

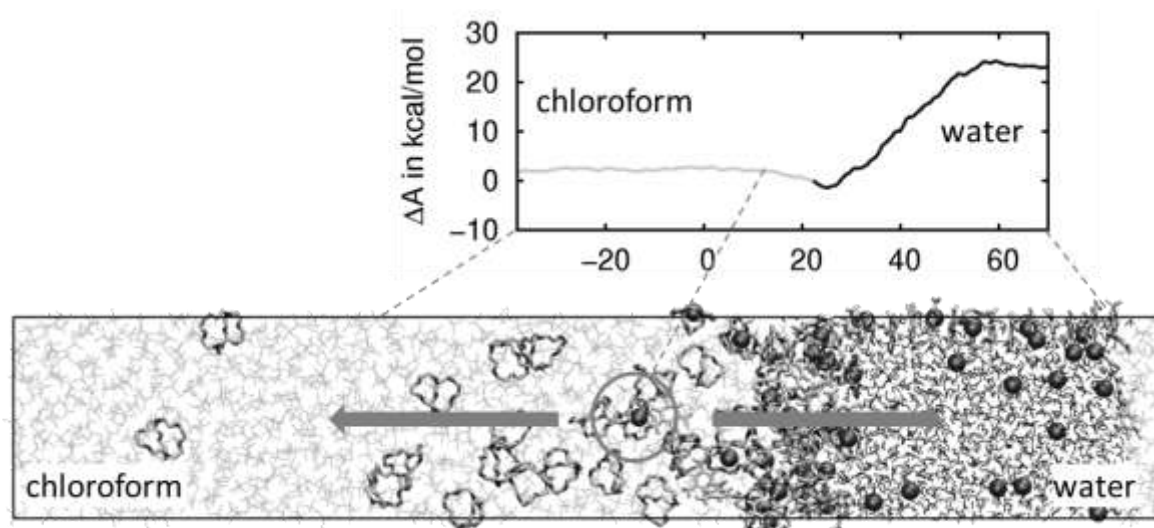
[P18] Complexation and extraction of $K^+ \subset 222$ cryptates across a liquid-liquid interface studied by MD and PMF simulations.

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We report molecular dynamics "MD" studies of systems involved in the extraction of potassium picrate $K^+ Pic^-$ by the 222 cryptand from an aqueous to a chloroform phase.

We focus on (i) the complexation reaction in the two phases and at the interface, and on (ii) the surface activity and partitioning of $K^+ \subset 222$ cryptates. The free energy profiles for K^+ complexation by 222 and for interface crossing by $K^+ \subset 222$ are investigated by potential of mean force "PMF" calculations. These account for the affinity of 222 for K^+ in bulk aqueous and organic phases, as well as at the interface. Furthermore, using different electrostatic representations of the solvents and solutes, we show that, in spite of their "spherical" shapes, the free 222 and its complex are surface active. The free $K^+ Pic^-$ ions also display some surface activity, contributing to lower the interfacial tension. As a result, (i) the cation uptake process is promoted "right at the interface", i.e. a nanosized thin domain (ii) diffusion of the complex from the interface to the oil phase becomes facilitated. This feature is confirmed by MD simulations of a biphasic concentrated solution of cryptates, free ligands and $K^+ Pic^-$ ions, as well as by the PMF free energy profiles for interface crossing.



Mixture of 10 $K^+ \subset 222 Pic^-$ + 20 222 + 20 $K^+ Pic^-$ species at the interface (chloroform, *left* and water, *right*). *Top*: Free energy profile (ΔA in kcal.mol⁻¹) for interface crossing by the $K^+ \subset 222$ complex. *Bottom*: snapshot after 10 ns of dynamics.

This work is performed in the context of the "Labex Chimie des Systèmes complexes". Chimie supramoléculaire.