2001) Detergent-like action of the antibiotic peptide surfactin on lipid membranes. *Biophys J* **81**, 1547-1554.

Abstract: Surfactin is a bacterial lipopeptide with powerful surfactant-like properties. High-sensitivity isothermal titration calorimetry was used to study the self association and membrane partitioning of surfactin. The critical micellar concentration (CMC), was 7.5 μ M, the heat of micellization was endothermic with $\Delta H(w \rightarrow m)(Su) = +4.0$ kcal/mol, and the free energy of micellization $\Delta G(O, w \rightarrow m)(Su) = -9.3$ kcal/mol (25 degrees C; 100 mM NaCl; 10 mM TRIS, 1 mM EDTA; pH 8.5). The specific heat capacity of micellization was deduced from temperature dependence of $\Delta H(w \rightarrow m)(Su)$ as $\Delta C(w \rightarrow m)(P) = -250 \pm 10$ cal/(mol.K). The data can be explained by combining the hydrophobicity of the fatty acyl chain with that of the hydrophobic amino acids. The membrane partition equilibrium was studied using small (30 nm) and large (100 nm) unilamellar POPC vesicles. At 25 degrees C, the partition coefficient, K , was $(2.2 \pm 0.2) \times 10^4 M^{-1}$ for large vesicles leading to a free energy of $\Delta G(O, w \rightarrow b)(Su) = -8.3$ kcal/mol. The partition enthalpy was again endothermic, with $\Delta H(w \rightarrow b)(Su) = 9 \pm 1$ kcal/mol. The strong preference of surfactin for micelle formation over membrane insertion explains the high membrane-destabilizing activity of the peptide. For surfactin and a variety of non-ionic detergents, the surfactant-to-lipid ratio, inducing membrane solubilization, $R(sat)(b)$, can be predicted by the simple relationship $R(sat)(b)$ approximately $K \cdot CMC$.

Hildebrand A., Beyer K., Neubert R., Garidel P., and Blume A. (2004) Solubilization of negatively charged DPPC/DPPG liposomes by bile salts. *J Colloid Interface Sci* **279**, 559-571.

Abstract: The interactions of the bile salts sodium cholate (NaC) and sodium deoxycholate (NaDC) in 0.1 M NaCl (pH 7.4) with membranes composed of 1,2-dipalmitoyl-sn-glycero-3-phosphatidylcholine (DPPC), 1,2-dipalmitoyl-sn-glycero-3-phosphatidylglycerol (DPPG) and mixtures of DPPC and DPPG at molar ratios of 3:1 and 1:1 were studied by means of high-sensitivity isothermal titration calorimetry (ITC), dynamic light scattering (DLS), and differential scanning calorimetry (DSC). The partition coefficients and the transfer enthalpies for the incorporation of bile salt molecules into the phospholipid membranes were determined by ITC. The vesicle-to-micelle transition was investigated by ITC, DLS, and DSC. The phase boundaries for the saturation of the vesicles and their complete solubilization established by ITC were in general agreement with DLS data, but systematic differences could be seen due to the difference in detected physical quantities. Electrostatic repulsion effects between the negatively charged bile salt molecules and the negatively charged membrane surfaces are not limiting factors for the vesicle-to-micelle transition. The membrane packing constraints of the phospholipid molecules and the associated spontaneous curvature of the vesicles play the dominant role. DPPG vesicles are transformed by the bile salts into mixed micelles more easily or similarly compared to DPPC vesicles. The saturation of mixed DPPC/DPPG vesicles requires less bile salt, but to induce the solubilization of the liposomes, significantly higher amounts of bile salt are needed compared to the concentrations required for the solubilization of the pure phospholipid

systems. The different solubilization behavior of DPPC/DPPG liposomes compared to the pure liposomes could be due to a specific "extraction" of DPPG into the mixed micelles in the coexistence region.

Huang X., Han Y., Wang Y. and Wang Y. (2007) Aggregation behavior of nitrophenoxy-tailed quaternary ammonium surfactants. *J Phys. Chem B* **111**, 12439-12446.

Abstract: Cationic surfactants N,N,N-trimethyl-10-(4-nitrophenoxy)decylammonium bromide (N10TAB) and N,N,N',N'-tetramethyl-N,N'-bis[10-(4-nitrophenoxy)decyl]-1,6-hexanediammonium dibromide (N10-6-10N), bearing aromatic nitrophenoxy groups in the ends of their hydrophobic chains, have been synthesized, and their self-assembling properties in aqueous solutions have been studied by conductivity, isothermal titration microcalorimetry, ¹H NMR spectroscopy, and dynamic light scattering. Below the critical micelle concentration, N10-6-10N can form premicelles with 2 or 3 surfactant molecules. Beyond the critical micelle concentration, the two surfactants have strong self-aggregation ability and can form micelles of rather small size and with small aggregation numbers *N*, which are 30 ± 3 for N10TAB and 20 ± 2 for N10-6-10N, respectively. Also, the variations in ¹H NMR signals at different surfactant concentrations provide the information on the environmental change of the surfactants upon their micellization progress. The most prominent phenomenon is the shielding effect of the aromatic groups over the protons in the aliphatic chains, implying that the nitrophenoxy groups partially insert into the micelles and face the several middle methylenes of the hydrophobic side chains.

Jiang L., Wang K., Deng M., Wang Y. and Huang J. (2008) Bile salt-induced vesicle-to-micelle transition in cationic surfactant systems: steric and electrostatic interactions. *Langmuir* **24**, 4600-4606.

Abstract: The vesicle-to-micelle transition (VMT) was realized in cationic surfactant systems by the addition of two kinds of bile salts, sodium cholate (SC) and sodium deoxycholate (SDC). It was found that steric interaction between the bile salt and cationic surfactant plays an important role in cationic surfactant systems that are usually thought to be dominated by electrostatic interaction. The facial amphiphilic structure and large occupied area of the bile salt are crucial to the enlargement of the average surfactant headgroup area and result in the VMT. Moreover, bile salts can also induce a macroscopic phase transition. Freeze-fracture transmission electron microscopy, dynamic light scattering, isothermal titration calorimetry, and absorbance measurements were used to follow the VMT process

Kresheck G. C. (2006) The temperature dependence of the heat capacity change for micellization of nonionic surfactants. *J Colloid Interface Sci* **298**, 432-440.

Abstract: The thermodynamic parameters that govern micelle formation by four different nonionic surfactants were investigated by ITC and DSC. These included n-dodecyldimethylphosphine oxide (APO12), Triton X-100 (TX-100), n-octyltetraoxyethylene (C8E4), and N,N-dimethyloctylamine-N-oxide (DAO8). All of these surfactants had been previously investigated by solution calorimetry over smaller temperature ranges with conflicting conclusions as to the temperature dependence of the heat capacity change, ΔC_p , for the process. The temperature coefficient of the heat capacity change, *B* (cal/mol K²), was derived from the enthalpy data that were obtained at small intervals over a broad temperature range. The values obtained for each of the surfactants at 298.2 K for ΔC_p and *B* were -155 ± 2 and 0.50 ± 0.36 (APO12), -97 ± 3 and -0.24 ± 0.18 (TX-100), -105 ± 2 and 1.0 ± 0.3 (C8E4), and -82 ± 1 and 0.36 ± 0.04 (DAO8), cal/mol K and cal/mol K², respectively. The resulting *B*-values did not correlate with the cmc, aggregation number, or structure of the monomer in an obvious way, but they were found to reflect the relative changes in hydration of the polar and nonpolar portions of the surfactant molecule as the micelles are formed. An analysis of the data obtained from DSC scans was used to describe the temperature dependence of the critical micelle concentration, cmc. An abrupt increase in heat capacity was observed for TX-100 and C8E4 solutions of 36.5 ± 0.5 and 21 ± 5 cal/mol K, respectively, as the temperature of the scan passed through the cloud point. This change in heat capacity may reflect the increased monomer concentration of the solutions that accompanies phase separation, although other interpretations of this jump are possible.

Lah J., Bester-Roga C. M., Perger T. M., and Vesnaver G. (2006) Energetics in correlation with structural features: the case of micellization. *J Phys Chem B Condens Matter Mater Surf Interfaces Biophys* **110**, 23279-23291.

Abstract: Understanding micellization processes at the molecular level has direct relevance for biological self-assembly, folding, and association processes. As such, it requires complete characterization of the

micellization thermodynamics, including its correlation with the corresponding structural features. In this context, micellization of a series of model non-ionic surfactants (poly(ethylene glycol) monoethyl ethers, C(8)E(γ)) was studied by isothermal titration calorimetry (ITC) and differential scanning calorimetry (DSC). The corresponding structural properties of C(8)E(γ) micelles were investigated by small-angle X-ray scattering (SAXS). The C(8)E(γ) micellization, characterized independently from ITC, DSC, and structural data, reveals that $\Delta H(M)(o) > 0$, $\Delta S(M)(o) > 0$, and $\Delta C(P)(M)(o) < 0$, while the dissection of its energetics shows that it is primarily governed by the transfer of 20-30 C(8) alkyl chains from aqueous solution into the nonpolar core (r approximately 1.3 nm) of the spherical micelle. Moreover, thermodynamic parameters of micellization, estimated from the structural features related to the changes in solvent-accessible surface areas upon micellization, are in a good agreement with the corresponding parameters obtained from the analysis of ITC and DSC data. We have shown that the contributions to $\Delta S(M)(o)$ other than from hydration ($\Delta S(M)(other)(o)$), estimated from experimental data, appear to be small ($\Delta S(M)(other)(o) < 0.1 \Delta S(M)(other)(o)$) and agree well with the theoretical estimates expressed as a sum of the corresponding translational, conformational, and size contributions. These $\Delta S(M)(other)(o)$ contributions are much less unfavorable than those estimated for a rigid-body association, which indicates the dynamic nature of the C(8)E(γ) micellar aggregates. the dynamic nature of the C8EY micellar aggregates.

Lasch J. and Hildebrand A. (2002) Isothermic titration calorimetry to study CMCs of neutral surfactants and of the liposome-forming bolaamphiphile dequalinium. *J Liposome Res* **12**, 51-56.

Abstract: Isothermic titration calorimetry was used to measure the heat of micelle formation (molar enthalpy of transfer of surfactants monomers from water into micellar aggregates. The problems associated with the estimation of the CMC and the whole thermodynamic profile of micellization of surfactants via Gibbs-Helmholtz-Equation are discussed. CMC's of octylthioglucoside and the peculiar bolaamphiphile dequalinium which concentrates in mitochondria are measured. In contrast to earlier reports, no CMC of dequalinium could be found inspite of extensive systematic measurements.

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 $C(p) \geq 0.05\%$ 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.

Li X., Wettig S. D., Wang C., Foldvari M., and Verrall R. E. (2005) Synthesis and solution properties of gemini surfactants containing oleyl chains. *Phys Chem Chem Phys* **7**, 3172-3178.

Abstract: Gemini surfactants 18:1- s -18:1, where $s = 2, 3,$ and 6 methylene groups and 18:1 refers to oleyl carbon chains, have been synthesized, characterized and a number of micelle solution properties measured

by using electrical conductance, fluorescence probe emission, light scattering (DLS), surface tension and isothermal titration calorimetry (ITC) methods at 25 degrees C. The cmc values of 18:1-2-18:1, 18:1-3-18:1, and 18:1-6-18:1 were found to be 26.9, 23.4, and 18.0 microM, respectively, using the electrical conductance method. Surface tension results suggest that in 0.01 N NaCl solutions, the s = 2 and 3 members of the series form multilayer rather than monolayer structures, while the s = 6 homologue adopts a close-packed arrangement. This is consistent with DLS and EM measurements which show vesicle formation for the s = 2 and 3 compounds, and micelle formation for the s = 6 compound. The enthalpies of micellization (ΔH degrees (M)) are more exothermic for the 18:1-s-18:1 series of surfactants, than for the 12-s-12 series. The differences are rationalized in terms of steric and configurational contributions to ΔH degrees (M) arising from difficulties associated with packing of the bulky cis-9-octadecene tails.

Li Y., Li P., Wang J., Wang Y., Yan H., and Thomas R. K. (2005) Odd/Even effect in the chain length on the enthalpy of micellization of gemini surfactants in aqueous solution. *Langmuir* **21**, 6703-6706.

Abstract: The micellization properties of cationic symmetric gemini surfactants, $[\text{C}_m\text{H}(2m+1)(\text{CH}_3)_2\text{N}(\text{CH}_2)_6\text{N}(\text{CH}_3)_2\text{C}_m\text{H}(2m+1)]\text{Br}_2$ (designated as $\text{C}_m\text{C}_6\text{C}_m\text{Br}_2$, with $m = 7, 8, 9, 10, 11, 12,$ and 16), has been investigated by isothermal titration microcalorimetry. The critical micelle concentration (CMC) and enthalpy of micellization (ΔH_{mic}) were determined from calorimetric titration curves. The linear decreasing of $\log \text{CMC}$ with increasing the length of the hydrophobic chain is consistent with an increase in the hydrophobicity of the alkyl chain. Interestingly, with increasing the length of the alkyl chain, the ΔH_{mic} values of the surfactants with even numbered alkyl chains vary from endothermic to exothermic, whereas the ΔH_{mic} values of the surfactants with odd numbered alkyl chains are all endothermic and tend to become more endothermic. The pronounced even/odd effect in ΔH_{mic} is discussed with respect to the "donor-acceptor" interaction.

Li Y., Li P., Wang J., Wang Y., Yan H., Dong C., and Thomas R. K. (2005) Thermodynamics of micellization for partially fluorinated cationic gemini surfactants and related single-chain surfactants in aqueous solution. *J Colloid Interface Sci* **287**, 333-337.

Abstract: A series of partially fluorinated cationic gemini surfactants and their corresponding monomeric surfactants have been studied by isothermal titration microcalorimetry. The critical micelle concentration (CMC) and enthalpy of micellization (ΔH_{mic}) were obtained from calorimetric curves. The CMCs of the gemini surfactants are much lower than those of the corresponding monomeric surfactants and decrease with an increase in the number of fluorine atoms on the hydrophobic chain. The micellization of partially fluorinated cationic gemini surfactants is much more exothermic than that of the corresponding monomeric surfactants. Because of the incompatibility of hydrocarbon spacer and partially fluorinated chain, ΔH_{mic} values of the surfactants with a C(6) spacer are more negative than those of the surfactants with a C(12) spacer. The variations in the architecture of the fluorocarbon chain segments may be the reason of the irregularities in the change of ΔH_{mic} for the gemini surfactants. Moreover, the contribution of the enthalpy generally increases with an increase in the number of fluorine atoms.

Li Y., Li P., Dong C., Wang X., Wang Y., Yan H., and Thomas R. K. (2006) Aggregation properties of cationic gemini surfactants with partially fluorinated spacers in aqueous solution. *Langmuir* **22**, 42-45.

Abstract: The aggregation properties of cationic gemini surfactants alkanediyl- α,ω -bis(dodecyldimethylammonium bromide), $[\text{C}(12)\text{H}(25)(\text{CH}_3)_2\text{N}(\text{CH}_2)_m(\text{CF}_2)_n(\text{CH}_2)_m\text{N}(\text{CH}_3)_2\text{C}(12)\text{H}(25)]\text{Br}_2$ [where $2m + n = 12$ and $n = 0, 4,$ and 6 ; designated as 12-12-12, 12-12(C(4)(F))-12, and 12-12(C(6)(F))-12, respectively] have been studied by microcalorimetry, time-resolved fluorescence quenching, and electrical conductivity. Compared with a fully hydrocarbon spacer of 12-12-12, the fluorinated spacer with a lower ratio of CF_2 to CH_2 in 12-12(C(4)(F))-12 tends to disfavor the aggregation, leading to larger critical micelle concentration (cmc), lower micelle aggregation number (N), and less negative Gibbs free energy of micellization (ΔG_{mic}). However, the fluorinated spacer with a higher ratio of CF_2 to CH_2 in 12-12(C(6)(F))-12 may prompt the aggregation, resulting in lower cmc, higher N, and more negative ΔG_{mic} . It is also noted that enthalpy change of micellization (ΔH_{mic}) for 12-12(C(4)(F))-12 is the most exothermic, but the values of ΔH_{mic} for 12-12-12 and 12-12(C(6)(F))-12 are almost the same. These results are rationalized in terms of competition among the enhanced hydrophobicity and the rigidity of the fluorinated spacer, and the variation of immiscibility of the fluorinated spacer with the hydrocarbon side chains.

Li Y., Cao M., and Wang Y. (2006) Alzheimer amyloid beta(1-40) peptide: interactions with cationic gemini and single-chain surfactants. *J Phys Chem B Condens Matter Mater Surf Interfaces Biophys* **110**, 18040-18045.

Abstract: The aggregation of amyloid beta-peptide [Abeta(1-40)] into fibril is a key pathological process associated with Alzheimer's disease. The effect of cationic gemini surfactant hexamethylene-1,6-bis-(dodecyldimethylammonium bromide) [C(12)H(25)(CH(3))(2)N(CH(2))(6)N(CH(3))(2)C(12)H(25)]Br(2) (designated as C(12)C(6)C(12)Br(2)) and single-chain cationic surfactant dodecyltrimethylammonium bromide (DTAB) on the Alzheimer amyloid beta-peptide Abeta(1-40) aggregation behavior was studied by microcalorimetry, circular dichroism (CD), and atomic force microscopy (AFM) measurements at pH 7.4. Without addition of surfactant, 0.5 g/L Abeta(1-40) mainly exists in dimeric state. It is found that the addition of the monomers of C(12)C(6)C(12)Br(2) and DTAB may cause the rapid aggregation of Abeta(1-40) and the fibrillar structures are observed by CD spectra and the AFM images. Due to the repulsive interaction among the head groups of surfactants and the formation of a small hydrophobic cluster of surfactant molecules, the fibrillar structure is disrupted again as the surfactant monomer concentration is increased, whereas globular species are observed in the presence of micellar solution. Different from single-chain surfactant, C(12)C(6)C(12)Br(2) has a much stronger interaction with Abeta(1-40) to generate larger endothermic energy at much lower surfactant concentration and has much stronger ability to induce the aggregation of Abeta(1-40).

Li Y., Wang X., and Wang Y. (2006) Comparative studies on interactions of bovine serum albumin with cationic gemini and single-chain surfactants. *J Phys Chem B Condens Matter Mater Surf Interfaces Biophys* **110**, 8499-8505.

Abstract: The interactions of bovine serum albumin (BSA) with cationic gemini surfactants alkanediyl-alpha,omega-bis(dodecyldimethylammonium bromide) [C12H25(CH3)2N(CH2)(S)N(CH3)2C12H25]Br2 (designated as C12C(S)C12Br2, S = 3, 6, and 12) and single-chain surfactant dodecyltrimethylammonium bromide (DTAB) have been studied with isothermal titration microcalorimetry, turbidity, fluorescence spectroscopy, and circular dichroism at pH 7.0. Comparing with DTAB, C12C(S)C12Br2 have much stronger binding ability with BSA to induce the denaturation of BSA at very low molar ratio of C12C(S)C12Br2/BSA, and C12C(S)C12Br2 have a much stronger tendency to form insoluble complexes with BSA. The binding of C12C(S)C12Br2 to BSA generates larger endothermic peaks. The first endothermic peak is much stronger than that of the second endothermic peak. The double charges and strong hydrophobicity of the gemini surfactants are the main reasons for these observations. In addition, the spectra results show that the binding of DTAB to BSA only promotes BSA unfolding and aggregation, whereas the secondary structure of BSA is possibly stabilized by a small amount of C12C(S)C12Br2, even if the small amount of binding C12C(S)C12Br2 could induce the loss of the tertiary structure of BSA. This result may be related to the double tails of gemini surfactants, which may generate the hydrophobic linkages between the nonpolar residues of BSA.

Malmquist N. A., Baldwin J. and Phillips M. A. (2007) Detergent-dependent kinetics of truncated Plasmodium falciparum dihydroorotate dehydrogenase. *J Biol Chem* **282**, 12678-12686.

Abstract: The survival of the malaria parasite Plasmodium falciparum is dependent upon the de novo biosynthesis of pyrimidines. P. falciparum dihydroorotate dehydrogenase (PfDHODH) catalyzes the fourth step in this pathway in an FMN-dependent reaction. The full-length enzyme is associated with the inner mitochondrial membrane, where ubiquinone (CoQ) serves as the terminal electron acceptor. The lipophilic nature of the co-substrate suggests that electron transfer to CoQ occurs at the two-dimensional lipid-solution interface. Here we show that PfDHODH associates with liposomes even in the absence of the N-terminal transmembrane-spanning domain. The association of a series of ubiquinone substrates with detergent micelles was studied by isothermal titration calorimetry, and the data reveal that CoQ analogs with long decyl (CoQ(D)) or geranyl (CoQ(2)) tails partition into detergent micelles, whereas that with a short prenyl tail (CoQ(1)) remains in solution. PfDHODH-catalyzed reduction of CoQ(D) and CoQ(2), but not CoQ(1), is stimulated as detergent concentrations (Tween 80 or Triton X-100) are increased up to their critical micelle concentrations, beyond which activity declines. Steady-state kinetic data acquired for the reaction with CoQ(D) and CoQ(2) in substrate-detergent mixed micelles fit well to a surface dilution kinetic model. In contrast, the data for CoQ(1) as a substrate were well described by solution steady-state kinetics. Our results suggest that the partitioning of lipophilic ubiquinone analogues into detergent micelles needs to be an important consideration in the kinetic analysis of enzymes that utilize these substrates.

Mitra D., Bhattacharya S. C. and Moulik S. P. (2008) Physicochemical studies on the interaction of gelatin with cationic surfactants alkyltrimethylammonium Bromides (ATABs) with special focus on the behavior of the hexadecyl homologue. *J Phys. Chem B* **112**, 6609-6619.

Abstract: The interaction of a denatured interfacially active protein, gelatin (G) (at pH 9, above its isoelectric pH 4.84, and ionic strength $\mu=0.005$), with a cationic amphiphile, hexadecyl (or cetyl) trimethylammonium bromide, CTAB, has been elaborately studied using a variety of techniques. Two types of protein-surfactant complexes at a concentration below the normal critical micellar concentration (cmc) were formed in solution. The first, G-CTAB (monomer) combined complex (GS(n)(I)) adsorbed at the air/solution interface, followed by its gradual transformation to the poor interfacially active second G-CTAB (aggregate) complex (GS(m)(B)) at a critical aggregation concentration (cac) of the interacting oppositely charged surfactant. In the higher concentration range, upon completion of GS(m)(B) formation, coacervation (association of GS(m)(B)) led to add turbidity. With increasing addition of CTAB, the coacervates became disintegrated and ultimately remained dissolved in the free micellar solution of CTAB. The above features were studied using the techniques of tensiometry, conductometry, turbidimetry, fluorimetry, and microcalorimetry. The interaction features were prominent at $[G] \geq 0.05$ g %, and several of these were either marginal or absent at $[G] < 0.05$ g %. The denatured protein was found to form viscous as well as gel-forming consistencies at higher $[G]$ and at lower temperature. A temperature variation study on the interaction of G with CTAB has revealed that enhanced interaction takes place at higher temperature. The effect of $[G]$ on its interaction with cationic surfactants of varying chain length in the alkyltrimethylammonium bromide (ATAB) series has been also studied; a similar interactional profile as that of CTAB has been exhibited by octadecyltrimethylammonium bromide; however, the lower homologues (dodecyl- and tetradecyl-) of ATAB have offered different profiles. It has been found that the ATABs with higher alkyl chain lengths were more interactive with negatively charged G than their lower homologues. Quantification of the results in terms of different transition points, counterion binding of the protein-bound surfactant aggregates and free micelles, the enthalpy of binding interactions and energetics of ATAB micellization, and so forth have been studied. The results have been rationalized in terms of an interaction model

Opatowski E., Lichtenberg D., and Kozlov M. M. (1997) The heat of transfer of lipid and surfactant from vesicles into micelles in mixtures of phospholipid and surfactant. *Biophys J* **73**, 1458-1467.

Abstract: We study the heat associated with the transformation of vesicles into micelles in mixtures of bilayer-forming phospholipids and micelle-forming surfactants. We subdivide the total heat evolution $\Delta Q(\text{coex})$ within the range of coexistence of vesicles and micelles into three contributions related to the transition of $dN(D)m-b$ molecules of surfactant and $dN(L)m-b$ molecules of lipid from micelles to vesicles and to the extraction of $dN(D)m-w$ molecules of surfactant from micelles to the aqueous solution, so that $\Delta Q(\text{coex}) = \Delta H(D)m-w \times dN(D)m-w + \Delta H(D)m-b \times dN(D)m-b + \Delta H(L)m-b \times dN(L)m-b$ where $\Delta H(D)m-w$, $\Delta H(L)m-b$, and $\Delta H(D)m-b$ are the respective molar "transfer" enthalpies. We design a method for the evaluation of all three molar enthalpies, from isothermal calorimetric titrations conducted according to two different protocols of titration of lipid-surfactant mixtures. In the first protocol the mixture is titrated with an aqueous solution of pure lipid vesicles, and in the second the mixture is titrated with an aqueous solution of pure surfactant. Titration of the mixed systems by a buffer solution serves to verify the results obtained under these protocols. In addition to the values of molar enthalpies, our method yields the cmc value of the pure surfactant. We apply our method to investigating the heat evolution in mixtures of egg yolk phosphatidylcholine and the nonionic surfactant octylglucoside in a phosphate-buffered saline solution at 28 degrees C. These studies gave the following values: $\Delta H(D)m-w = -1732$ cal/mol, $\Delta H(L)m-b = -592$ cal/mol, $\Delta H(D)m-b = 645$ cal/mol, and $\text{cmc} = 23.5$ mM. We discuss the possible physical insight of these values and the perspectives of applications of the proposed method.

Otzen D. E., Sehgal P. and Westh P. (2009) alpha-Lactalbumin is unfolded by all classes of surfactants but by different mechanisms. *J Colloid Interface Sci* **329**, 273-283.

Abstract: We show that all four classes of surfactants (anionic, cationic, non-ionic, and zwitterionic) denature alpha-lactalbumin (alphaLA), making alphaLA an excellent model system to compare their denaturation mechanisms. This involves at least two steps in all surfactants but is more complex in charged surfactants due to their strong binding properties. At very low concentrations, charged surfactants bind specifically as monomers, but the first denaturation process only sets in when 4-10 surfactant molecules are bound to form clusters on the protein surface and is followed by a second loss of structure as 20-25

surfactant molecules are bound. Sub-micellar interactions can be modeled as simple independent binding at multiple sites which does not achieve saturation before micelle formation sets in. In contrast, no specific sub-micellar surfactant binding is detected by calorimetry in the presence of zwitterionic and non-ionic surfactants, and denaturation only occurs around the cmc. Unfolding rates are very rapid in charged surfactants and reach a similar plateau level around the cmc, indicating that monomers and micelles operate on a mutually exclusive basis. In contrast, unfolding occurs slowly in zwitterionic and non-ionic surfactants and the rate increases with the cmc, suggesting that monomers cooperate with micelles in denaturation

Pahi A. B., Kiraly Z., Mastalir A., Dudas J., Puskas S. and Vago A. (2008) Thermodynamics of Micelle Formation of the Counterion Coupled Gemini Surfactant Bis(4-(2-dodecyl)benzenesulfonate)-Jeffamine Salt and Its Dynamic Adsorption on Sandstone. *J Phys. Chem B*. (epublication)

Abstract: A novel counterion-coupled gemini (cocogem) surfactant, DBSJ, was synthesized via the 2:1 coupling reaction between 4-(2-dodecyl)benzenesulfonic acid (Lutensit A-LBS) and polypropyleneglycol-bis(2-aminopropyl) ether (Jeffamine D230). The surfactant had a polydispersity index of $M_w/M_n = 1.04$, as determined by electrospray-ionization mass spectrometry. The micellar properties of DBSJ in water were investigated in the temperature range 283-348 K by conductometry and titration microcalorimetry. The critical micelle concentration (cmc) of the cocogem was found to be more than 1 order of magnitude less than that of monomeric sodium 4-(2-dodecyl)benzenesulfonate (SDBS). The mean degree of dissociation in the temperature range studied proved to be $\alpha = 0.39$. The calorimetric enthalpies of micelle formation agreed well with the enthalpies calculated via the van't Hoff relation. The cmc versus T curve passes through a minimum just below room temperature, after which the micelle formation changes from endothermic to exothermic. The Gibbs free energy of micelle formation was nearly constant as the temperature was increased, due to enthalpy/entropy compensation. The isotherm for DBSJ adsorption from aqueous solution onto sandstone was determined by continuous flow frontal analysis solid/liquid chromatography at 298 K and 60 bar. The adsorption of DBSJ on sandstone followed an S-type isotherm. Surface aggregation occurred over an extended range of concentration. Surface saturation was reached at a solution concentration more than 1 order of magnitude less than for monomeric SDBS. This finding is a point of concern in the chemical flooding of oil reservoir rocks to enhance oil recovery

Panyukov Y. V., Nemykh M. A., Dobrov E. N. and Drachev V. A. (2008) Surfactant-induced amorphous aggregation of tobacco mosaic virus coat protein: a physical methods approach. *Macromol. Biosci.* **8**, 199-209.

Abstract: The interactions of non-ionic surfactant Triton X-100 and the coat protein of tobacco mosaic virus, which is an established model for both ordered and non-ordered protein aggregation, were studied using turbidimetry, differential scanning calorimetry, isothermal titration calorimetry, and dynamic light scattering. It was found that at the critical aggregation concentration (equal to critical micelle concentration) of 138×10^{-6} M, Triton X-100 induces partial denaturation of tobacco mosaic virus coat protein molecules followed by protein amorphous aggregation. Protein aggregation has profound ionic strength dependence and proceeds due to hydrophobic sticking of surfactant-protein complexes (start aggregates) with initial radii of 46 nm. It has been suggested that the anionic surfactant sodium dodecyl sulfate forms mixed micelles with Triton X-100 and therefore reverses protein amorphous aggregation with release of protein molecules from the amorphous aggregates. A stoichiometric ratio of 5 was found for Triton X-100-sodium dodecyl sulfate interactions

Portnaya I., Cogan U., Livney Y. D., Ramon O., Shimoni K., Rosenberg M., and Danino D. (2006) Micellization of bovine beta-casein studied by isothermal titration microcalorimetry and cryogenic transmission electron microscopy. *J Agric Food Chem* **54**, 5555-5561.

Abstract: The association behavior, critical micellization concentration (CMC), and enthalpy of demicellization (ΔH_{demic}) of bovine beta-casein were studied, for the first time by isothermal titration calorimetry, in a pH 7.0 phosphate buffer with 0.1 ionic strength and in pure water. In the buffer solutions, the CMC decreased asymptotically from 0.15 to 0.006 mM as the temperature was raised from 16 to 45 degrees C. ΔH_{demic} decreased with increasing temperature between 16 and 28 degrees C but increased from 28 to 45 degrees C. Thermodynamic analysis below 30 degrees C is consistent with the Kegeles shell model, which suggests a stepwise association process. At higher temperatures, this model exhibits limitations, and the micellization becomes much more cooperative. The CMC values in water, measured between 17 and 28 degrees C, decreased with increasing temperature and, expectedly, were higher than

those found in the buffer solutions. beta-Casein micelles were visualized and characterized, for the first time in their hydrated state, using advanced digital-imaging cryogenic transmission electron microscopy. The images revealed small, oblate micelles, about approximately 13 nm in diameter. The micelles shape and dimensions remained nearly constant in the temperature range of 24-35 degrees C.

Prasad M., Moulik S. P., and Palepu R. (2005) Self-aggregation of binary mixtures of alkyltriphenylphosphonium bromides: a critical assessment in favor of more than one kind of micelle formation. *J Colloid Interface Sci* **284**, 658-666.

Abstract: The micellization behavior of binary combinations of alkyltriphenylphosphonium bromides (ATPBs) with alkyl chain carbons 10, 12, 14, and 16 has been studied by conductometry and calorimetry. The combinations C(10)-C(12), C(10)-C(14), C(10)-C(16), C(12)-C(14), C(12)-C(16), and C(14)-C(16) were found to form two cmc's by both the methods, with good agreement, except C(14)-C(16)TPB, which has evidenced only a single cmc by calorimetry for all combinations. The combinations C(10)-C(12) (for both cmc(1) and cmc(2)) and C(10)-C(14)TPB (for cmc(2)) formed ideal mixtures, whereas the rest were nonideal. In the nonideal binary mixtures, the ATPB components showed antagonistic interaction with each other. The cmc, interaction parameter (beta), mixed micellar composition, extent of counterion binding, and thermodynamic parameters for the micellization process have been reported and discussed. The enthalpy of mixed micelle formation has been found to have a fair correlation with a Clint-type relation applicable to ideal binary mixtures of surfactants.

Prasad M., Chakraborty I., Rakshit A. K., and Moulik S. P. (2006) Critical evaluation of micellization behavior of nonionic surfactant MEGA 10 in comparison with ionic surfactant tetradecyltriphenylphosphonium bromide studied by microcalorimetric method in aqueous medium. *J Phys Chem B Condens Matter Mater Surf Interfaces Biophys* **110**, 9815-9821.

Abstract: The micellization behavior of MEGA 10 has been studied at nine different temperatures by isothermal titration calorimetry (ITC), and thermodynamics of the process have been evaluated and examined in detail. The aggregation number of the nonionic surfactant has been estimated from the ITC results by a simulation procedure based on the mass action principle of micellization of the surfactant. The cmc of MEGA 10 has shown a minimum in temperature dependence as observed for ionic surfactants. For a comparison, the cmc and related thermodynamic parameters of an ionic surfactant, tetradecyltriphenylphosphonium bromide (C(14)TPB) studied at several temperatures in aqueous medium has been considered. The contributions of the headgroups of both the surfactants to the free energies of their respective micellization have been deciphered and presented.

Ray G. B., Chakraborty I., Ghosh S., Moulik S. P., Holgate C., Glenn K. and Palepu R. M. (2007) Studies on binary and ternary amphiphile combinations of tetradecyltrimethylammonium bromide (C14TAB), tetradecyltriphenylphosphonium bromide (C14TPB), and tetradecylpyridinium bromide (C14PB). A critical analysis of their interfacial and bulk behaviors. *J Phys. Chem B* **111**, 9828-9837.

Abstract: Mixed surfactants play a promising role in surface chemical applications. In this study, interfacial and bulk behaviors of binary and ternary combinations of tetradecyltrimethylammonium bromide (C(14)TAB), tetradecyltriphenylphosphonium bromide (C(14)TPB), and tetradecylpyridinium bromide (C(14)PB) have been examined in detail using the methods of tensiometry, conductometry, fluorimetry, and microcalorimetry. The state of micellar aggregation, amphiphile composition in the micelle, extent of counterion binding by the micelle, and interaction among the surfactant monomers in the binary and ternary combinations have been quantitatively assessed in the light of the regular solution theories of Rubingh and that of Rubingh and Holland. The monomer packing in the micelles and their expected shapes have also been estimated from topological considerations. Conceptual rationalization of results has been presented together with associated energetics of the interfacial adsorption and self-aggregation in the bulk.

Rozycka-Roszak B., Zylka R., and Sarapuk J. (2001) Micellization process--temperature influence on the counterion effect. *Z Naturforsch [C]* **56**, 154-157.

Abstract: The micellization process of dodecyltrimethylammonium chloride (DTAC) and bromide (DTAB) was studied at 313 K. Nuclear magnetic resonance and calorimetric methods were used. The calorimetric titration curves permitted determination of the critical micelle concentration (CMC) and enthalpy of the micellization process (ΔH_m) of the compounds studied. The results obtained were compared

to those obtained at 298 K. It was found that calorimetric curves obtained at 313 K for both compounds were similar to each other in contrast to 298 K. Especially a great difference in the shape of curves was observed for DTAC. NMR (^1H NMR and ^{13}C NMR) spectra were taken below and above the CMC values and chemical shifts (Δ) analysed as a function of concentration of the compounds. Comparison of chemical shift-concentration plots with those obtained from measurements performed at lower temperature showed that chemical shifts are of very similar character in both cases for analyzed groups. However, there are some quantitative differences that indicate at smaller difference in hydration of DTAB and DTAC micelles at elevated temperature. This may be the reason of decrease of differences between micellization processes of DTAC and DTAB compounds. The smaller hydration may be, in turn, the result of diminishing differences in physicochemical properties of bromide and chloride ions with temperature.

Samakande A., Chaghi R., Derrien G., Charnay C. and Hartmann P. C. (2008) Aqueous behaviour of cationic surfactants containing a cleavable group. *J Colloid Interface Sci* **320**, 315-320.

Abstract: The aggregation behaviour of two novel cationic RAFT agents (transfer surfactants); N,N-dimethyl-N-(4-(((phenylcarbonothioyl)thio)methyl)benzyl)ethan ammonium bromide (PCDBAB) and N-(4-(((dodecylthio)-carbonothioyl)thio)methyl)benzyl)-N,N-dimethylethana mmonium bromide (DCTBAB) in diluted solutions have been investigated by surface tension, conductimetry and microcalorimetry measurements. The thermodynamic parameters i.e. the critical micelle concentration (cmc), the degree of micelle ionization (α), the head group surface area (a_0), ΔH_{mic} , ΔG_{mic} and $T \Delta S_{\text{mic}}$ are reported at 303 K. The thermodynamic parameters have been compared to those of the conventional surfactant cetyltrimethylammonium bromide (CTAB) in order to specify structural relationships. The obtained results have been discussed considering the hydrophobic behaviour of the S-C=S- linkage and the specific interactions that arise from the introduction of the benzene ring into the hydrophobic part

Shimizu S., Pires P. A., and El Seoud O. A. (2004) Thermodynamics of micellization of benzyl(2-acylaminoethyl)dimethylammonium chloride surfactants in aqueous solutions: a conductivity and titration calorimetry study. *Langmuir* **20**, 9551-9559.

Abstract: The enthalpies of micellization of the surfactant series benzyl(2-acylaminoethyl)dimethylammonium chlorides, RABzMe_2Cl , have been determined by calorimetry and conductivity measurements in the temperature range 15-75 degrees C. Here R stands for an acyl group containing 10-16 carbon atoms and A, Bz, and Me stand for $\text{NH}(\text{CH}_2)_2\text{N}^+$, benzyl, and methyl groups, respectively. The enthalpy of micellization, ΔH_{mic} degrees, and the critical micelle concentration, cmc, were calculated directly from calorimetric data. The free energy of micellization, ΔG_{mic} degrees, was obtained from the cmc and the conductance-based degree of counterion dissociation. There is an excellent agreement between ΔG_{mic} degrees calculated from the data of both techniques, but the ΔH_{mic} degrees, the entropy of micellization, values differ. The dependence of the thermodynamic parameters of micellization on the chain length of the hydrophobic group and on the temperature has been analyzed by considering the delicate balance between the factors that contribute to micelle formation, including transfer of the surfactant hydrocarbon chain from the aqueous environment to the micelle, with concomitant release of the solvating water molecules, and the effect of temperature on the structure of water. ΔG_{mic} degrees is more negative, that is, more favorable for RABzMe_2Cl than for the structurally related alkylbenzyl dimethylammonium chlorides. This is attributed to direct and water-mediated H bonding between the amide groups of molecules of the former series.

Soderman O., Jonsson B., and Olofsson G. (2006) Titration of fatty acids solubilized in cationic and anionic micelles. Calorimetry and thermodynamic modeling. *J Phys Chem B Condens Matter Mater Surf Interfaces Biophys* **110**, 3288-3293.

Abstract: The electrostatic properties of charged surfactant micelles are investigated through titrations of fatty acid probes solubilized in the micelles. The titration process is followed by means of calorimetric measurements and by determining the pH values as a function of added base. This approach yields a complete thermodynamic description of the titration process. In particular, we find that the process is endothermic at 298 K. This is contrary to the titration of carboxylic acids in water, where ΔH is approximately 0. To identify the main effect underlying the difference in ΔH between titration in a micelle and water, a thermodynamic model has been developed which focuses on the transfer properties of charged and uncharged species from bulk water to the surface of a micelle and which incorporates a

dielectric discontinuity at the micellar surface. The model relies on the use of the Poisson-Boltzmann equation which is solved using a finite element method. Experimental results and the model calculations imply that the dielectric discontinuity at (or near) the micellar surface plays a major role and hence must be included when analyzing the titration behavior of an acid functionality at the surface of a charged micelle.

Stodghill S. P., Smith A. E., and O'haver J. H. (2004) Thermodynamics of Micellization and Adsorption of Three Alkyltrimethylammonium Bromides Using Isothermal Titration Calorimetry. *Langmuir* **20**, 11387-11392.

Abstract: Studies of the thermodynamic properties of micellization, as well as the enthalpy change of adsorption (displacement), were conducted using isothermal titration calorimetry (ITC). The cationic surfactants, dodecyltrimethylammonium bromide, tetradecyltrimethylammonium bromide, and hexadecyltrimethylammonium bromide or cetyltrimethylammonium bromide were used. Adsorption studies were performed utilizing HiSil 233 precipitated silica as the substrate. The thermodynamics of micellization were studied at 28, 30, and 35 degrees C using ITC. ΔH_{dil} was calculated and graphed versus concentration in order to determine ΔH_{mic} and critical micelle concentration. From these data, ΔG_{mic} and ΔS_{mic} were also determined and found to be in agreement with values previously determined using traditional temperature-variation methods. The thermodynamics of adsorption were also determined at the above temperatures using ITC. Using the results, the heat of displacement, Q_{disp} , and enthalpy of displacement, ΔH_{disp} , were calculated. A plot of ΔH_{disp} as a function of concentration was generated and used to interpret the mechanism of adsorption in the four regions of a typical cationic surfactant adsorption isotherm.

Suksai C., Figueiras G. S., Chhabra A., Liu J., Skepper J. N., Tuntulani T., and Otto S. (2006) Controlling the morphology of aggregates of an amphiphilic synthetic receptor through host-guest interactions. *Langmuir* **22**, 5994-5997.

Abstract: A new amphiphilic receptor containing a macrocyclic anionic headgroup and a single alkyl chain was prepared through an efficient templated synthesis. The interdependence of the aggregation behavior and the host-guest chemistry was studied. In the absence of any guest the terminus of the alkyl chain of the receptor is included inside the hydrophobic cavity of the macrocycle (as evident from $(1)H$ NMR studies) leading to self-assembly into micrometer-long nanotubes (as evident from TEM studies). The alkyl chain can be displaced by an acridinium bromide guest (as evident from $(1)H$ NMR and ITC), which leads to a dramatic change in aggregate size and morphology (as evident from DLS). Studies of the solubilization of Nile red suggest that the resulting aggregates are micelles with a cmc of around 35 microM. These results represent a new addition to the still small number of water-soluble amphiphilic receptors and one of the first examples in which specific host-guest chemistry controls the size and shape of nanoscale aggregates.

Talhout R., Stafforst T., and Engberts J. B. (2004) Aggregation behavior of p-n-alkylbenzamidinium chloride surfactants. *J Colloid Interface Sci* **276**, 212-220.

Abstract: The aggregation behavior of a novel class of surfactants, p-n-alkylbenzamidinium chlorides, has been investigated. The thermodynamics of aggregation of p-n-decylbenzamidinium chloride mixed with cationic and anionic cosurfactants has been studied using isothermal titration calorimetry. For mixtures of p-n-decylbenzamidinium chloride with n-alkyltrimethylammonium chlorides, the aggregation process is enthalpically more favorable than for the pure n-alkyltrimethylammonium chlorides, probably caused by diminished headgroup repulsion due to charge delocalization in the amidinium headgroup. A critical aggregation concentration between 3 and 4 mM has been extrapolated for p-n-decylbenzamidinium chloride at 40 degrees C, around two times lower than that of similar surfactants without charge delocalization in the headgroup and well comparable to that of similar surfactants with charge delocalization in the headgroup. In mixtures of p-n-decylbenzamidinium chloride with either sodium n-alkylsulfates or sodium dodecylbenzenesulfonate, evidence is found for the formation of bilayer aggregates by the pseudo-double-tailed catanionic surfactants composed of p-n-decylbenzamidinium and the anionic surfactant. These aggregates are solubilized to mixed micelles by excess free anionic surfactant at the measured critical aggregation concentration.

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 Y., Bai G., Marques E. F., and Yan H. (2006) Phase behavior and thermodynamics of a mixture of cationic gemini and anionic surfactant. *J Phys Chem B Condens Matter Mater Surf Interfaces Biophys* **110**, 5294-5300.

Abstract: We present the phase behavior and thermodynamics of the catanionic mixture of the gemini surfactant hexanediyl- α,ω -bis(dodecyltrimethylammonium bromide), designated here as 12-6-12Br(2), and sodium dodecyl sulfate (SDS) over the full range of composition, at the water-rich corner. Visual and turbidity measurements of the mixtures provide some basic macroscopic information on phase behavior. The structure of the aggregates formed spontaneously in the mixtures has been observed with TEM. As the molar fraction of SDS, X(SDS), is increased, at constant total surfactant concentration, the aggregation morphologies change gradually from gemini-rich micelles, through multiphase regions containing a precipitate (catanionic surfactant) and a vesicle region, to SDS-rich micelles. From isothermal titration calorimetry measurements, the phase boundaries and corresponding enthalpy changes for phase transitions have been obtained. The formation of the different microstructures, in particular, the spontaneously formed vesicles in the SDS-rich side, is discussed on the basis of geometric and electrostatic effects occurring in the SDS-gemini mixture.

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 α -helical content of cellulase. With further increasing the concentration of SDS, however, a re-formation of the α -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.

Zhang S., Li N., Zheng L., Li X., Gao Y. and Yu L. (2008) Aggregation behavior of pluronic triblock copolymer in 1-butyl-3-methylimidazolium type ionic liquids. *J Phys. Chem B* **112**, 10228-10233.

Abstract: Three amphiphilic poly(oxyethylene)-poly(oxypropylene)-poly(oxyethylene) ethers triblock copolymers, denoted Pluronic L61 (PEO3PPO30PEO3), Pluronic L64 (PEO13PPO30PEO13), and Pluronic F68 (PEO79PPO30PEO79) were shown to aggregate and form micelles in ionic liquids (ILs) 1-butyl-3-methylimidazolium tetrafluoroborate (bmimBF₄) and 1-butyl-3-methylimidazolium hexafluorophosphate (bmimPF₆). The surface tension measurements revealed that the dissolution of the copolymers in ILs depressed the surface tension in a manner analogous to aqueous solutions. The cmcs of three triblock copolymers increase following the order of L61, L64, F68, suggesting that micellar formation was driven by solvophobic effect. cmc and gamma cmc decrease with increasing temperature because hydrogen bonds between ILs and hydrophilic group of copolymers decrease and accordingly enhance the

solvatophobic interaction. Micellar droplets of irregular shape with average size of 50 nm were observed. The thermodynamic parameters ΔG_m^0 , ΔH_m^0 , ΔS_m^0 of the micellization of block copolymers in bmimBF₄ and bmimPF₆ were also calculated. It was revealed that the micellization is a process of entropy driving, which was further confirmed by isothermal titration calorimetry (ITC) measurements