THE SALT CURVE REVISITED – ELECTROSTATIC CHARGES GOVERN THE VISCOELASTIC PROPERTIES OF MICELLAR SOLUTIONS

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In ionic surfactant micelles, interactions among surfactant monomers, their counterion, and additives are fundamental to tune molecular self-assembly and thus the rheological properties (see Figure 1). Here we propose a combination of ^{1}H-NMR, integrated small-angle neutron scattering (SANS) and small-angle X-ray scattering, and rheology to probe the molecular arrangements of the individual molecules within the micelle and the resulting flow properties [1, 2]. Shifts in the ^{1}H-NMR signal show the penetration of counterions and additives into the micellar surfactant structure while SANS and SAXS determine specific intramicellar length scales and intermicellar interactions. SANS signals are sensitive to the contrast between the solvent (deuterium) and the hydrocarbonic tails in the micellar core (hydrogen) and SAXS access the inner structure of the polar shell because the headgroups, counterions, and penetrated salt have higher electron densities compared to the solvent and to the micellar core.

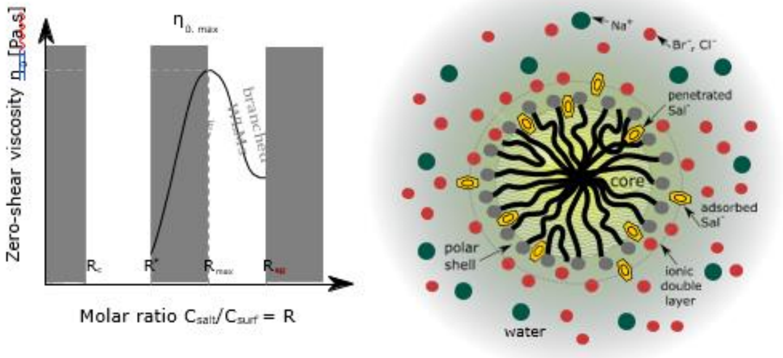

Figure 1: Schematic representation of the variation of zero-shear viscosity (left). Micellar cross-section in the presence of an aromatic salt (right). The ionic interactions among headgroups and counterions are identified in the polar shell as well as core and ionic double layer formation [1].

The number density, intermicellar distances, aggregation number, and inter/intramicellar repulsions are discussed on the basis of the dependence of the structure factor and form factor on the micellar aggregate morphology. The results allow us to propose a modified packing parameter model taking electrostatic charges into account. As a consequence, micellar growth and structure can be discussed by variations in the flexibility and size of the headgroup as well as the ionic dissociation rate of its counterion. Additionally, we show that the counterion binding is even more significant to the development of viscoelasticity than the headgroup structure of a surfactant molecule [2-4]. This somewhat surprising finding shows the importance of electrostatic charges in the self-assembly process and its consequences on the rheological fingerprint of viscoelastic surfactant solutions.

References

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