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Investigation of the role of alkali cation in early stage of oligomerization in silicate fluids: a molecular dynamics study

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Context
- Solutions of activation (= alkali media) of aluminosilicate are environmentally friendly and considered as green chemistry (used for ground stabilization, painting,...)
- The formulation is complex since the parameters are various and numerous
- Understanding the ion-ion interactions for the oligomerization process where the nature and concentration of alkali drives the final properties of the gel [1]
- Molecular dynamics is a useful tool to fill the gap between theoretical and experimental studies
- Molecular dynamics allows the calculation of the structural and dynamical properties of the solutes in solution
- Effect of water, alkali and hydroxide are explicitly taking into account

Method
- Classical Molecular Dynamics (MD)
  - Molecular dynamics simulations using explicit polarization with AMBER14 [3]
  - Development of a polarizable silicate force field for describing all the silicate oligomers by assembling neutral and anionic fragment (10 types of atom)
  - MD simulations focused on 3 species:
    - SiO(OH)$_2^-$
    - Si$_2$O$_2$(OH)$_4^-$
    - Si$_4$O$_6$(OH)$_8^-$
- X-ray scattering intensity from MD simulation
  - Calculation of I(q) from radial distribution functions
    \[
    I(q) = \sum_{\alpha \beta} f_\alpha f_\beta q^2 \sqrt{N_\alpha N_\beta S_{\alpha\beta}(q)}
    \]
  - Theoretical I(q) directly comparable to experimental one
  - Efficient method for describing alkali media [4] study of silicate oligomers in such media

Silicate in NaOH concentrated media
- Pure oligomer solutions
  - [Si]/[Na]$^+$ = 1
    - 300 Na$^+$
    - 300 SiO(OH)$_2^-$
    - 150 Si$_2$O$_2$(OH)$_4^-$
    - 150 OH$^-$
  - [Si]/[Na]$^+$ constant
  - Provide a “buffer media”
- Mixtures of oligomers
  - [Na]$^+$ free, constant
  - Si$_4$O$_6$(OH)$_8^-$ rich mixture
    - 300 Na$^+$
    - 37 Si$_2$O$_2$(OH)$_4^-$
    - 37 Si$_2$O$_2$(OH)$_4^-$
    - 152 Si$_2$O$_2$(OH)$_4^-$
- Scattering intensities from MD
  - Same structure for Q > 1 Å$^{-1}$
  - Rise for Q < 0.4 Å$^{-1}$ (aggregation)
  - Presence of monomers decreases the I(Q) at small angles

Conclusions and Outlines
- Structure of the solution depends on the oligomer composition and nature:
  - Spontaneous aggregation of dimers in solution: aggregates composed of silicates and Na$^+$
  - Dimers Si$_2$O$_2$(OH)$_4^-$ interact strongly with Na$^+$
  - Monomers SiO(OH)$_2^-$: small aggregates, and destabilize the aggregation (entropic effect)
- Similar behaviors of Na$: “buffer media” with the hydroxide anions
- MD simulations of “real” solutions:
  - Different [Si]/[Na]$^+$ ratios with respect to NMR experiments
  - Influence of the alkali nature on the aggregation

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References

Ground stabilization on building site (Institut National de la Recherche Agronomique, Domaine de Bagnols-sur-Cèze)

Stability diagram for soluble silicates at 298 K [3]

Concentrated aqueous solutions of NaOH

Experiments

Dynamiste (CNRS, Université Montpellier - UMR 5257 CEA - Université Montpellier - CNRS - ENSCM, BP 17111, F-30207 Bagnols-sur-Cèze)

CEA, Nuclear Energy Division, Research DE2D (SEAD, LCBC) BP 17111, F-30207 Bagnols-sur-Cèze