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Non-ideal mixing drives complex micellization morphology and phase behavior of mixed nonionic surfactants

There is considerable interest in replacing perfluoroalkyl surfactants (PFAS) with more environmentally benign substitutes in a range of industrial and consumer applications. Since individual alkyl and silicone-based surfactants consistently underperform against PFAS,
mixtures of surfactants are being considered as potential substitutes. In many cases, property data are interpreted assuming that chemically homologous co-surfactants completely mix at the molecular scale, often with ideal mixing thermodynamics. However, limited studies with co-
surfactant mixtures involving large differences in spontaneous curvature lead to a number of non-ideal phenomena including non-monotonic mixture phase behavior and complex assembled structures in solutions and emulsions. To better elucidate the molecular origins of this behavior we report combined structural, thermodynamic, and chemical characterization in model mixed ethoxylated alkane (CiEj) co-surfactants in aqueous solutions (water/surfactant). Phase behavior
and calorimetric studies in these mixtures exhibit a significant non-monotonic dependence of critical temperatures and micellization thermodynamics that indicate non-ideal mixing in co-surfactants with disparate spontaneous curvature (e.g., C12E5/C4E1) relative to geometrically similar co-surfactant pairs (e.g., C12E5/C12E6). Using a combination of viscometry, dynamic light scattering (DLS), and contrast-variation small angle neutron scattering (CV-SANS) measurements to resolve micelle morphology and intermolecular interactions, we show that this behavior corresponds with significant temperature-dependent differences in solvation between the mixed surfactants and their pure component counterparts. Ultimately, we hypothesize that differential solvation structures between co-surfactants in the mixed state provide a potential explanation for all the observed non-ideal behavior, and we test this hypothesis against molecular dynamics and field-theoretic simulations.

Topical Area

Biology and life sciences

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