Aggregation behavior and surface tension lowering ability of anionic surfactants having highly-methylated tails

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A fluorinated surfactant can reduce aqueous surface tension effectively. However, it is quite expensive and environmentally burden compared with a hydrocarbon one. Previous studies [1] have reported that double branched-nonyl-tail surfactants are able to reduce aqueous surface tension to ~24 mN/m, even at low hydrocarbon tail layer densities of 0.47-0.53 g/cm^3. Based on the air/liquid interfacial properties of liquid n-alkanes (e.g. 22.4 mN/m at a mass density of 0.71 g/cm^3 for n-nonane at 25 ºC), if the layer density of this double branched-nonyl-tail layer can be increased to ~0.70 g/cm^3, comparable to that seen in the analogue liquid alkane, the surface tension could approach as low as ~22 mN/m.

Aiming to develop hydrocarbon surfactants able to lower aqueous surface tension as effective as a fluorinated surfactant does, this study synthesized surfactants having highly methylated tails, namely, double, and triple 3,3-dimethylbutyl tails (namely, $ROCO-CH_2-CH(-SO_3Na)-COOR$ four double tail surfactant di-BC_4ESS, and $ROCO-CH_2-C(-SO_3Na)(-COOR)-CH_2-COOR$ for triple tail surfactant tri-BC_4ETS, where R is 3,3-dimethylbutyl tail), and examined their surface tension lowering ability in water and aggregation behavior in nonpolar solvents (*n*-hexane, *n*-heptane and supercritical CO_2) of these surfactants.

Critical micelle concentration (cmc), surface tension at cmc (γ_{cmc}), minimum effective area per surfactant molecule (A_{min}) of the surfactants were obtained from relationship between surface tension and surfactant concentration in water at 35 ℃. The cmc, γ_{cmc} and A_{min} were 3.9×10^{-2} M, 26.0 mN/m and 150 Å^2 for di-BC_4ESS and 4.6×10^{-3} M, 24.6 mN/m and 183 Å^2 for tri-BC_4ETS, respectively.

To investigate effects of various salts on the surface tension lowering ability, sodium, magnesium or calcium chloride was added to the aqueous surfactant solution at twice the critical micelle concentration, and the surface tension was measured as a function of salt concentration. Addition of salts in the surfactant solutions decreased surface tension until the certain salt concentrations. At its lowest, the aqueous surface tensions reached 22.5 mN/m and 23.2 mN/m for the CaCl/di-BC_4ESS and CaCl/tri-BC_4ETS systems, respectively. These values are very close to the surface tension of liquid *n*-nonane, and γ_{cmc} of a short fluorocarbon-tail surfactant. The structure-surface tension lowering ability correlation suggests that the order parameter, layer density and tail length are key in the design of a hydrocarbon surfactant with fluorinated surfactant-like low surface energy.

Nanostructures of those surfactants in the nonpolar solvents were examined by small angle neutron scattering apparatus (LOQ, Rutherford Appleton laboratory, UK) at 25 ℃. Tri-BC_4ETS was found to yield transparent single phases with water/n-heptane and water/n-hexane systems even with water-to-surfactant molar ratios (W_0) higher than 10, but di-BC4ESS could not so. The SASN measurements and data analysis suggested aqueous cores of the 50mM tri-BC4ETS/D_2O/*n*-heptane microemulsion with $W_0 = 30$ to be spherical with the radius of ~20 Å. On the other hand, in water/supercritical CO_2 mixtures at 45 ℃, 50 mM tri-BC_4ETS formed a transparent single phase with $W_0 < 3$, but it turned into a turbid phase with an increase in W_0. SANS profile of the turbid phase with $W_0 = 5$ showed a Bragg peak ascribed to the layer spacing of 27 Å. Then the turbid phase was identified as a liquid crystal phase like a lamellar one but not a simple W/CO_2 macroemulsion phase.

[1] M. Sagisaka, T. Narumi, M. Niwase, S. Narita, A. Ohata, C. James, A. Yoshizawa, E. T. Givenchy, F. Guittard, S. Alexander and J. Eastoe, *Langmuir*, 2014, **30**, 6057.