

588d Molecular Dynamics Studies on the Stability of Cage-like Polysilicate Ions in Tma Aqueous Solution

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Zeolite crystallization assisted by organic cations, typically tetraalkylammonium cations (TAA), involves complex solution and colloidal chemistry. A host of modern analytical techniques have been employed in studies aimed at elucidating the molecular processes that take place. A detailed understanding of the atomic scale mechanisms of the template-assisted formation of these materials is a prerequisite before we are able to develop rational strategies for their design which remains chiefly an empirical endeavour and usually requires very costly trial-and-error modifications to reagents and conditions.

We shall present results from fully atomistic simulations with explicit solvent on the interactions between tetramethylammonium (TMA) and two cage-like, silicate polyions: the cubic octamer Si_8O_{20} , and the prismatic hexamer Si_6O_{15} . Our interest in these model systems is motivated by the fact that, in spite of their sub-nanoscale dimensions, they already manifest clear signs of control over speciation. Specifically, and as opposed to the multitude of small, often asymmetrical silicate anions found in alkali-metal silicate solutions, concentrated TMA--silicates are dominated by a few compact, cage-like species such as the cubic octamer and to a lesser extent the prismatic hexamer. The relatively small size of these polyions makes them amenable to computer simulation by means of which we can study the interactions between the silica species and the organic cation on an atomic scale, while taking into account the full effects of the solvent explicitly. Our objective is by careful analysis of the structure and dynamical behaviour of these tractable paradigms to obtain insights into the structure and stabilization of silica nanoparticles which form during zeolite synthesis under hydrothermal conditions. It is well-established that under such conditions synthesis of several zeolite types (silicalite-1, Si-MTW, Si-BEA, and LTA,) proceeds through a long-lived metastable state which involves the formation of small colloidal particles, 10 nm or less in diameter. A major step in answering a host of questions in zeolite crystallization would be to understand the structure and stabilization of these nanoparticles and the mechanism by which they contribute to the growth of larger crystallites. Central, in all these questions, is the role of the organic cations. Very little consensus exists regarding these issues. Controversy arises primarily because the analytical techniques that are used (NMR, neutron scattering, x-ray scattering) are either not sensitive to the detailed microscopic structure of these species or else require a considerable degree of interpretation to obtain structural information.

The stability of silica octamers, Si_8O_{20} , observed in aqueous tetramethylammonium (TMA) solutions by NMR spectroscopy, has been investigated in connection with the TMA concentration by performing equilibrium molecular dynamics simulations of octamer--TMA--water mixture at two concentrations. At the experimental concentration at which the silica octamers have been observed spectroscopically, we find that on the average six TMA molecules surround the silica octamer, coordinated so that each cation occupies a face of the cubic octamer. Our simulations reveal that as TMA adsorbs, it expels water molecules from the surface of the octamer but, remarkably, it appears to do so in a fashion that does not disrupt the hydrogen-bond network in which the silanol (surface) oxygens participate. The water molecules that leave the surface are those previously found in the vicinity of the siloxane (bridge) oxygens, which themselves participate in hydrogen bonds due to the negative partial charge that they carry, albeit smaller than that of the silanol oxygens. On the other hand, at concentrations at which no octamers have been observed experimentally, our simulations show that practically no TMA adsorption takes place. Moreover, in this case the solvent structure in the vicinity of the silica solute remains unaltered and in essence the same one we calculate for TMA-free solution.

The stability of the prismatic hexamers, Si_6O_{15} , in TMA solution has similarly been investigated by performing equilibrium molecular dynamics simulations of the hexamer--TMA--water mixture. We have found that on the average 2.8 TMA molecules surround the hexamer, coordinated preferentially opposite the four-ring faces. On account of the fact that the remaining faces get exposed to the water molecules, and thus the corresponding siloxane bonds are vulnerable to hydrolysis, we have concluded that in aqueous TMA solution the hexamer is not as stable a species as the cubic octamer. These results are in complete agreement with experimental findings that under the concentration conditions examined the hexamer is always pitted against the octamer.

We have studied the energetics of this preferential stabilization by calculating the relative change in the free energies of formation between the complexes $\text{Si}_8\text{O}_{20}.8\text{TMA}$ and $\text{Si}_6\text{O}_{15}.6\text{TMA}$ --- the former is found to be more stable by 70 kcal/mol.

These findings reinforce the theory that adsorption of TMA at the surface of these cage-like polyions protects the siloxane group from hydrolysis by expelling water in the vicinity of the bridge oxygens.