23b Ion – Exchange of Monovalent and Bivalent Cations with Naa Zeolite Membranes : a Molecular Dynamics Study

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Molecular simulations using the method of molecular dynamics have been carried out to study the dynamics and energetics of ion exchanges between monovalent and bivalent cations in supercritical and subcritical (liquid) electrolyte solutions (here Li+, and Ca++ in aqueous solutions of LiCl and CaCl2) and an ion exchange membrane (NaA zeolite) using direct simulations of upto a nano-second or more. NaA zeolites are widely used in many commercial ion-exchange processes including detergents. Our results show that with appropriate driving forces, such ion exchange processes can be clearly witnessed and investigated using molecular simulations at these time scales, especially for supercritical solutions. We have also attempted to understand the phenomenon of ion exchange at the molecular level. Our results have shown that the ion-exchange process is primarily energetically driven and entropic forces do not appear to be playing a significant role in the exchanges observed. For supercritical LiCl solutions, we found small differences between the energy of the Li+ inside and outside the membrane. In contrast, for Na+ there was a considerable energetic advantage in being outside the membrane, making the overall exchange process energetically favorable. In subcritical (liquid) LiCl solutions we found an exchange to be more favorable energetically than supercritical solutions. For Ca++ similar trends were observed, except the differences in the energies were much larger (compared to the corresponding Li+ exchanges), making them more energetically efficient, as has also been observed experimentally. In addition to clarifying the molecular basis for these exchanges, simulations can also potentially be very useful to determine the behavior (e.g. state dependence, etc.) of hydrodynamic parameters commonly used to characterize ion-exchange processes at a fundamental molecular level, and to determine if the hydrodynamic equations used for ion-exchange processes are applicable to nano-systems that can be studied using simulations.