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Diffusion Coefficients of Arsenate and Arsenite in Water at Various pH

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Diffusion coefficients (*D*) of arsenite and arsenate at various pH, or degrees of dissociation, were reported by diffusion cell, some values of which are newly reported in this letter. Systematic decrease of *D* depending on the dissociation of arsenite and arsenate shows that *D* is closely related to the size of the hydrated ions.

Recently, environmental behavior of arsenic in natural waters has been of great interest in environmental chemistry, especially in groundwater–sediment systems due to the arsenic contamination of groundwater in large areas in Southeast Asia.[1,2] For the understanding of the migration of arsenic in stagnant water such as in sediments, diffusion of dissolved arsenic species should be quantified based on the diffusion coefficients (*D*) in water. Actually, the diffusion of arsenic species across soil–water[2] and sediment–water[3] interfaces has been discussed in environmental studies. However, *D* values for arsenite and arsenate, two main arsenic species in natural water, have been reported only for (i) H_3AsO_3 and (ii) H_3AsO_4 and $H_2AsO_4^-$.[4,5] The *D* values for $H_2AsO_3^-$, $HAsO_4^{2-}$, and $HAsO_4^{3-}$ were not determined, though they can be present under circumneutral and alkaline conditions in natural waters. Thus, *D* values of arsenite and arsenate at various degrees of ionization including $H_2AsO_3^-$, $HAsO_4^{2-}$, and $HAsO_4^{3-}$ were determined in this study from the viewpoint of environmental chemistry, based on which we can also discuss their hydration at various pH.

In this study, *D* values of arsenite and arsenate species were determined by diffusion-cell method following previous studies.[6–8] The diffusion cell in this study is made of acrylic plastic consisting of two chambers (source and the measurement cells; each cell is a 5.0-cm cube), partitioned by a membrane filter (polycarbonate) with the following dimensions: pore diameter 0.80 µm, thickness 11 µm, and porosity 0.15. At the beginning of the experiment, the source cell was filled with a solution containing arsenite or arsenate ($[As] = 0.10\,mg\,kg^{-1}$), while the measurement cell was filled with Milli-Q water. The concentration gradient between the source and measurement cells induces the diffusion of the ions from the source to measurement cells through the membrane. The *D* values of arsenic species were determined by the dependence of the concentration on the elapsed time (C_1 and C_2: concentrations in source and measurement cells, respectively) at 25.0 ± 0.2 °C and ionic strength of 0.10 M ($NaNO_3$). The solution in each chamber was stirred by a magnetic stirrer at 600 rpm. The concentrations of arsenic as well as cesium (Cs) and strontium (Sr) (internal standards to obtain *D*) were determined by ICP-MS.

In the model by Deen et al.,[6] the dependence of $\ln[(C_1 - C_2)_0/(C_1 - C_2)_t]$ on time gives a slope $2Ak/V$ (A: membrane area; k: mass-transfer coefficient; V: volume of the solution in the cells). The k value reflects the mass-transfer resistance, which must be calibrated to determine the unknown diffusion coefficients. Moreover, k is expressed by k_1, k_2, k_3, and D as $1/k = (k_1 + k_3)/D + k_2/D_{2/3}$ (eq 1). The three constants k_1, k_2, and k_3 are characterized by the rate of mass transfer in the diffusion cell, which depends on the membrane properties, cell geometry, and stirring speed but not on the nature of the solutes. Since k can be measured from the diffusion experiment, D can be calculated from eq 1 if we knew $(k_1 + k_3)$ and k_2. To determine D for arsenic, we simultaneously obtained the diffusion curves for Cs^+ and Sr^{2+} ions with known diffusion coefficients[4] added into the solution to obtain the $(k_1 + k_3)$ and k_2 (Figure 1). The D values of arsenic species were determined by the diffusion curves of the arsenic species (to obtain k for the species) with calibrated $(k_1 + k_3)$ and k_2.

Typical diffusion profiles shown in Figure 1 were straight lines with different slopes for Cs^+, Sr^{2+}, and arsenate, showing that our experiments obeyed the model written above. Thus, we could obtain *D* for arsenite and arsenate at various pH, or degrees of dissociation. The pH dependence of *D* for arsenite shows that the *D* was constant between pH 2 and 6 (Figure 2a), where arsenite was not dissociated. The *D* for H_3AsO_3 was $(11.6 \pm 0.1) \times 10^{-6}\,cm^2\,s^{-1}$, which was consistent with $11.1 \times 10^{-6}\,cm^2\,s^{-1}$ in Leaist (2007).[5] However, *D* values for $H_2AsO_3^-$ and $HAsO_3^{2-}$ were not reported. Above pH 7 where it starts to dissociate, the *D* decreased as the increase in pH. In general, diffusion coefficient in water as hydrated ion reflects the size of the species diffusing in water, hydrated ion. Thus, the decrease of *D* coupled with the dissociation shows that the number of water molecules associated with $HAsO_3^{2-}$ increases by the dissociation due to the larger electrostatic interaction.

Based on the pH dependence, *D* for $H_2AsO_3^-$ was estimated to be $(9.71 \pm 0.02) \times 10^{-6}\,cm^2\,s^{-1}$ (pH 11.0; $H_2AsO_3^-$ fraction: 91%). The value is ca. 16% smaller than that of H_3AsO_3, showing that diffusion distance in natural systems estimated using *D* for

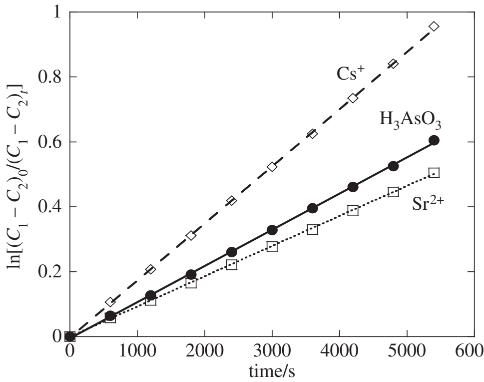

Figure 1. Diffusion profiles of arsenite, Cs^+, and Sr^{2+} at pH 4.5.

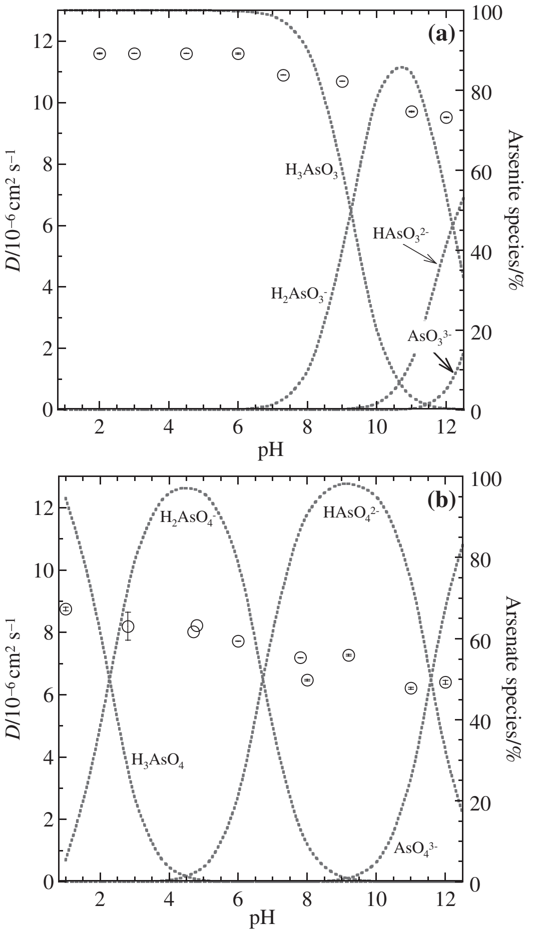

Figure 2. *D* of arsenite and arsenate and their dissolved species.

arsenite species by H_3AsO_3 can be overestimated at pH above 8, frequently encountered in natural waters. Our data in Figure 2 can be apparent values when more than two species coexist at certain pH but can be used directly to estimate precisely the diffusivity in environmental and hydrological studies.

Similar results were also obtained for arsenate at various pH (Figure 2b). The *D* of arsenate decreased with increasing pH. The *D* starts to decrease from lower pH compared with arsenite due to the lower pK_{a1} (=2.2) of arsenate. The *D* continuously decreased with increasing pH possibly due to the subsequent dissociation to $HAsO_4^{2-}$ and AsO_4^{3-}. More dissociated species has thicker hydration layer, resulting in the slower diffusivity. The pH dependence allows us to estimate *D* for H_3AsO_4, $H_2AsO_4^-$, and $HAsO_4^{2-}$ as $(8.75 \pm 0.06) \times 10^{-6}\,\mathrm{cm^2\,s^{-1}}$ (the value at pH 1.0), $(8.12 \pm 0.10) \times 10^{-6}\,\mathrm{cm^2\,s^{-1}}$ (pH 4.75), and $(7.27 \pm 0.03) \times 10^{-6}\,\mathrm{cm^2\,s^{-1}}$ (pH 9.2), respectively. The *D* for AsO_4^{3-} can be lower than $(6.40 \pm 0.06) \times 10^{-6}\,\mathrm{cm^2\,s^{-1}}$, the value at pH 12.0 where the proportion of AsO_4^{3-} is 72%. The *D* for $HAsO_4^{2-}$ has not been reported elsewhere. The first two values were reported previously as 8.09×10^{-6} and $8.3 \times 10^{-6}\,\mathrm{cm^2\,s^{-1}}$.[5] Considering that the species with more charges usually diffuse slower, the *D* values for H_3AsO_4 and $H_2AsO_4^-$ reported in this letter may be more reasonable, though the difference is not very large.

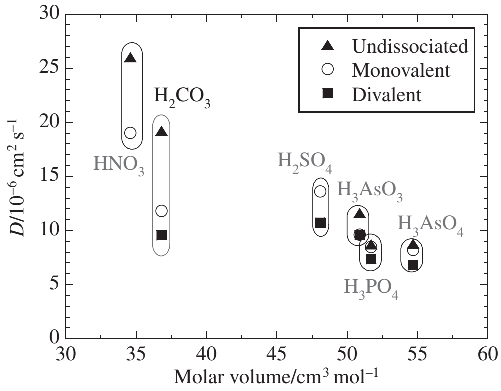

Figure 3. *D* vs. molar volumes of corresponding oxoacids.

Compared with arsenate, arsenite, which is more toxic than arsenate, diffuses faster than arsenate. The degree of decrease of *D* with pH was larger for arsenate than arsenite due to the presence of ions with more charges, or thicker hydration layers. Even for neutral species, however, *D* for H_3AsO_3 is larger than H_3AsO_4 possibly caused by the larger size of the latter species. Based on the Stokes–Einstein equation for spherical ion ($D = k_BT/6\pi\mu R_H$), size (radius) of the diffusing species (R_H) of H_3AsO_4 was calculated to be 280 pm. On the other hand, the size of H_3AsO_4 is assumed to be $R_{As\text{–}O} + R_O$ ($R_{As\text{–}O}$: interatomic distance between As and O; R_O: ionic radius of O^{2-}), which was 300 pm. The results suggest that the hydration layer for H_3AsO_4 is thin for the neutral species.

The relationship between *D* values[4,5,9–12] and molar volumes of corresponding undissociated oxoacids (Figure 3; Supporting Information[13]) showed that for smaller ions such as nitrate and carbonate, decrease of *D* by the dissociation is much larger than those of arsenate. However, *D* value is smaller for arsenate than nitrate and carbonate, which may be caused by the size of the species, suggesting thinner hydration layer for larger oxyanions such as arsenate.

As shown in this study, *D* can be different among different arsenic species (arsenite vs. arsenate; various degrees of dissociation), which must be taken into account for the precise evaluation of environmental behaviors of arsenic in natural waters.

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13 Supporting Information is available electronically on the CSJ-Journal Web site, http://www.csj.jp/journals/chem-lett/index.html.