From aluminum electrolysis up to nuclear reactors: some experimental and theoretical approaches of molten salts organization.

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In aluminum production, the alumina (Al_2O_3) dissolution in the electrolyte is of major importance in the industrial process. The electrolyte is a cryolitic bath containing mainly NaF and AlF_3 at around 1000°C where the main anionic species are fluoroaluminates ions such as $[AlF_6]^{3-}$, $[AlF_5]^{2-}$, $[AlF_4]^-$ and F^-. During Al_2O_3 dissolution, different kinds of oxyfluoroaluminates species are formed. However, due to the difficult experimental conditions and the large number of potential ions, no quantitative speciation could be made up to now. A speciation of alumina-cryolite melts combining in situ NMR experiments, classical molecular dynamics simulations and electronic structure calculations, allows us to establish the nature and quantities of each species, depending on the Al_2O_3 concentration. In particular, we have shown that the oxygen atoms are always linked to at least two Al atoms, leading to the formation of polymeric oxyfluorides. From the dynamic point of view, the simulations also show that the lifetime of the O-Al bonds is also much longer than the F-Al ones. The same approach can be proposed to describe thee speciation of molten fluoride mixtures based on ThF_4 and UF_4 actinides used in molten salt reactors. The local structure of molten AF-MF_4 systems ($A=Li^+$, Na^+, K^+; $M= Th^{4+}$, U^{4+}) is studied in situ by combining measurements by high temperature X-ray absorption spectroscopy and molecular dynamics simulations. In the molten state, these mixtures are composed of free fluorine and anionic species $[MF_7]^{3-}$, $[MF_8]^{4-}$ and $[MF_9]^{5-}$ whose distribution varies with the amount of MF_4 ($M= Th^{4+}$, U^{4+}).
We are now able to calculate directly the chemical shifts and the EXAFS spectra corresponding to the system, thanks to the coupling between molecular dynamic calculations and theoretical approach with experimental measurements. This new step towards a better description of the speciation in such molten salts will provide a new capability to determine the physical and chemical properties of molten fluorides.

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