

Probing the electrical potential gradient of charged micelles using Benzoic-derived pH-probes

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Introduction: Surfactants can associate spontaneously in aqueous solutions forming aggregates with a variety of structures (e.g., micelles, liposomes, vesicles, bilayers). Micelles are dynamic aggregates and some of their interfacial properties can be related with those from biological membranes. pH-indicator properties change dramatically when charged surfactants are added to the solution. This property can be used to study the electrical potential profile of different aggregates using interfacially-bound pH-indicators, because the apparent pK_a changes can be related with both H⁺ (or OH⁻) distribution between the surface and bulk solution, as well as possible changes in the intrinsic pK_a of the pH probe.

Objectives: We have synthesized benzoic acid-derived probes containing a quaternary ammonium group to ensure interfacial binding in negatively charged micelles. These probes, in principle, could allow us to experimentally map the electrical potential gradient extending from the charged interface to bulk solution.

Methods and Results: N-amino-N-dimethyl-N-dodecyl-N-ethyloxi benzoic acid and two other probes with one or two additional ethyloxi extensor groups were used in this study. The pK_{a(app)}, defined as the bulk pH where the sum of the dissociated forms of the probe were equal to the protonated forms, were determined by spectrophotometric measurements in buffers with different pHs. The pK_{a(app)} in the presence of SDS increased markedly in relation to the pK_a in the bulk, decreasing discretely with [salt] and [SDS]. We found no significant differences in the pK_{a(app)} as the number of ethyloxy groups varied from 1–3. The intrinsic pK_a (pK_i) and the effect of [salt] on the pK_i was estimated by measuring the pK_{a(app)} of highly soluble probe analog of the probes.

Conclusion: Our results indicate that the three probes occupy similar environments in the SDS micelle surface.

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