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The Discovery of Nanostructural Optical Activity in Solutions of Surfactants¹

A. I. Rusanov and A. G. Nekrasov

St. Petersburg State University, St. Petersburg, 199034 Russia

e-mail: rusanov@ar1047.spb.edu

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Optical activity (the ability to rotate the polarization plane of linearly polarized light) is inherent to solutions whose molecules have neither centers nor planes of symmetry, i.e., to substances possessing chirality. The term ‘supramolecular chirality’ was introduced in supramolecular chemistry for a case of a molecular complex possessing chirality is formed as a result of the chemical interactions of both chiral and achiral compounds. In this work, only aggregative processes in the absence of chemical interactions are discussed. In this case, a hydrophobic effect of entropic origin causes the formation of nanostructures. It is this mechanism that characterizes the micelle-formation processes in polar media (with the formation of direct micelles [1, 2]). This work is dedicated to the detection of nanostructural optical activity in colloid (micellar) surfactants. These substances are themselves not optically active, but unexpectedly exhibit optical activity in the course of aggregation in aqueous solutions. The phenomenon actually arises in the area of critical micelle concentration (CMC) but starts to develop well before reaching CMC. Experiments indicate the emergence of dextrorotatory submicellar aggregates. This is illustrated by the examples of aqueous solutions of sodium dodecylsulfate (as a representative of anionic surfactants), hexadecyltrimethylammonium bromide (as a representative of cationic surfactants), and polyoxyethylene(4) dodecyl ether (Brij-30, as a representative of nonionic surfactants). All of these surfactants are achiral chemical compounds and do not exhibit optical activity in the monomer form. Nevertheless, molecular aggregates exhibiting optical activity appear during the micelle formation. They emerge above the Kraft point and gather strength before reaching CMC. Experiments conducted below the Kraft point demonstrate the absence of optical activity and, since there are no micelles below the Kraft point, this indicates the generation of chiral aggregative structures from the surfactant molecules.

During aggregation, the above surfactants form spherical micelles in which a center of symmetry logically appears and optical activity disappears. The optical activity of the solution (along with the formation of such micelles) falls to some nearly constant level corresponding to the contribution from the chiral fraction of the equilibrium distribution of aggregates according to their aggregation numbers (a further increase in concentration leads only to a rise in the number of optically inactive spherical micelles). It should be noted that, even though the phenomenon of nanostructural optical activity has been observed in various types of surfactants, it cannot be considered universal. It has been found, for instance, that solutions of N-dodecanoyl-N-methylglucamide (nonionic colloidal surfactant) do not exhibit optical activity. This means that aggregative chirality, just like chirality on the whole, is associated with the individual properties of chemical compounds.

Nanostructured optical activity of surfactant solutions associated with the micellar aggregation of achiral surfactants due to the hydrophobic effect has thus been discovered. Such supramolecular chirality can be referred to an aggregative or concentrational chirality, since it occurs only over a certain interval of concentrations. Optical activity can be considered a new tool for colloid chemical studies. If CMC registers the initial stage of the formation of direct micelles, then the rapid decrease in optical activity associated with the formation of spherical micelles indicates the completion of micelle formation; at the same time, these two characteristics are separated by a considerable concentration interval. Regrettably, this optical criterion is not universal, since it is associated with individual specifics of surfactants as well.

REFERENCES

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