Effect of electrolyte and counterion hydrophicity on the macroscopic properties of dilute micellar solutions

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The shear thickening transition (STT) in dilute surfactant solutions was first reported in the early 1980’s [1]. Afterwards, it was detected in concentrated suspensions [2], monodisperse and bidisperse colloidal dispersions [3] and associative polymer solutions [4]. This transition is typified by a large viscosity rise when the micellar solution is sheared at or above a critical shear rate \( \dot{\gamma} \) or a critical shear stress \( \sigma \) due to the formation of shear-induced structures (SIS) [5].

Shear stress against shear rate under stress (●) or strain controlled (□) conditions. Inset: \( \sigma - \dot{\gamma} \) flow curve without re-entrant region for CTAT solutions.

Most reports on the STT in micellar solutions have been done with cationic surfactant solutions, usually cetyltrimethylammonium (CTA) or cetylpyridinium (CPy) halides, with added inorganic electrolytes or salts containing strongly binding organic counterions. Cationic surfactants that have a strongly binding counterion such as salicylate (Sal), tosilate (T) or vinylbenzoate (VB), exhibit the STT at dilute concentrations without the addition of salts.

In this work, the effect of adding electrolytes (with different counterion valence) to dilute CTAT micellar solutions, and the effect of varying the counterion hydrophobicity in dilute solutions of cetyltrimethylammonium-type cationic surfactants, on the shear thickening behavior and furthermore, on the transition to shear thinning, are examined.