STRUCTURING OF TRISILOXANES-BASED SUPERSPREADERS AT INTERFACE AND IN BULK BY NEUTRON SCATTERING

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Trisiloxanes-based surfactants, known as superspreaders, are widely used in agricultural industry [1]. However, some trisiloxane surfactants are toxic agents for honeybees and insect-pollinators, and pose a potential threat to human health. To develop biocompatible surfactants enabling the same effectiveness as trisiloxane surfactants, it is crucial to understand mechanism behind the superspreading effect. The mechanism is likely related to formation of multilayer aggregates of trisiloxane surfactant molecules in the bulk and at interfaces. Conditions at which trisiloxane surfactant solutions exhibit superspreading were proposed: (i) temperature of solutions is close to the phase transition temperature, T_{cp}, from transparent to turbid solution; and (ii) concentration of surfactants is above the critical wetting concentration (cwc) which is above the critical micelle concentration (cmc).
The aim of the current work was to investigate using neutron scattering how temperature variation influences structural conformation of molecular aggregates of trisiloxane surfactants during their adsorption at a solid interface (by specular neutron reflectometry) and self-organization in a bulk phase (by small-angle neutron scattering). The solutions of trisiloxane surfactant with 9 ethoxy units (TEO_9) and commercial trisiloxane surfactant Silwet L-77 with 7.5 EO units were studied at concentrations of 1.5 cmc, 1.5 cwc, 5 cwc in D_2O. For comparison, the solution of hydrocarbon surfactant $C_{12}EO_8$ at 5 cmc in D_2O was also investigated. Measurements were performed at different temperatures in the ranges below and above T_{cp} for each surfactant: Silwet L-77 (T_{cp}= 40°C), TEO_9 (35°C), $C_{12}EO_8$ (78°C). In the experiments on neutron reflectometry, silicon substrate was coated (magnetron deposition) by Ti film which then was oxidized to increase the wetting angle. Among three surfactants under study the adsorption layer of TEO_9 showed very low temperature sensitivity. For L-77 and $C_{12}EO_8$ the changes of the layer are observed at $T \geq T_{cp}$. For TEO_9 at 20°C SANS data showed a transition from compact micelles (1.5 cwc) to anisotropic lamellar type micelles (5 cwc). The same transition takes place with the temperature increase (up to T = 50°C) at 1.5 cwc. An increase in the temperature up to 75°C results in the partial formation of a macrophase (with the Porod law in the scattering curve). The more the concentration the lower the temperature when this process starts.

[1] Ivanova, N.A., Kovalchuk, N.M., Sobolev, V.D., Starov, V.M., Soft Matter, 2015, 12(1), 26–30