STRUCTURAL STUDIES OF SURFACTANT MICELLES INTERACTING WITH POLYMERS IN BULK AND AT INTERFACES BY NEUTRON SCATTERING

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The interaction of surfactants and polymers in solutions, including the adsorption of surfactants and surfactant micelles on polymers, is characterized by a wide variety of structures, offering extensive opportunities for controlling the properties of colloidal systems. Identification of the structural features of such systems enables more effective development of their scientific and industrial applications, particularly those related to their unique viscoelastic properties. Neutron scattering methods are widely used for this purpose. The high penetration depth of neutron radiation allows for studies to be conducted in bulk solutions and for investigation of hidden interfaces modified for the adsorption of components from the solution. This paper presents aspects of structural studies using neutron scattering methods for a number of relevant surfactant-polymer systems, based on experiments conducted at the IBR-2 reactor at JINR (Dubna).

Small-angle neutron scattering (SANS) was used to study aqueous solutions of polymer-like worm-shaped micelles of the "traditional" surfactant potassium oleate and the gemini surfactant C18-4-C18 [1]. Surfactant solutions are widely used in the oil industry as smart thickeners that lose their viscoelasticity upon contact with oil. Their rheological properties can be improved by adding both inorganic and organic (including polymeric) nanoparticles, which act as cross-linking agents between the micelles. The improvement of the viscoelastic properties of solutions while maintaining sensitivity to hydrocarbons is possible by incorporating a self-organizing percolation network of cellulose nanocrystals. Nanocrystals have been shown to increase the viscosity and elastic modulus of a solution of potassium oleate micelles by an order of magnitude and ensure temperature stability of these properties. This phenomenon can be explained by the formation of a fused network consisting of worm-like micelles and of nanocrystals. SANS data showed that within this network, the shape and size of both micelles and nanocrystals remain unchanged, indicating that the micelle network structure is preserved in the presence of nanocrystals and that additional nanocrystal aggregation does not occur.

Surfactant-polymer interactions can also lead to significant changes in the structural parameters as determined by SANS, as in the case of the addition of polyethyleneglycol (PEG) to aqueous micellar solutions of dodecylbenzenesulfonic acid (DBSA)[2]. The interaction between DBSA and PEG molecules occurs primarily through hydrogen bonds, leading to the formation of lamellar structures. A mechanism also occurs due to the hydrophobic interaction of surfactant tails and the adsorption of individual micelles onto the polymer chain, forming "necklace"-type structures. The coexistence of free spherical micelles and surfactant-polymer complexes in a "necklace" structure was demonstrated using SANS. The influence of PEG molar mass on the formation of multimicellar complexes in these systems was observed.

The interaction of micelles and polymers near a flat quartz surface can be studied using polymer grafting. This approach chemically anchors densely packed polymer chains to the surface, forming a coating in the form of a polymer "brush." Polyacrylamide polymer brushes with thickness of tens of nanometers have been synthesized using the "grafting-through" technique [3]. This approach allows for the production of films with a relatively high grafting density, resulting in strong elongation of the polymer chains in the film compared to a free polymer coil. Reflectometry methods allow for obtaining the scattering length density profile of the film on the surface, followed by analysis of the thickness and structure of the internal layers. The "grafting-through" method demonstrated to be scalable to large substrates for neutron reflectometry. The proposed approach opens a relatively simple path for modifying the surface with polymer nanolayers of controlled thickness as a model surface, on which neutron methods can be used to analyze the adsorption of objects and their interaction with the polymer.

Using polyacrylamide polymer brushes, we analyzed the adsorption of surfactant micelles from aqueous solutions onto a surface. When a polymer brush comes into contact with water, it partially swells, effectively increasing its thickness and roughness compared to the dry state. When micelles are added to the solution, they interact with the polymer chains via one of the mechanisms previously described for the bulk case, initiating their adsorption. In neutron reflectometry, this interaction can be observed by constructing and analyzing a depth profile of the scattering length density, effectively changing the density, thickness, and roughness of the polymer layer. In the case of a polyacrylamide film, the addition of a surfactant increases the layer thickness and roughness comparable to the micelle diameter, thus detecting micelle adsorption.

Thus, based on the information obtained in neutron scattering experiments, studies of the structure of surfactant micelles interacting with polymers, which combine studies in the bulk and on the surface, are promising in the field of soft matter investigation.

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