Hydration of 3-(*N*,*N*-Dimethyldodecylammonio)propanesulfonate micelles using Dielectric Relaxation Spectroscopy

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INTRODUCTION: Salt addition alters surface hydration of ionic micelles affecting, among other properties, micellar growth. Using dielectric relaxation spectroscopy, DRS we demonstrated (Langmuir, **2013,**13;29(32):10037-46), that Trifluoromethanesulfonate ($CF_3SO_3^-$) counterion causes large interfacial hydration changes in positively charged micelles. Here we used DRS to investigate the hydration of zwitterionic 3-(*N*,*N*-dimethyldodecylammonio)propanesulfonate micelles (DPS), with added sodium salts (methanesulfonate, bromide, trifluoromethanesulfonate and trifluoroacetate). **OBJECTIVES**: Investigate the effect of salts on the hydration of zwitterionic micelles. **MATERIAL AND METHODS**: We measured solutions with different DPS concentrations (25-150 mM) and DPS 150mM with added salts (NaBr, NaMs, NaTfa, NaTfl) (50 and 100mM). The dielectric spectra were obtained in the range $0.01 \leq \nu/GHz \leq 89$, by combining multiple equipments. **RESULTS AND DISCUSSION**: The DRS spectra can be fitted by a sum of equations that describe physical processes occurring at different frequencies (modes). One mode is assigned to the relaxation of (bulk) water unaffected by the presence of the solutes. Other mode can be assigned to bound ('slow') water molecules hydrating the DPS head group. The difference between analytical water concentration and DRS detected water is the irrotationaly bound (ib) water. From the fitting, the amount of slow and ib water per surfactant, for pure DPS were: Z_s^{DPS} = 15.6±0.1, Z_{ib}^{DPS} = 3.9±0.8. For DPS+salts: Z_s^{salt} = 9.0±1.1, Z_{ib}^{salt} = 11.9±0.6. **CONCLUSION**: Part of the additional ib water was hydrating Na^+ where $Z_{ib}(Na^+)$ = 5.2±0.2 at $c \to 0$ (and $Z_s(Na^+)$ = 0). We may conclude that the additional (Z_{ib}^{salt} - $Z_{ib}(Na^+)$ ≈ 6-7) ib H_2O were only weakly bound by DPS in the salt-free solutions and were frozen because by simultaneously interacting with the DPS head groups and the added ions. This implies that the DPS head groups and the added cations and anions strongly interact in aqueous solutions.

Palavra chave: Dielectric Relaxation Spectroscopy, Hydration, Zwitterionic Micelles
Patrocínio: FAPESP, CNPq, NAP-FCx and INCT-Fcx.