Reversible binding of multivalent ions by surfactant self-assembly
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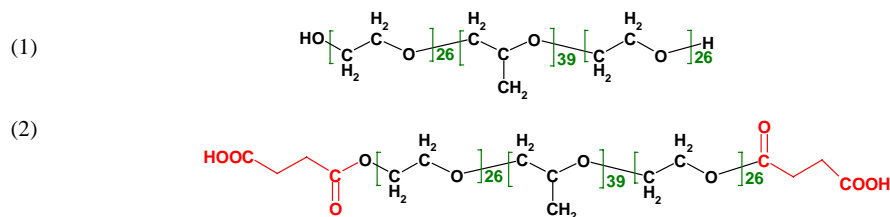**Supporting Information**

Chemical Structures - In this work Pluronic P85 surfactant (1) and CAE-85 surfactant (2) are used. Pluronic P85 (EO_{26}-PO_{39}-EO_{26}, BASF) is a poly(ethylene oxide) - poly(propylene oxide) - poly(ethylene oxide) triblock copolymer.

(1)

(2)

Synthesis and characterization - In the synthesis of the CAE-85 surfactant, first 50 g of Pluronic P85 surfactant is purified by dissolving the polymer in 200 g diethyl ether. The cloudy turbidity is removed in a centrifuge, followed by precipitation of the surfactant in 200 g cold (5 °C) pentane. Succinic anhydride is recrystallized from dichloromethane/hexane. 40 g of purified P85 is dissolved in 160 mL toluene, followed by the addition of 5.04 g succinic anhydride. The reaction is performed for two hours at 90 °C and for two hours at 100 °C, respectively. The water is removed before reaction by azeotropic distillation. After the reaction, the solvent is evaporated, and the product is dissolved in water (20 wt%), followed by addition of sodium carbonate until pH>9 and diluted sulphuric acid until pH<2, respectively. The product is then extracted with butanol and dried overnight above a layer of anhydrous sodium sulphate. Finally, butanol is evaporated and the product is redissolved in 200 g diethyl ether, followed by precipitation with an equal amount of cold (5 °C) pentane. The final product is obtained after filtering and drying under vacuum conditions at room temperature. The product is characterized by titration of a 1wt% solution CAE-85 with 0.5 M NaOH, which is shown in the graph. A pKa value of about 4.51 was found. The product CAE-85 has about $5.0*10^{-4}$ mol acid groups per gram surfactant. The fact that Pluronic P85 is polydisperse makes it difficult to give an absolute number for the conversion, despite the purification steps.
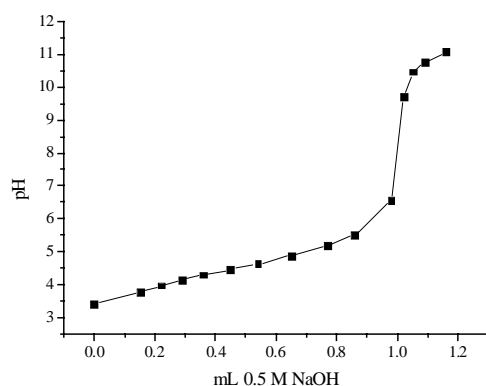

Figure S1. Titration curve for CAE-85.

Isothermal titration calorimetry and data analysis - ITC experiments were performed using a MicroCal VP-ITC apparatus with a cell volume of 1.4431 mL. The experimental procedure consisted of adding 70 injections of 4 μL of calcium, barium, magnesium or lanthanum chloride salt solution (10.0 mmol/L) to 1 wt% solutions of CAE-85 surfactant. The isotherms (Figure 3) are obtained from the thermal data (Figure 2) using Origin (MicroCal Software, Inc.). From an isothermal titration experiment the calorimetric enthalpy ΔH, the binding constant K and the stoichiometric constant n are obtained by fitting the experimental thermal data. The equations, used to fit the data, consist of a binding model, the mass balance for the binding sites, and a relation for the heat content. By specifying the binding model, a single relation for the heat content equation is obtained that is a function of ΔH, K, and n. It is assumed that a "single set of identical sites" model, i.e. a Langmuir model, will describe the binding mechanism the best. The isotherms of Figure 3 for CAE-85 and PAA are obtained with a K value of $1.3*10^3$ and $2.0*10^4$ [L mol^{-1}], respectively, and using the following relation for the fractional binding as a function of the the unbound calcium concentration:

$$\theta = \frac{K[Ca^{2+}]}{1 + K[Ca^{2+}]}$$

Membrane permeation - In the reversibility experiment a crossflow of 150 L/h was used, while the total system had a volume of about 2 L. The total membrane area of the cellulose acetate membrane was $6.49*10^{-3}$ m^2 with an applied pressure of 20 Psi during the experiment. The surfactant concentration was 0.5 w%.