

## The difference of diffusion coefficients in water for arsenic compounds at various pH and its dominant factors

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Toxicity of arsenic is significantly variable depending on its speciation and it is important to understand the migration behaviors of this speciation, where diffusion can control transport mechanism in the impermeable layer such as in the pore waters of sediments and rocks. Diffusion coefficients ( $D$ s) of arsenite, arsenate, methylarsonic acid (MMA), and phenylarsonic acid (PAA) as a function of pH were determined in this study, which contributes to the better understanding of transport of various arsenic speciation in the environment. By aid of *ab initio* molecular orbital (MO) calculations and Monte Carlo (MC) simulations, this study sheds light on the origin of pH dependence on the diffusion coefficients for the arsenic compounds.

Diffusion experiments were conducted by diffusion cell method, and  $D$ s were determined by measuring the concentrations of arsenic species every 10 minutes during the diffusion. The concentrations were measured by ICP-MS. The molar volumes and electrostatic potential maps were calculated by means of *ab initio* MO method to estimate the molecular size and the degree of polarization of arsenic compounds. Radial distribution functions of distances between arsenic and oxygen atoms in water molecule for arsenic compounds were determined by MC simulations to obtain hydration structures of arsenic species.

The  $D$ s of arsenic compounds decreased with increasing pH, and the trends were different depending on the type of compounds. With particular reference to the arsenate derivatives,  $D$  was different reflecting difference of functional groups at low pH, but  $D$  became similar at high pH even though they have different solute sizes. The molecular simulations indicate that for the neutral speciation at low pH, the diffusion is dominated not only by the molecular size but also by charge distribution in the molecule (degree of polarization). On the other hand, for the dissociated speciation at high pH, the diffusion is dominated by charged oxyanion due to high association of water molecules regardless their functional groups. This effect is common for all the arsenic species, which causes that the differences in their  $D$ s become smaller as the pH increases, especially for arsenate, MMA, and PAA.

Keywords: arsenic compound, diffusion coefficient, pH dependence, *ab initio* MO method, Monte Carlo simulation, hydration structure