Free energy of metal ion binding to some functional groups of concrete admixtures in water

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Concrete is the most used man-made materials on earth and has played a fundamental role in shaping our word, ranging from the cities we live in, roads and railways, to the infrastructure to support lower-carbon energy solutions [1]. Compared to other building materials, concrete is inherently a low carbon constructional material. However, as a result of the large volumes of concrete used, the production of Portland cement, the main binder of concrete, contributes 5–8% of annual anthropogenic global CO_2 production [2,3] What can we do to reduce the carbon footprint and to further improve the environmental performance of concrete? Various solutions have been proposed and practiced, such as partial cement replacement by supplementary cementitious materials, development of low-carbon binders, reducing the amount of cementitious material altogether, and enhancement of concrete strength and durability; however, such solutions are often not possible without the development of efficient concrete admixtures, which have now become indispensable ingredients for the production of modern advanced concrete.

There are two main types of concrete admixtures—chemical admixtures and mineral admixtures, both of which can be further grouped into various categories according to their function and chemical constituents. Our work focuses on the development of chemical admixtures, such as superplasticizers, slump-retaining admixtures, rheology modifying agents, and air entraining admixture. While those molecules are designed to sever different functions, most of them contain anionic functional groups and are supposed to act at interfaces [4]. However, the aqueous phase where chemical admixtures are dissolved in contains various metal cations, which may bind to the anionic functional groups of the chemical admixtures and play a profound role in their functions. We believe it is crucial to understand such binding interactions in order to understand the working mechanisms of chemical admixtures and to develop more efficient admixtures. Our current work has focused on calculations of the binding free energies of two different metal cations (Ca^{2+} and K^{+}) with several different functional groups of chemical admixtures via two different methods—the quantum density functional theory (DFT) method and classical the force-field-based Metadynamics method. The binding free energies for potassium and calcium cations with different functional groups such as phosphonate, phosphate, carboxylate, sulfonate, sulfate, and alkoxide, as the complexes, have been explored in detail by the two methods.

References

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