Quantification of counterion binding to and its effects on aqueous dispersions of dialkyl cationic surfactants

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Dialkyl cationic surfactants, such as dioctadecyl dimethyl ammonium chloride (DODAC) or bromide (DODAB) form multilamellar vesicles upon dispersion in water. In order to study the influence of the surfactant's counterion on its behaviour in aqueous dispersion, a method was developed that enabled to prepare the same dialkyl surfactant with different counterions, ranging from fluoride to iodide. Visually, quite transparent and hence rather uni- or oligolamellar vesicles were prepared when fluoride was selected as counterion, whereas very turbid dispersions were obtained using iodide instead, whereby the chloride and bromide surfactant had an intermediate behaviour. These observations seemed to indicate an increasing degree of surface charge neutralization by the heavier anions, in line with the Hofmeister series, which was indeed confirmed by electrophoretic light scattering measurements. The increased surface charge density also induced more interlamellar electrostatic repulsion, which was reflected by the increased d-spacing of DODAF as compared to DODAB.

In order to further quantify the surfactant-counterion interaction, diffusion H-NMR measurements were performed on dispersions of a dialkyl cationic surfactant with methyl sulphate counterion in deuterated water. The diffusion data clearly showed that the organic anion was largely surfactant bound in aqueous dispersions: whereas the diffusion coefficient of methyl sulphate in an aqueous solution of its sodium salt was 9.46 10^{-10} m²/s, this value was reduced to 1.79 10^{-10} m²/s when the methylsulphate was present as the counterion of cationic vesicles (whose diffusion coefficient was only 0.25 10^{-10} m²/s). When adding different sodium halides to the vesicular dispersion with methyl sulphate counterion, the mobility of the latter anion gradually increased from fluoride over chloride and bromide or iodide, which clearly indicated its gradual displacement from the vesicular surface by the stronger binding anions.

The data obtained indicate that the cationic dialkyl surfactant's counterion has a significant influence on its behaviour upon dispersion in water. Hence, selection of an appropriate counterion may enable to adjust or control the properties of vesicular dispersions. In addition, it was shown that the binding characteristics of inorganic anions may be indirectly determined from their effect on the diffusion properties of an organic counterion, which may be determined by H-NMR.