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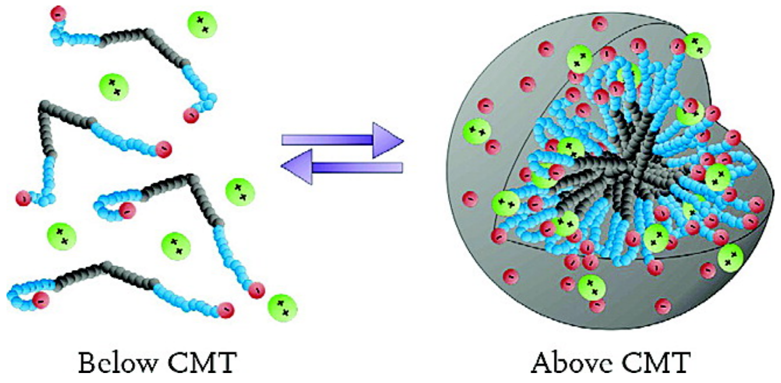

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Reversible Binding of Multivalent Ions by Surfactant Self-Assembly

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Binding of multivalent cations is relevant for many phenomena occurring in aqueous environments, ranging from biophysical systems[1] (e.g., binding to lipid bilayers and ion pumping) to processes for large-scale water purification.[2] Most ion binding processes differ in the uptake and release behavior of ions, and this has led to a great interest in developing systems for multivalent ion binding with tunable properties.[3] Here, we demonstrate the use of multifunctional amphiphiles that bind multivalent cations in a reversible way. High molecular weight nonionic surfactants[4] have been chemically modified by introducing acid groups that provide sufficient charge density to bind multivalent ions only above the critical micellization temperature (CMT), that is, in the micellar form. Lowering the temperature below the CMT causes the disintegration of the micellar structure, releasing the bound cations as no binding occurs to the free surfactant molecules.

At this moment, aggregates of ionic surfactants are being used to bind divalent ions in an irreversible way, which is usually performed in combination with micellar-enhanced ultrafiltration (MEUF).[5] Contrary to most ionic surfactants,[6] nonionic polymeric surfactants can be dissolved in water in high concentrations in the presence of multivalent cations.[7] This is applied to bind multivalent ions to aggregates of mixtures of ionic and nonionic surfactants, where the nonionic surfactants are used to increase the solubility of the mixed micelles. However, the binding of the cations to the ionic surfactants is still irreversible, and below the CMT of the nonionic surfactant, the ionic surfactants will precipitate in the presence of the cations.[8]

To allow for the thermoreversible binding of multivalent cations in the aqueous shell of micelles, Pluronic P85 ((ethylene oxide)$_{26}$−(propylene oxide)$_{39}$−(ethylene oxide)$_{26}$) has been modified with succinic anhydride, yielding a high molecular weight (MW = 4748 g/mol) triblock copolymer with carboxylic acid end-standing (CAE) groups. This polymer is denoted as CAE-85. The large amount of ethylene oxide in the CAE-85 surfactant ensures that the surfactant remains soluble up to high concentrations of multivalent ions. Initially, at temperatures below the CMT, the CAE-85 surfactant and the multivalent cations are present in solution as "free molecules". The affinity of isolated carboxylic acid groups for multivalent cations is very low.[9] Increasing the temperature above the CMT brings the charged carboxylic acid groups present on different surfactant chains together, thus allowing for the sequestering of the multivalent cations. Subsequent lowering of the temperature to values below the CMT will release the bound cations because the micellar structure breaks up.

First, CAE-85 was characterized using differential scanning calorimetry (DSC). Figure 1 shows that CAE-85 at pH > 5 has a CMT of about 32 °C at low ionic strength, a value that decreases to about 26 °C at an ionic strength of 0.8 mol/L. Unmodified P85 displays a CMT of 31 °C at low ionic strength, a value that decreases to about 27 °C at 0.8 mol/L. From the DSC measurements, it can be concluded that the modification of P85 has, besides a small pH effect, only a minor influence on the micellization behavior. From titration curves, a pK_a value of 4.51 has been determined for CAE-85.

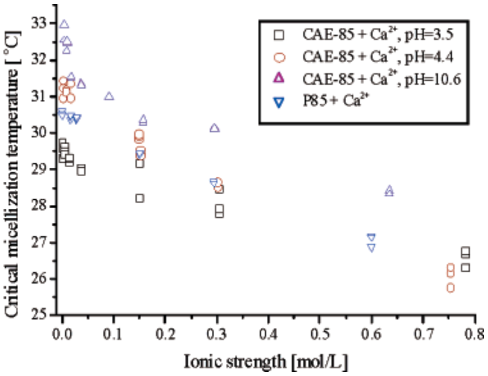

Figure 1. Differential scanning calorimetry results for the critical micellization temperatures as a function of the ionic strength for 1 wt % solutions of P85 and CAE-85 surfactants at different pH and in the presence of $CaCl_2$.

Next, experiments were performed using isothermal titration calorimetry (ITC) to investigate the binding between the CAE-85 surfactant aggregates and different cations. ITC has proven to be an effective method for evaluating the heat effects occurring upon aggregation of surfactants and during ion binding and release.[9,10] In the ITC measurements, a solution of the chloride salt of known concentration was added to a surfactant solution. Performing ITC experiments, at pH > 5 and 50 °C, with Ca^{2+}, Ba^{2+}, Mg^{2+}, and La^{3+} salts and CAE-85 yields the results shown in Figure 2. For Ca^{2+} also, the result of an ITC experiment at a temperature of 25 °C (i.e., below the CMT) is given. There is no significant binding of Ca^{2+} to CAE-85 when the surfactant molecules are freely dissolved in solution at 25 °C. However, the cations strongly bind to CAE-85 when present in a micellar form at 50 °C. At 50 °C, about the same heat effect is observed for the three different divalent ions, which is an indication that the binding of the cations to the CAE-85 aggregates follows a charge compensation mechanism. Binding of La^{3+} results in a higher heat effect than that observed for the divalent cations. For comparison also, ITC experiments have been performed to study the binding of Ca^{2+} to poly(acrylic acid) (PAA, MW = 2000 g/mol). Two acid groups on the same PAA molecule bind one single Ca^{2+} ion, without the formation of micelles.[11]

Figure 3 compares the Ca^{2+} binding isotherm for PAA and CAE-85 at pH = 9 and 50 °C. The fractional counterion binding[12] θ, defined as the ratio of occupied active sites per total active sites, is

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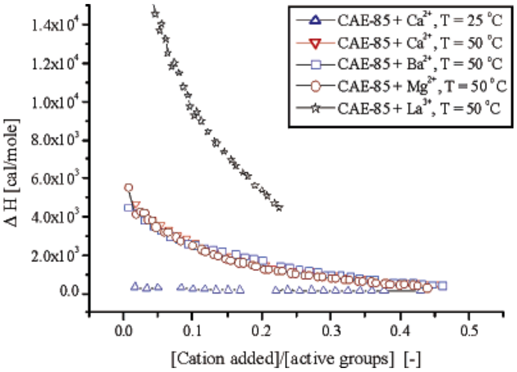

Figure 2. Results of the isothermal titration calorimetry experiments with CAE-85 at 50 °C. The heat effect per injection (ΔH/inj) is given as a function of the ratio between the moles cation added and total moles active carboxylic acid groups. For calcium, the result at 25 °C is also given.

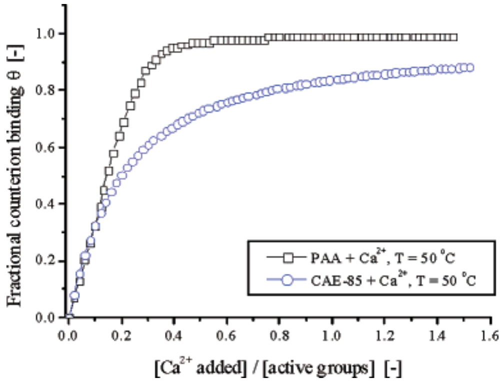

Figure 3. Results for the fractional counterion binding θ of calcium to PAA and CAE-85 as a function of the ratio between the moles Ca^{2+} added and total moles active carboxylic acid groups, at a temperature of 50 °C. The fractional counterion binding θ is calculated from the binding constant, which was obtained from the measured ITC data.

calculated from the ITC data. For both systems, the binding isotherm is described by the Langmuir model. From the fact that the binding isotherms for PAA and the CAE-85 aggregates have the same initial slope, it follows that Ca^{2+} is bound with the same affinity in the two systems at low Ca^{2+} concentrations. The Langmuir model properly describes the binding of the cations to the CAE-85 aggregates, which indicates a similar interaction mechanism for the CAE-85 surfactant as that observed for conventional ionic surfactants, such as SDS (sodium dodecyl sulfate).[13] To verify if binding of Ca^{2+} to unmodified triblock copolymers occurs, ITC experiments with unmodified Pluronic P85, below and above the CMT, have been carried out. From these experiments, it can be concluded that no noticeable Ca^{2+} binding to P85 occurs.

Finally, to verify the reversibility of the metal ion binding to CAE-85 micelles and to demonstrate that the surfactants can be regenerated, a continuous membrane filtration experiment has been performed. In this experiment, a temperature cycle was applied, while a solution of CAE-85 and $CaCl_2$ was led through a cross-flow flat membrane module containing a regenerated cellulose acetate ultrafiltration membrane with a cutoff value of 3 kDa. The calcium concentration at the permeate side of the membrane was measured by colorimetric titration.[14] The membrane retains the CAE-85 surfactant molecules, whereas Ca^{2+} ions can permeate through the membrane. During the experiment, the temperature of the solution is switched from 20 °C (below CMT) to 50 °C (above CMT) and back to 20 °C. Each temperature was maintained for at least 1 h, in which a steady-state Ca^{2+} flux through the membrane was obtained. Below the CMT, the Ca^{2+} concentration in the permeate stream equals the feed concentration, and increasing the temperature above the CMT reduces the amount of free calcium in the system. As a result, a clearly lower Ca^{2+} permeate concentration has been measured, in accordance with the isotherm. By lowering the temperature back to 20 °C, the Ca^{2+} concentration in the permeate stream becomes, again, equal to the feed concentration, confirming the complete release of all of the bound Ca^{2+} ions.

Current technologies to remove divalent cations, like calcium and barium in water softening, are commonly based on the use of ion-exchange resins.[15] The regeneration of the resins involves consecutive washing steps with acid and caustic, which results in a substantial amount of waste salt.[16] The fact that a thermoreversible binding process for divalent ions is now available allows for the development of environmentally friendly water purification processes without the use of additional chemicals during the regeneration steps. The proposed surfactant modification provides a generic approach to obtain CAE surfactants. The CAE aggregates result in a binding system with an on/off mechanism that responds to a moderate temperature stimulus, which can also offer attractive opportunities for responsive delivery systems[17] and the design of ligands[9,18] in the biomedical field.

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Supporting Information Available: Details of surfactant synthesis, isothermal titration calorimetry, membrane permeation, and chemical structures. This material is available free of charge via the Internet at http://pubs.acs.org.

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