

Anion Exchange on Cross-Linked Cationic Surfactant Micelles Across Ultrafiltration Membranes

Ming Chen

Abstract

Surfactant micelles combined with ultrafiltration can partially, or sometimes nearly completely, separate various ionic and nonionic pollutants from water. To this end, the selectivity of aqueous micelles composed of either cetyltrimethylammonium (CTA⁺) bromide or cetylpyridinium (CP⁺) chloride towards many environmentally relevant anions (IO_3^- , F^- , Cl^- , HCO_3^- , NO_2^- , Br^- , NO_3^- , H_2PO_4^- , HPO_4^{2-} , SO_4^{2-} , and CrO_4^{2-}) was investigated. Selectivity coefficients of CTA⁺ micelles (with respect to Br^-) and CP⁺ micelle (with respect to Cl^-) for these anions were evaluated using a simple thermodynamic ion exchange model. The sequence of anion affinity for the CTA⁺ micelles and for the CP⁺ micelles were the same, with decreasing affinity occurring in the order: $\text{CrO}_4^{2-} > \text{SO}_4^{2-} > \text{HPO}_4^{2-} > \text{NO}_3^- > \text{Br}^- > \text{NO}_2^- > \text{Cl}^- > \text{HCO}_3^- > \text{F}^- \approx \text{H}_2\text{PO}_4^-$. From the associated component mass balance and ion exchange (i.e., mass action) equations, an overall speciation model was developed to predict the distribution of all anions between the aqueous and micellar pseudo-phase for complex ionic mixtures. Experimental results of both artificial and typical surface waters were in good agreement to model predictions.

A significant issue with surfactant micelle enhanced ultrafiltration is the significant and constant loss of surfactant monomers across the membranes due to the fact that surfactant monomers within the micelles are in rapid equilibrium with the aqueous phase surfactant monomers. To overcome this issue, a new quaternary ammonium hydroxypropyl conjugated linoleic acid ester (QACLE) cationic surfactant was synthesized through the reaction of conjugated linoleic acid (CLA) and (2,3-epoxypropyl) trimethylammonium chloride (ETAC). When QACLE was present in aqueous micellar form, it was easily crosslinked, forming stable cross-linked quaternary ammonium linoleate ester (QALE) nanoparticles with high anion exchange capacity.

The selectivity coefficients of the QACLE micelles towards the common anions in natural water were evaluated using the ion exchange thermodynamic model, and was compared to those measured for micelles composed of two commercially available cationic surfactants, cetyltrimethylammonium bromide (CTAB) and cetylpyridinium chloride (CPC). The sequence in anion affinity for all the three micellar phase was the same. Using the necessary mass balance and ion exchange reactions, a model was developed to predict the distribution of all anions between the aqueous and nanoparticle phases. The model was applied to predict anion association to QALE nanoparticles, contained in dialysis membranes, in phosphate-enriched river water, and the results indicate that the cross-linking of QACLE monomers did not alter the values of the selectivity coefficients for any of the anions. The relatively large affinities of the divalent anions and NO_3^- , and the experiment results (using artificial and real surface waters), indicate that the new QALE nanoparticles have the potential to recover anionic nutrients from natural and polluted waters.