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Silica oligomerization in presence of divalent cations[†]

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Solvation of monocalcium silicate

The criteria for selection of an optimum number of water molecules is to maximize the number of water molecules surrounding and interacting with Ca as well as maximizing the stabilization energy per water molecule ($\Delta E_{stb}/n$). The stabilization energy per water molecule can be expressed in terms of both change in enthalpy (ΔH) as well as change in Gibbs free energy (ΔG). Here stabilization energy can be defined as

$$\Delta E_{stb} = E(monocalciumsilicate) + n.E(H_2O)$$
$$-E(monocalciumsilicate.nH_2O) \tag{1}$$

The stabilization energy involves contribution from ionic interaction H_2O-Ca and hydrogen bond $Si-O \cdots H-OH$. Fig. 1 shows the variation of stabilization energy with change in the number of added water molecules. It clearly demonstrates that beyond 2 water molecules $\Delta E_{stb}/n$ starts decreasing. Here it should be noted that water molecules can be added at random configuration. The following graph was plotted using configurations with the least energy. In case of 2 water system each water molecule forms an ionic bond with Ca and a hydrogen bond with separate oxygen atoms as $O \cdots H-OH$. When this number is raised to 4, still each water molecule remains ionic bonded with Ca but they form hydrogen bonds as $HO-H \cdots O \cdots H-OH$, which ultimately results in loss of individual hydrogen bond strength and hence $\Delta E_{stb}/n$ reduces. Any further ex-

plicitly added water molecules fail to undergo interaction with both Ca and silicate ion. This observation motivated us to select the configuration with 4 water molecules for further calculation. It should also be noted that consideration of 4 explicit water molecules satisfies the hexacoordination of Ca^{2+} ion.
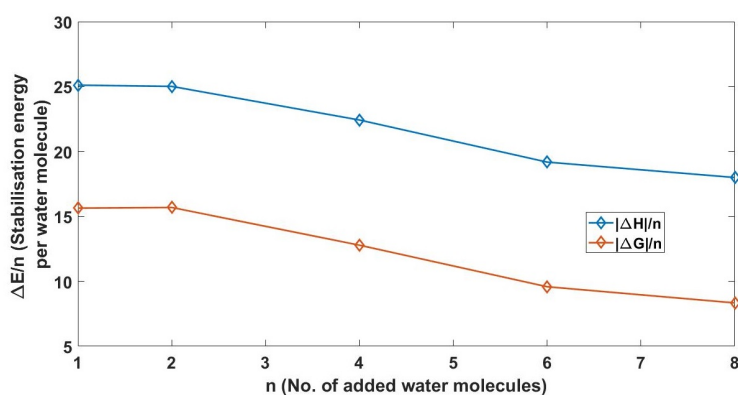

Fig. 1 Stabilisation energy per water molecule shown in terms of enthalpy (ΔH) as well as gibbs' free energy (ΔG) for system with number of added water molecules varying from 1 to 8.

Thermochemisrty

The Finite temperature calculation of Gibbs free energy (G) requires enthalpy (H) as well as entropy (S). Enthalpy (H), entropy (S), and Gibbs free energy (G) are related to each other as

$$G = H - TS = U + PV - TS \tag{2}$$

where PV is approximated to $\kappa_B T$ ($\kappa_B =$Boltzmann's constant). Internal Energy (U) is expressed as the sum of the electronic energy of the system (ε) and kinetic energy having a contribution from translational, electronic, vibrational, and rotational motion. Electronic energy (ε) is the direct outcome of SCF calculation while the kinetic energy components are derived from partition function q obtained for different types of aforementioned motions. Entropy (S) and thermal energy (E) is calculated from the partition function q as follows.

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$$S = R + R\ln(q(V,T)) + RT\left(\frac{\partial \ln q}{\partial T}\right)_V \qquad (3)$$

$$E = N\kappa_B T^2 \left(\frac{\partial \ln q}{\partial T}\right)_V \qquad (4)$$

Finally, G is calculated as

$$G = \varepsilon + E + \kappa_B T - TS \qquad (5)$$

Where E and S include the contribution from all different kinds of motion. E includes the zero point vibrational energy also.