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Anion-Exchangers Highly Recognizing Differences in Ionic Hydration and Origin of Separation Selectivity

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Summary

A novel charge-stacked zwitterionic surfactant, dodecyltetramethylethylenediammonio- propanesulfonate (DEP) bromide, has been synthesized, and the properties of its micelle has been studied by electrophoretic mobility measurements, potentiometry, NMR, and X-ray absorption fine structure (XAFS). Although the dissociation degree of Br⁻ from the micelle evaluated by potentiometry almost agrees with that determined by NMR, the former is slightly smaller than the latter over the entire range of the concentration of DEPB. This is explained by assuming that the bromide ions in the micellar system have several different peripheral structures. XAFS has given a significant insight into the hydration structures of Br⁻ involved in the system. Some of the bromide ions partitioned into the micelle are dehydrated and directly bound by the ammonium groups in the DEP molecules. However, a part of the bromide ions are still completely hydrated even when they are partitioned into the micelles. The average hydration number of the bromide ions directly bound by the ammonium groups was determined to be ca 3.3. The partial dehydration of Br⁻ is possibly facilitated by the characteristic hydration circumstances provided by the charge-stacked structure of the surfactant and by the resulting thick palisade layer of the DEP micelle.

The structure of DEP has been introduced onto a polymer resin to allow the preparation of a novel zwitterionic anion-exchange resin. The separation selectivity of this resin has been chromatographically studied, and the results are compared with those obtained with usual anion-exchange resins. The DEP-resin shows higher selectivity toward poorly hydrated ions and lower selectivity toward multivalent anions than conventional resins. This characteristic separation selectivity has been confirmed for the chromatographic retention of dicarboxylic acids; their retention becomes weaker as the pH of the mobile phase increases.