Ion Transport Mechanisms in Liquid−Liquid Interface

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Here, we study by combining atomistic MD simulations with experimental measurements the molecular mechanisms of extractant facilitated ion transport through the liquid−liquid interface. Formulation of a water-in-oil microemulsion with density and dimensions amenable to MD simulations provides the feasibility of investigating mechanics of the nanoscale liquid−liquid ion exchange process. Our results show no evidence of extractant participation at the water/oil surface in the microemulsion, contrary to current hypotheses. Instead, we propose that ions are exchanged via water channels that penetrate the interfacial zone and connect the extractant molecules with the aqueous phase.

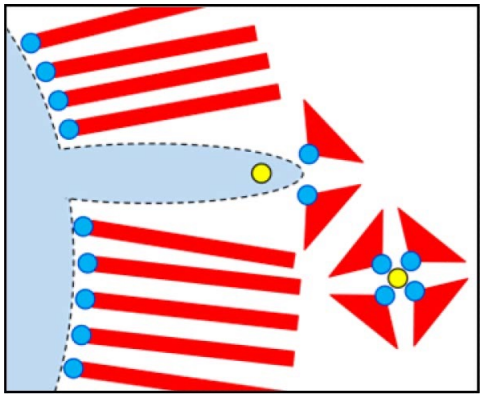

Figure. A scheme summarizing the cation exchange mechanism suggested by the convergent experiment and simulation results. The scheme illustrates how the molecular geometry of extractants like HDEHP (wedge-shaped molecules) differs from surfactants like CTAB (rod-shaped molecules). Polar heads are in blue and lipophilic tails are in red. The relatively low packing parameter of the CTAB surfactant allows the formation of low curvature monolayers at the oil−water interface. The very high packing parameter of extractants caused by multiple short branched tails disfavors participation in flat structures and forces highly negative curvature. The very high curvature offered by the water channel “finger” provides a location where several extractant molecules may converge and exchange ions.

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