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NMR Study of Organic Counterion Binding to Perfluorinated Micellar Structures DOBRIN BOSSEV, Indiana University, MUSTUO MATSUMOTO, MASARU NAKAHARA, Kyoto University — In this study we have applied our previously developed NMR method to study the adsorption of tetramethylammonium (TMA^+) and tetraethylammonium (TEA^+) counterions to micelles formed by perfluorooctylsulfonate (FOS^-) surfactant in water at 30 °C. These two counterions induce formation of threadlike surfactant structures that result in well pronounced viscoelastic properties of the solution. To selectively probe the degree of counterion binding we have used ^1H and ^{19}F NMR chemical shifts and self-diffusion coefficients that are sensitive to the *Stern* and *diffuse double layers*, respectively. The competitive adsorption of TMA^+ and TEA^+ was examined as a function of the $\text{TMA}^+/\text{TEA}^+$ ratio at a constant FOS^- concentration of 100 mM. The two counterions were found to form Stern layer around the FOS^- micelles with comparable packing; about one counterion per two micellized FOS molecules. When mixed at intermediate proportions, however, the TEA^+ counterion shows preferential binding; the concentration of TEA^+ in the *Stern layer* is found to be twice higher than that of TMA^+ at equal total respective concentrations in the solution. These results are discussed in terms of counterion size and hydrophobicity and presented in parallel with those that involved the smaller and more hydrophilic lithium counterion.

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