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Supramolecular chirality of surfactants

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Aggregative or concentration chirality has been discovered in the process of micellization of ionic surfactants.

Chirality is known to be recognized *via* optical activity, *i.e.*, the capability of rotating the polarization plane of linearly polarized light. The rotation angle α obeys Biot's law

$$\alpha = [\alpha]\, lc, \qquad (1)$$

where l is the optical path length in a matter under investigation, c is the concentration of a chiral component, and $[\alpha]$ is the proportionality coefficient that is called specific optical rotation when the concentration is expressed in g/100 ml or molar optical rotation when the concentration is given in mol/100 ml. Since solids and liquid solutions differ by two orders of magnitude in their optical activity, they measure l in mm for solids and in dm for solutions. The constant $[\alpha]$ is a standard characteristic of a chiral substance.

The concept of supramolecular chirality was introduced in supramolecular chemistry.[1] It is natural when a supramolecule acquires chirality from its chiral constituents. At the same time, two different achiral compounds can form chiral supramolecules, *i.e.*, chirality appears in the supramolecular state only. In other respects, chiral supramolecules behave in a usual way and obey equation (1) if c designates the concentration of chiral supramolecules. However, supramolecular chemistry typically deals with non-covalent synthesis (even when considering self-assemblies[2]). At the same time, an aggregative mechanism of forming supramolecular chiral structures (even from achiral molecules or ions) exists. The simplest example is crystallization when achiral compounds (such as $NaClO_3$ or $NaBrO_3$) form chiral crystals from optically non-active solutions. The phenomenon is detectable at the stage of nucleation in supersaturated solutions.[3,4] We observed one more case of supramolecular chirality in the process of molecular aggregation of achiral surfactants.

Colloidal surfactants are capable of forming micelles at a temperature above the Krafft point and a concentration above the critical micelle concentration (CMC). We optically tested sodium dodecylsulfate (SDS, Fluka, >99% purity) as an anionic surfactant and hexadecyltrimethylammonium bromide (HTAB, Acros, >99% purity) as a cationic one in aqueous solutions. Both of the surfactants are achiral, and they do not possess optical activity in ordinary solutions. Summarizing the experimental data published,[5] the Krafft point ranges within 8–16 °C for SDS and lies at 26 °C for HTAB. For both of the surfactants, our optical experiments carried out below the Krafft point (at 7 °C for SDS and at 20 °C for HTAB) showed no optical activity. The results obtained above the Krafft point (at 20 °C for SDS and at 30 °C for HTAB) are presented in Figures 1 and 2. Both the surfactants exhibit dextrorotatory optical activity in a concentration range close to the CMC. The fact that the CMC value for HTAB lies to the left from the maximum of optical activity in the contrast with

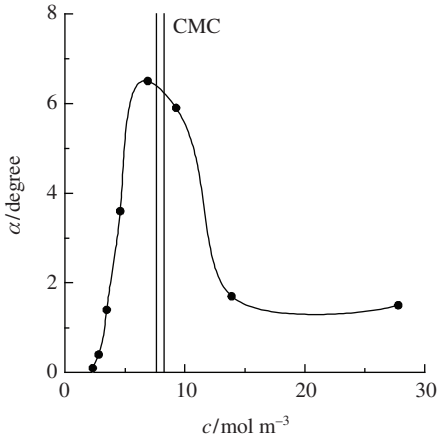

Figure 1 White-light optical rotation *vs.* concentration for an aqueous solution of SDS at 20 °C.

the case of SDS, can be explained, to some extent, by the CMC definition. It follows from the quasi-chemical theory of micellization[6] that the critical degree of micellization (corresponding to the CMC) is the smaller the larger is the aggregation number of a micelle. In turn, the aggregation number increases with the length of the hydrocarbon chain of a surfactant molecule. As compared with SDS, HTAB has a lengthier hydrocarbon chain, and, as a result, the CMC for HTAB corresponds to an earlier stage of micellization.

To exclude a possible influence of surfaces and walls, we verified the linearity between the optical rotation α and the solution length l as it follows from equation (1). The linearity was

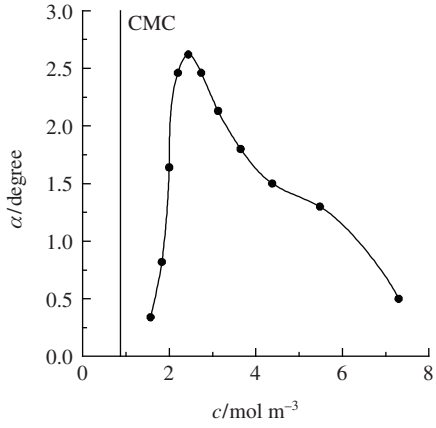

Figure 2 White-light optical rotation *vs.* concentration for an aqueous solution of HTAB at 30 °C.

confirmed with the coefficient of determination 0.98. This shows that the optical activity observed relates to the bulk solution, and it cannot be ascribed to surfaces (at forming, for example, liquid crystals at the cuvette wall). Taking into account that (a) the optical activity appears only above the Krafft point where micellization occurs and (b) both of the surfactants form spherical micelles that should be incapable of optical activity by the symmetry condition, we may conclude that the optical activity observed is caused by the formation of chiral micellar ionic aggregates. The optical activity wanes with concentration as aggregates acquire a more perfect shape and the number of spherical micelles increases. Figures 1 and 2 also indicate that the formation of spherical micelles is completed at a concentration significantly larger than the CMC (for example, at ~15 mol m^{-3} for SDS, whereas its CMC lies at ~8 mol m^{-3}).

Concerning now the proportionality between the optical rotation α and the concentration c in equation (1), Figures 1 and 2 show it to be not fulfilled. This occurs for two reasons. First, Biot's law operates with particles of a given nature and size, but we have a system with the particle size distribution depending on concentration. Second, Biot's law implies dealing with the concentration of optically active particles, whereas we use the total concentration of matter (the fraction of optically active matter remains unknown). For these two reasons, the introduction of specific rotation $[\alpha]$ seems questionable, and we presented our results in the primary form, *i.e.*, in absolute units of α. Naturally, this requires indicating the optical path length: we had $l = 0.8$ dm in our experiments.

The above experiments were carried out with white light, which is insufficient for characterization of optical activity. Biot's second law predicts that optical rotation is roughly inversely proportional to the square of the wavelength of monochromatic light. To verify whether aggregative optical activity obeys Biot's second law, we repeated experiments with SDS for various light wavelengths. The results are shown in Figure 3. They confirm the result obtained with white light (Figure 1): all maxima of optical activity (α_{max}) lie at the same concentration, and the concentration is close to the CMC. Figure 4 represents the plot of α_{max} *vs.* λ^{-2}, where λ is the wavelength of monochromatic light. The plot is approximated with a straight line with the coefficient of determination 0.91, which is sufficient to conclude that aggregative optical activity obeys Biot's second law and, therefore, belongs to optical activity at all.

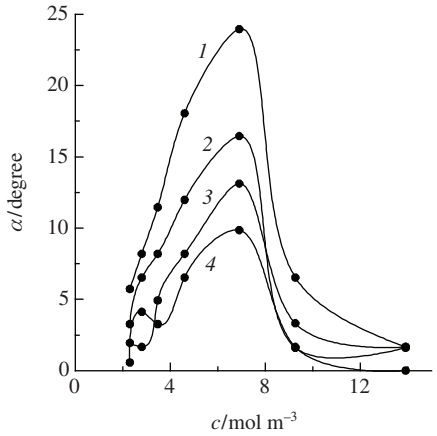

Figure 3 Optical activity of SDS using monochromatic light of the wavelengths (*1*) 0.45, (*2*) 0.48, (*3*) 0.57 and (*4*) 0.61 μm.

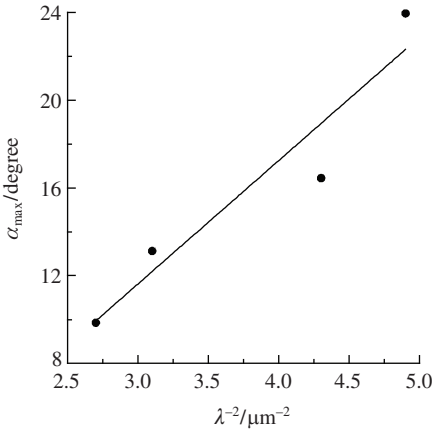

Figure 4 Verification of Biot's second law for maximum values (α_{max}) of aggregative optical activity (λ is the wavelength of monochromatic light).

The last question to be discussed is the origin of optical activity in an initially symmetrical system consisting of achiral components. What factor makes the preference of D-aggregates against L-aggregates in the case of surfactants? A similar problem was disputed for small crystals.[4] It was earlier accepted that equal numbers of L- and D-crystals are formed from an achiral solution. However, published data[7] gave evidence for the preference of a certain type of chirality, which was explained by the presence of cryptochiral (undetectable) admixtures. Such admixtures, although contributing negligibly to the total optical activity, can induce the formation of chiral structures of a certain sign. Since we used the surfactants certainly containing impurities (there are no pure surfactants at all), the most reasonable explanation (at least, at this stage of research) of the surfactant optical activity is the possible presence of cryptochiral admixtures. This makes the phenomenon observed not less interesting, not speaking that it creates a new tool for studying micelles in colloid science.

Thus, the above experiments show that we deal with a kind of supramolecular chirality originating from the micellar aggregation of surfactants. This kind of chirality can be called concentration chirality since it displays itself within a certain concentration range.

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