Microstructural changes in m-s-m type of gemini surfactant solutions

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Viscometric measurements have been performed at 30°C to see the effect of inorganic (KBr, KNO₃, KSCN) and organic salts (NaBen, NaSal) on the evolution of microstructure in gemini alkanediyl-α,ω-bis(dimethylalkylammonium bromide) surfactant (Br⁻, n-CₙH₂n+₁N⁺Me₂-(CH₂)ₛ-Me₂-N⁺n-CₙH₂n+₁, Br⁻, n = 14,16, s = 4,5,6) solutions. In pure aqueous solutions, the relative viscosity results were found with the geminis in comparison to their monomeric counterparts tetradecyltrimethylammoniumbromide (Cₙ-C₁₄H₂₉N⁺Me₃, Br⁻, TTAB) and cetyltrimethylammoniumbromide (Cₙ-C₁₆H₃₃N⁺Me₃, Br⁻, CTAB). As evidenced by further rise in viscosity, the presence of salts results in structural changes (spherical to nonspherical) of gemini micelles in aqueous solutions. The nature and size of the added counterions is mainly responsible for the micellar growth in gemini surfactants. The effect of inorganic counterions on the micellar growth is observed following the lyotropic series (Br⁻< NO₃⁻< SCN⁻) and the effect of organic counterions are discussed on the basis of probable solubilization sites of the substrate molecule in the gemini micelles, which follows the order Sal⁻>Benz⁻. To get further insight of this, the ¹H NMR studies have also been performed on the 14-s-14 gemini surfactants, which strongly supported the viscometric results. The results are confirmed in terms of the obtained values of relative viscosity (ηr), chemical shifts (δ), and line width at half height (lw). Also it was observed among geminis of same series the growth was more pronounced shorter the spacer (i.e., s = 4>5>6). This was attributed to the unique molecular structure of gemini surfactant micelles having flexible polymethylene spacer chain linking the two polar headgroups.