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Chemical speciation of inorganic and methylarsenic(III) compounds in aqueous solutions†

Hiroshi Hasegawa[1]*, Yoshiki Sohrin[2], Masakazu Matsui[2], Noriko Takeda[1] and Kazumasa Ueda[1]

[1]Department of Chemistry and Chemical Engineering, Faculty of Engineering, Kanazawa University, Kodatsuno 2-40-20, Kanazawa 920-8667, Japan
[2]Institute for Chemical Research, Kyoto University, Uji, Kyoto 611-0011, Japan

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Speciation of inorganic and methylarsenic(III) species in aqueous hydrochloric acid solutions has been studied by the solvent extraction method. In a hydrochloric acid–carbon tetrachloride system, inorganic and methylarsenic(III) species formed the corresponding chlorides and were extracted into the organic phase. The extractability of inorganic and methylarsenic(III) species increased as the number of methyl groups attached to the arsenic atom increased. In addition, dimerization of dimethylarsinous acid occurred with decreasing acidity in the aqueous phase. On the basis of the data obtained, we determined the stability constants for the proposed species, and evaluated the effect of methyl groups on the speciation and the reactivity of inorganic and methylarsenic(III) species in aqueous solutions. Copyright © 2002 John Wiley & Sons, Ltd.

KEYWORDS: arsenic; speciation; methylarsenic(III) species; solvent extraction; halogen substitution; aqueous solution

INTRODUCTION

Biological availability and toxicological impact of trace elements are directly related to their chemical speciation in aquatic systems. From the viewpoint of arsenic speciation, inorganic species (arsenate [$AsO(OH)_3$] and arsenite [$As(OH)_3$]) and organic species (methylarsonic acid [$CH_3AsO(OH)_2$; MMAA(V)], dimethylarsinic acid [$(CH_3)_2AsO(OH)$; DMAA(V)], trimethylarsine oxide, arsenobetaine, arsenosugars, etc.) have been reported.[1–5] Most of the organoarsenic species are metabolized via the pathway for arsenic biosynthesis, which involves reduction of arsenic(V) species to arsenic(III) species followed by oxidative addition of methyl groups to the arsenic atom.[4–6] Recently, the existence of the metabolic intermediates, monomethylarsonous acid [$CH_3As(OH)_2$; MMAA(III)] and dimethylarsinous acid [$(CH_3)_2As(OH)$; DMAA(III)], has been reported in natural waters[7–9] and human urine.[10–11] Methylarsenic(III) species are more toxic and probably more reactive than methylarsenic(V) species in aquatic systems. Systematic studies on the aqueous chemistry of methylarsenic(III) species are of importance for the elucidation of arsenic biotransformation.

MMAA(III) and DMAA(III) have two types of bond between the central arsenic atom and the ligands.[12,13] One is the arsenic–carbon (As—C) bond, which is relatively nonpolar and kinetically inert. The other is the more polar and labile arsenic–oxygen (As—O) bond, as well as that of arsenite. Cleavage of the latter bond is involved in various reactions of inorganic and methylarsenic(III) species.[13] In aqueous solutions, hydroxides of inorganic and methylarsenic(III) species are converted into the corresponding halides by adding a hydrohalic acid. Halogen substitution has been investigated by using solvent extraction methods from the viewpoint of separation and preconcentration of arsenic.[14–19] Most attention has been focused on arsenite, in which arsenite was extracted as trihalide complexes (halogen: Cl, Br and I) by a number of organic solvents.[14–16] It is also reported that hydroxychlorides of arsenite coexist at equilibrium in aqueous hydrochloric acid solutions.[17] On the other hand, only a few studies have dealt with methylarsenic(III) species,[18,19] which is probably due to the instability of methylarsenic(III) species to oxidation.

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*Correspondence to: H. Hasegawa, Department of Chemistry and Chemical Engineering, Faculty of Engineering, Kanazawa University, Kodatsuno 2-40-20, Kanazawa 920-8667, Japan.
E-mail: hhiroshi@t.kanazawa-u.ac.jp

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MMAA(III) and DMAA(III) are extracted into benzene as iodide complexes when the corresponding pentavalent hydroxides are treated with an excess of reductant, such as iodide. Information on the speciation of MMAA(III) and DMAA(III) is lacking, since the complexity of coexisting ions and side reactions prevents quantitative analysis of the complexation in aqueous solutions.

In this paper, the solvent extractions of inorganic and methylarsenic(III) species with hydrochloric acid have been examined to gain a better understanding of arsenic speciation in aqueous solutions. In hydrochloric acid solutions, chloride ions occupy the coordination sites of the central arsenic atom, forming the chlorides of inorganic and methylarsenic(III) species. In order to prevent oxidation of MMAA(III) and DMAA(III), the extractions were performed under an inert atmosphere. The stability constants and the partition constants for the arsenic species were calculated from the distribution data. We also discussed the effect of methyl groups on the reactivity of inorganic and methylarsenic(III) species in aqueous solutions.

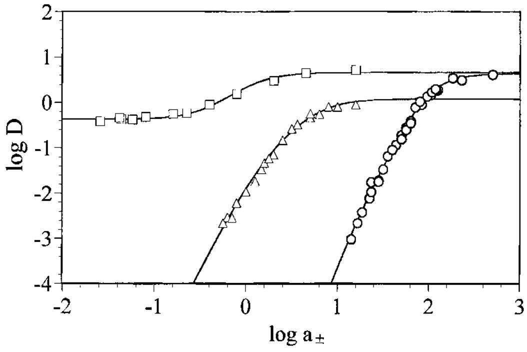

Figure 1. Distribution ratios of inorganic and methylarsenic(III) species and the mean activity of hydrochloric acid in aqueous solutions at 25 °C: ○, arsenite; △, MMAA(III); □, DMAA(III). The initial concentrations of arsenic are 1.0×10^{-4} mol l^{-1}. Solid curves are calculated using the stability constants and the partition constants in Table 1.

EXPERIMENTAL

Reagents

Stock solutions of 1.0×10^{-2} mol l^{-1} MMAA(III) and DMAA(III) were prepared by dissolving the corresponding bromides (Alfa, Morton Thiokol, Inc.) in 0.1 mol l^{-1} sodium hydroxide under a nitrogen atmosphere. MMAA(III) and DMAA(III) were dissolved as hydroxides by alkaline hydrolysis.[20] Stock solutions (1×10^{-2} mol l^{-1}) for the other arsenic compounds were prepared by dissolving the corresponding sodium salts ($CH_3AsO_3Na_2$ prepared by Quick's method,[21] and $NaAsO_2$, Na_2HAsO_4 and $(CH_3)_2AsO_2Na$, Nacalai Tesque) in 0.1 mol l^{-1} sodium hydroxide. These stock solutions were standardized by using inductively coupled plasma atomic emission spectrometry (ICP-AES, Japan Jarrel Ash, ICAP-500) after decomposition to arsenate. They were diluted to the desired concentrations just before use. Other reagents were of analytical reagent grade and distilled water was used throughout.

Safety Note. The arsenic compounds described in this paper can be severe toxins and should be handled with extreme care. Avoid inhaling arsenic chlorides and arsines.

Distribution measurements

10 ml of aqueous solution, of which arsenic species and hydrochloric acid were adjusted to the desired value, and 10 ml of carbon tetrachloride were placed in a 30 ml centrifuge tube under a nitrogen atmosphere. The tube was shaken for 30 min at 25.0 ± 0.1 °C, using a Taitec Bioshaker BR-30L. After centrifugation, the organic and the aqueous phases were separated. Since the sensitivity of ICP-AES is highly dependent on the valence of the arsenic species, the trivalent species was oxidized to the pentavalent state for accurate determination of the arsenic concentrations. Some aliquots of the aqueous phase were pipetted into a 10 ml polypropylene tube and adjusted to 0.1% hydrogen peroxide/0.1 mol l^{-1} sodium hydroxide solution by adding 1–10 mol l^{-1} sodium hydroxide, distilled water and 20% hydrogen peroxide in turn. The arsenic species in the organic phase were back-extracted with an equal portion of 0.1 mol l^{-1} sodium hydroxide solution containing 0.1% hydrogen peroxide. Then, the arsenic concentrations were determined by ICP-AES. The recovery was more than 95% for all the arsenic species. Distribution ratios D of the arsenic are defined as:

$$D = C_{\mathrm{As,o}}/C_{\mathrm{As}} \tag{1}$$

where $C_{\mathrm{As,o}}$ and C_{As} are the analytical molar concentrations of the arsenic species in the organic and the aqueous phases respectively.

Other aliquots of the aqueous phase were used for the measurements of the mean activity of hydrochloric acid. Concentrations of hydrochloric acid were measured by titration with 1.0 mol l^{-1} sodium hydroxide solution. The mean activity $a_{\pm}$, which was expressed on the molarity scale, was calculated from the measured concentration using values described in the literature.[22,23]

RESULTS AND DISCUSSION

Solvent extraction of inorganic and methylarsenic species in the chloride system

The distribution ratios of inorganic and methylarsenic(III) species are plotted against the mean activities on log–log scale (Fig. 1). The distribution equilibrium was reached after more than 15 min of shaking; no change was observed in the results of comparative measurements using equilibration periods of 15, 30 and 60 min. Inorganic and methylarsenic(III) species were extracted in the acidic region, whereas

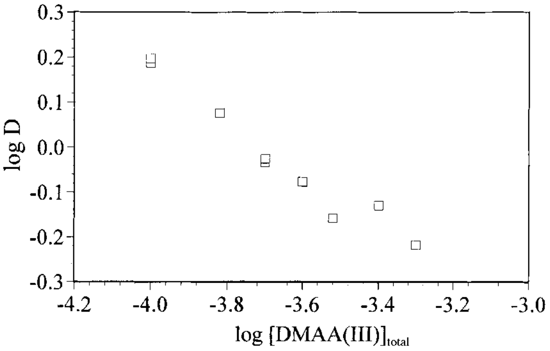

Figure 2. Effect of DMAA(III) concentration on the extraction of DMAA(III) at 25 °C in the 1.0 mol l^{-1} hydrochloric acid–carbon tetrachloride system.

none of the pentavalent species was extracted ($\log D < -3.5$). Cleavage of the As—C bonds and oxidation of inorganic and methylarsenic(III) species were not observed during the extraction procedure.

The distribution ratio of arsenic(III) species rises with increasing acidity. The log *D* of arsenite, MMAA(III) and DMAA(III) attains 0.55, −0.08 and 0.66 by 2.26, 0.90 and 0.65 of $\log a_{\pm}$ respectively and then remains relatively steady at higher concentrations of hydrochloric acid. The value obtained for arsenite in the present work is in agreement with other studies, in which arsenite is extracted as the trichloride complex.[14] Because of the hydrophilicity of the hydroxyl groups, MMAA(III) and DMAA(III) would also be extracted as the corresponding chlorides. The maximum in the slope of the log *D* versus $\log a_{\pm}$ plots decreases as the number of methyl groups attached to arsenic atoms increases. This is consistent with the following formation of arsenic chloride complexes:

$$(CH_3)_n As(OH)_{3-n} + (3-n)H^+ + (3-n)Cl^- \rightleftarrows (CH_3)_n AsCl_{3-n} + (3-n)H_2O \quad (2)$$

$$\beta = [(CH_3)_n AsCl_{3-n}]/[(CH_3)_n As(OH)_{3-n}][H^+]^{3-n}[Cl^-]^{3-n} \quad (3)$$

where β is the overall stability constant for $(CH_3)_n AsCl_{3-n}$, $n = 0, 1, 2$ and brackets signify activity. In the higher ranges of $\log a_{\pm}$, the dominant species is $(CH_3)_n AsCl_{3-n}$ in both the aqueous and the organic phases.

For DMAA(III), the plateau in the lower $\log a_{\pm}$ range appears in Fig. 1. In previous publications, DMAA(III) was shown to form $((CH_3)_2As)_2O$, the so-called cacodyloxide.[12,13] Since the formation of the chloride complex is negligible in the low $\log a_{\pm}$ range, the values of $\log D$ for DMAA(III) would depend on the partition of the dimer between aqueous and organic phases. Figure 2 shows the effect of DMAA(III) concentration on distribution ratios of DMAA(III) into carbon tetrachloride from 1.0 mol l^{-1} hydrochloric acid solution. The distribution ratio of DMAA(III) depends on the total quantity, $[DMAA(III)]_{total}$, and the slope of the log *D* versus $\log[DMAA(III)]_{total}$ plot is almost −1. This result provides experimental support for the dimerization of DMAA(III) in the chloride system. For As(III) and MMAA(III), experimental results showed no change in the arsenic distribution when the total quantity of arsenic was varied between 5.0×10^{-5} and 1.0×10^{-3} mol l^{-1} at constant hydrochloric acid concentration. It is considered that the chemical forms of As(III) and MMAA(III) are monomeric in both the aqueous and the organic phases.

Arsenic speciation in aqueous hydrochloric acid solutions

The analysis of the extraction reaction is carried out on the following assumptions.

(i) Hydroxide ions attached to the arsenic atom are stepwise substituted by chloride ions with increases in $\log a_{\pm}$. The description of the stepwise reactions is as follows:

$$(CH_3)_n As(OH)_{i+1}Cl_{j-1} + H^+ + Cl^- \rightleftarrows (CH_3)_n As(OH)_i Cl_j + H_2O \quad (4)$$

$$K_j = [(CH_3)_n As(OH)_i Cl_j]/[(CH_3)_n As(OH)_{i+1}Cl_{j-1}][H^+][Cl^-] \quad (5)$$

where K_j is the stepwise stability constant, and $n + i + j = 3$. Among these arsenic species, $(CH_3)_n AsCl_{3-n}$ alone is extracted into the organic phase. The partition constant P_{Cl}, of the arsenic chlorides is estimated using:

$$P_{Cl} = [(CH_3)_n AsCl_{3-n}]_o/[(CH_3)_n AsCl_{3-n}] \quad (6)$$

where subscript 'o' denotes corresponding species in the organic phase.

(ii) Arsenite, MMAA(III) and DMAA(III) are nonionic under acidic conditions.

(iii) DMAA(III) is dimerized into $((CH_3)_2As)_2O$. With regard to DMAA(III), the dimer is also extracted into the organic phase:

$$2(CH_3)_2AsOH \rightleftarrows ((CH_3)_2As)_2O + H_2O \quad (7)$$

$$K_{di} = [((CH_3)_2As)_2O]/[(CH_3)_2AsOH]^2 \quad (8)$$

$$P_{di} = [((CH_3)_2As)_2O]_o/[((CH_3)_2As)_2O] \quad (9)$$

where K_{di} and P_{di} are the formation constant and the partition constant for $((CH_3)_2As)_2O$.

(iv) Activity coefficients are unity for arsenic(III) species in both the aqueous and the organic phases. The activities of H^+ and Cl^- ions are equal to the mean activities $a_{\pm}$ of hydrochloric acid.

The stability constants and the partition constants for arsenic species are estimated from the extraction data by a

Table 1. Stability constants and partition constants for inorganic and methylarsenic(III) species in aqueous solutions at 25 °C[a]

Arsenic species	log β^b	log $K_1{}^b$	log $K_2{}^b$	log $K_3{}^b$	log $P_{Cl}{}^b$	log $K_{di}{}^b$	log $P_{di}{}^b$
Arsenite	−10.03 + 0.10	−2.02 ± 0.10	−4.02 ± 0.08	−3.99 ± 0.08	0.61 ± 0.02	–	–
MMAA(III)	−1.79 ± 005	−0.23 ± 0.05	−1.56 ± 0.05	–	0.07 ± 0.03	–	–
DMAA(III)	−0.08 ± 0.07	−0.08 ± 0.07	–	–	0.67 ± 0.03	4.14 ± 0.11	0.82 ± 0.02

[a] Numerical data and further details of computations methods are available on request from the authors.
[b] $\pm\sigma$.

nonlinear least-squares computation. Table 1 shows β, K_j, P_{Cl}, K_{di} and P_{di} at 25 °C. In Fig. 1, the solid curves calculated using the parameters listed on Table 1 agree well with the experimental data. The values of the stepwise stability constants for an equivalent coordination site increase in the order arsenite < MMAA(III) < DMAA(III). The same observation applies to the overall stability constants. These results suggest that hydroxyl groups bonded to an arsenic atom are easily replaced by chlorine atoms as the number of methyl groups attached to the arsenic atom increases. The stabilities of As—OH and As—Cl bonds would be affected by the inductive effect of the methyl groups, which are classified as weakly electron-donating. The transfer of a negative charge from the methyl groups increases the electron density on the central arsenic atom, and reduces the ionic interaction of As—OH and As—Cl bonds. The hydroxyl ions are harder bases than the chloride ions.

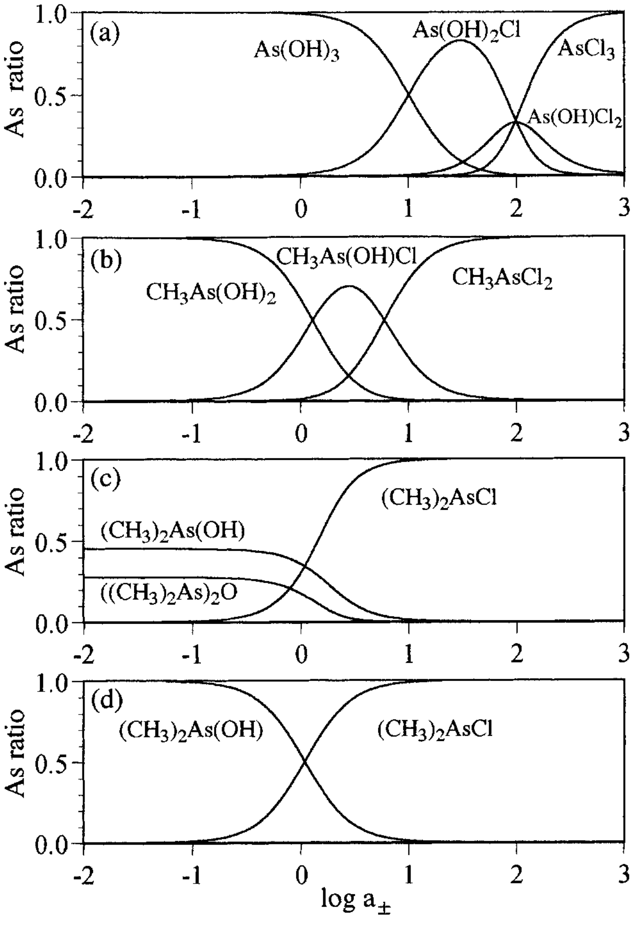

Figure 3. Equilibrium compositions of inorganic and methylarsenic(III) species in aqueous hydrochloric acid solutions at 25 °C: (a) arsenite; (b) MMAA(III); (c) DMAA(III), 1.0×10^{-4} mol l^{-1}; (d) DMAA(III), 1.0×10^{-8} mol l^{-1}.

Figure 3 demonstrates distribution diagrams of inorganic and methylarsenic(III) species in aqueous hydrochloric acid solutions. The range where the species composition of arsenite, MMAA(III) and DMAA(III) changes is shifted to a higher concentration of hydrochloric acid with a decrease in the number of methyl groups. Arsenite and MMAA(III) exist in monomeric forms in aqueous solutions, and the distribution diagrams demonstrated in Fig. 3(a) and (b) apply to a concentration range less than at least 1.0×10^{-3} mol l^{-1}. The speciation of DMAA(III) depends on the total concentration, which is due to the formation of the dimer (Fig. 3(c) and (d)). In the early literature, MMAA(III) and DMAA(III) in various organic solvents were formulated as $((CH_3)AsO)_n$ and $((CH_3)_2As)_2O$ on the grounds of NMR spectra and molecular weight data.[12,24,25] Our results suggest that the dominant species of MMAA(III) and DMAA(III) are monomeric in lower concentration ranges in aqueous solutions. Clearly, the chemical behavior of methylarsenic(III) species in aqueous solutions is different than those in organic solvents. The stabilities of organoarsenic compounds are related to the number and to the nature of various functional groups bonded to the arsenic atom. Much work remains to be done on the aquatic chemistry of organoarsenic compounds in the environment.

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