pH-induced structural changes in aqueous CTAB/NaSal solutions

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Cationic surfactants in the presence of hydrotropic salts exhibit pH-sensitive changes to rheological properties and can thus be utilized in ensuring effective stimulation of heterogeneous carbonate reservoirs. In this study, we investigate the pH-induced changes in microstructure and viscoelasticity of aqueous solutions of cetyltrimethylammonium bromide (CTAB) and sodium salicylate (NaSal), and their dependence on temperature, NaSal-to-CTAB ratio (CS/CD) and CTAB concentration (CD). It was observed that the solutions can be switched between gel-like (viscoelastic) and fluid-like (non-viscoelastic) behavior over a narrow pH range, and that the transition pH and associated change in viscoelasticity were strongly dependent on CS/CD. Dynamic light scattering and small-angle neutron scattering results revealed a hitherto unseen re-entrant transition in which micelles transition from cylindrical to spherical micelles but revert to flexible cylindrical micelles on reduction in pH. Our observations suggest that in addition to the well described electrostatic and hydrophobic interactions in cationic surfactant - hydrotrope mixtures, the pH-induced microstructural changes are governed by complementary cation-π interactions and hydrogen bonding.