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Speciation of astatine reacted with oxidizing and reducing reagents by thin layer chromatography: formation of volatile astatine

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Abstract

Radio-chromatography was conducted by using the astatine radionuclides ^{209,210,211}At produced in the ^{7}Li induced reaction of ^{209}Bi. The speciation of dissolved astatine chemical species of astatide (At^-), astatate (AtO_3^-) and perastatate (AtO_4^-) was carried out by thin layer chromatography on silica gel with an ethanol/water solution. Amounts of the astatine species varied with concentrations of oxidizing and reducing reagents, potassium periodate, sodium sulfate and hydrazine hydrate. The oxidation–reduction reactions between At^-(−I) and AtO_3^- (V) were found to form volatile At^0 (0) and release it from a silica gel thin layer in the development.

Keywords Astatine anions · Thin layer chromatography · Oxidation and reduction degree · Volatility of At^0

Introduction

^{211}At, an astatine radionuclide, with a half-life of 7.2 h is one of the prospective candidates for utilization in targeted alpha therapy of cancers. Astatine shows some different chemical behaviors in comparison with its homologue iodine. The understanding of basic chemical properties of astatine has been required to develop targeted alpha therapy reagents for cancers [1].

The speciation of astatine has been studied [2–14] but low amounts of astatine present could cause the difficulty in experimental identification [1]. In addition, identification of chemical species is generally affected by the preparation of samples and analytical methods. Some astatine chemical species in solutions were suggested; the identification of At^-, At^+ and AtO_3^- was proposed by Appelman [3] and supported by Rössler et al. [4]. The different identification of At^-, At^+ and AtO^+ has recently been proposed by Champion et al. [11]. In contrast, At^-, AtO_3^- and AtO_4^- were separated and identified with paper electrophoresis and paper chromatography by Dreyer et al. [5]. Two of the three astatine species, At^- and AtO_3^-, were identified with high-performance liquid chromatography (HPLC) by Balkin et al. [13].

In our previous study of thin layer chromatography (TLC) [14], the identification of the three astatine species has recently confirmed. The astatine speciation was carried out by comparing with retardation factors (R_f) of iodine anions. Furthermore, the behavior of the relative amounts of the astatine species with the oxidizing and reducing reagents, potassium periodate (KIO_4), sodium sulfate (Na_2SO_3) and hydrazine hydrate ($NH_2NH_2{\cdot}H_2O$), revealed that the astatine species were certainly identified as At^-, AtO_3^- and AtO_4^-. The oxidation numbers of astatine are At(−I) for At^-, At(V) for AtO_3^- and At(VII) for AtO_4^-. In the case of the TLC analysis for the solutions containing the reducing reagent of hydrazine hydrate, a marked loss of astatine activities in the development was observed. This observation suggests that the oxidation–reduction reactions between At^-(−I) and AtO_3^-(V) in dynamic equilibria enhance the probability to form At^0(0) characterized by high volatility [3] and release it from a silica gel thin layer in the development. The understanding the production of the volatile astatine species is required to conduct TLC experiments from a perspective of radiation safety.

The chemical nature of the volatile astatine species from solutions still remains uncertain. Distillation of astatine solution was found to take place under reduction conditions

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(0.05 M $FeSO_4$ in 0.5 M H_2SO_4) by Johnson et al. [2]. Such distillation technique under reductive conditions (0.75 M $FeSO_4$ in 1.5 M H_2SO_4) has recently used to purify ^{211}At from basic solutions; it is presumed that hydroastatic acid is distilled [13].

The aim of this work is to elucidate the relation between the production of the volatile species of At^0 and the oxidation–reduction behaviors among three dissolved astatine species of At^-, AtO_3^- and AtO_4^- in terms of not only radiation safety but also the fundamental interest in chemical properties of astatine. The TLC analysis for dissolved and volatile astatine species has been conducted by varying concentrations of KIO_4, Na_2SO_3 and hydrazine.

Experimental

Production of radionuclides

The astatine radionuclides were produced via the nuclear reaction of $^{nat}Pb(^7Li,xn)$ ^{209,210,211}At [15]. A stack of thin metal lead targets of approximately 1 mg/cm^2 in thickness was irradiated with 60 MeV $^7Li^{3+}$ ion beams supplied from the Japan Atomic Energy Agency (JAEA) tandem accelerator. Beam current was controlled to be approximately 180 nA during the irradiation of 3 h. After irradiation, radioactivity of astatine radionuclides ^{209,210}At produced in the target was measured by a high-purity germanium detector. Such target preparation, irradiation, γ-ray measurements as well as the preparation of astatine aqueous solutions described below were carried out in the similar way as described in our previous study [14].

Preparation of astatine aqueous solutions

The produced astatine radionuclides were separated from the irradiated targets by dry distillation. The dry distillation was conducted in the 180 × 18 mm (o.d.) glass test tube replaced air with nitrogen gas and sealed with polyethylene films. A third portion from the bottom of the test tube was inserted into a furnace at 650 °C for 20 min. After dry distillation, no-carrier-added astatine aqueous solutions were prepared as mother stock solutions by eluting the separated astatine radionuclides with 1.8 mL of distilled water. The activity of ^{211}At in the mother stock solutions was determined by α-ray spectrometry as described by Nishinaka et al. [15]. The sources for α-ray spectrometry were prepared by depositing a 5 μL portion of the astatine aqueous solutions on a silver sheet and evaporating them. Alpha particles from the sources were detected with a silicon surface barrier detector (ORTEC).

Preparation of astatine solutions containing an oxidizing or a reducing reagent in a concentration range

In order to investigate oxidation–reduction degree of astatine species, astatine in the mother stock solution was reacted with an oxidizing and two single reducing reagents in a concentration range as follows: (1) For oxidation by KIO_4, reaction mixtures were prepared by adding 50 μL KIO_4 solutions (3×10^{-5}, 3×10^{-4}, 3×10^{-3} and 3×10^{-2} mol L^{-1}) or 50 μL H_2O into 200 μL of the astatine aqueous solution as mother stock solution, and heating at 90 °C for 20 min. (2) For Na_2SO_3, reaction mixtures were prepared by adding 25 μL Na_2SO_3 solutions (5×10^{-4}, 5×10^{-3}, 5×10^{-2} and 5×10^{-1} mol L^{-1}) or 25 μL H_2O into 100 μL of the astatine aqueous solution as mother stock solution, and were kept at ambient temperature for 20 min. (3) For hydrazine, reaction mixtures were prepared by adding 10, 20, 30 and 40 μL $NH_2NH_2 \cdot H_2O$ solutions into 100 μL of the astatine aqueous solution, and were kept at ambient temperature for 20 min. The radioactivity concentrations of the reaction mixtures are different in the case of (3).

TLC for astatine

Thin layer chromatographic isolation was achieved in the same way described in our previous study [14]. A 5 μL portion of the reaction mixtures was spotted at 2 cm from the bottom of the silica gel TLC plate cut in strips 12 × 2 cm. A solvent mixture of ethanol/water (1:1, v/v) ascended the TLC plate in the distance of 8 cm from the spotted point. Distributions of activity on the TLC plate were measured with imaging plates and visualized by Bioimaging Analyzer System (BAS) (BAS-5000, FUJIFILM Life Science). All TLC plates each for KIO_4, Na_2SO_3 and hydrazine, and a plate for the corresponding astatine aqueous solution were exposed to an imaging plate. This enabled us to quantitaively compare the amounts of the astatin chemical spiecies reacted with each the oxidizing and reducing reagents in the concentration range.

Results and discussion

TLC successfully separated spots of astatine anions as shown in Figs. 1, 2, 3. Figures 1, 2, 3 each aligned the parts of the same BAS image in the area contacted with the TLC plates. The spots at the origin of the TLC plates correspond to AtO_4^-(VII), and the lower and the upper

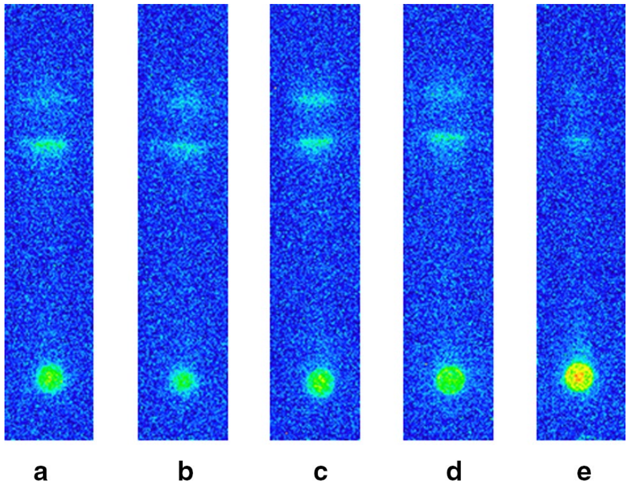

Fig. 1 Results of TLC experiments visualized by bioimaging analyzer system (BAS): **a** astatine aqueous solution, **b** 6×10^{-6} mol L^{-1} KIO_4, **c** 6×10^{-5} mol L^{-1} KIO_4, **d** 6×10^{-4} mol L^{-1} KIO_4, **e** 6×10^{-3} mol L^{-1} KIO_4

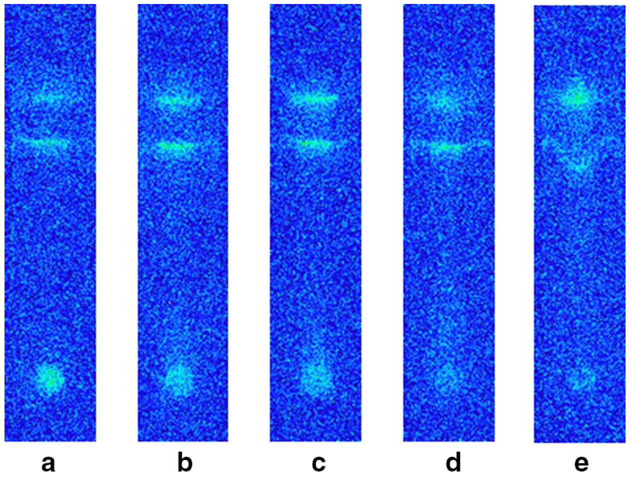

Fig. 2 Results of TLC experiments visualized by BAS: **a** astatine aqueous solution, **b** 1×10^{-4} mol L^{-1} Na_2SO_3, **c** 1×10^{-3} mol L^{-1} Na_2SO_3, **d** 1×10^{-2} mol L^{-1} Na_2SO_3, **e** 1×10^{-1} mol L^{-1} Na_2SO_3

bands correspond to AtO_3^-(V) and At^-(−I), respectively, as identified in Ref. [14].

The amounts of astatine radionuclides in the astatine aqueous solution at the time of contacting the TLC plates to an imaging plate were 26 ± 1 Bq ^{209}At, 44 ± 1 Bq ^{210}At and 33 ± 1 Bq ^{211}At for Fig. 1a, 19 ± 1 Bq ^{209}At, 26 ± 1 Bq ^{210}At and 34 ± 1 Bq ^{211}At for Fig. 2a, and 50 ± 2 Bq ^{209}At, 108 ± 3 Bq ^{210}At and 11 ± 1 Bq ^{211}At for Fig. 3a, respectively. These values were corrected for decay time from measuring activities to contacting the TLC plates to an imaging plate. It should be noted that TLC analysis was accomplished using the low amounts of no-carrier-added astatine present.

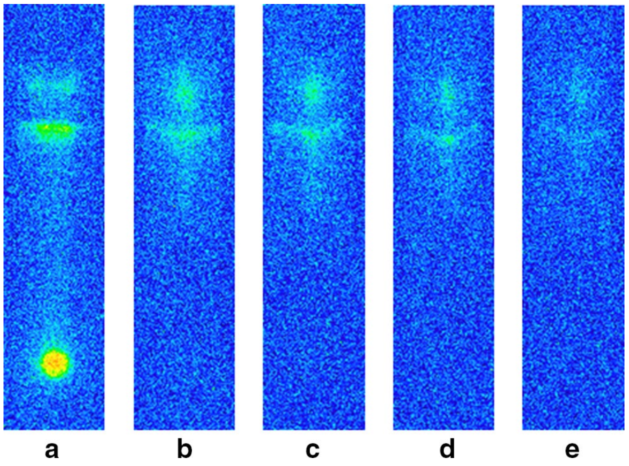

Fig. 3 Results of TLC experiments visualized by BAS for astatine aqueous solution with $NH_2NH_2{\cdot}H_2O$ at a volume ratio: **a** 0.0%, **b** 9.1%, **c** 16.7%, **d** 23.1%, **e** 28.6%

Images of Fig. 1 show that the increase in KIO_4 concentration heightens the intensity of the spots of AtO_4^-(VII) at the origin of TLC, and slightly lowers that of the bands of At^-(−I) and AtO_3^-(V), indicating the oxidation of astatine. In contrast, the reduction of astatine with increasing in concentrations of Na_2SO_3 and hydrazine is apparently observable as decreasing and disappearing the intensity of the spots of AtO_4^-, in Figs. 2 and 3, respectively. Additionally, loss of astatine activity is visible for hydrazine (Fig. 3).

Component analysis

To quantitate degrees of oxidation–reduction, a component analysis was carried out by using the chromatograms obtained from the BAS images in Figs. 1, 2, 3. Typical chromatograms are displayed in Fig. 4a–c. Figure 4a–c correspond to the BAS images for KIO_4 in Fig. 1a, e, those for Na_2SO_3 in Fig. 2a, d, and those for hydrazine in Fig. 3ad, respectively. Distributions of astatine activities on a plate are shown by intensity of a BAS image as a function of R_f. Solid and dashed lines correspond to the astatine aqueous solution with and without the oxidizing or the reducing reagent, respectively. The background level shown by dash-dotted line was taken from the average intensity of several areas of the BAS image. The intensities were normalized by the factor as the total intensity in the range of R_f = –0.25–1.25 for the corresponding astatine aqueous solution becames 100%.

Relative amounts of astatine species were obtained by integrating the normarized intensity in the ranges of R_f = –0.08–0.08 for AtO_4^-, 0.64–0.82 for AtO_3^- and 0.82–1.00 for At^-. These R_f ranges are shown by gray vertical line in Fig. 4. The results of the component analysis for

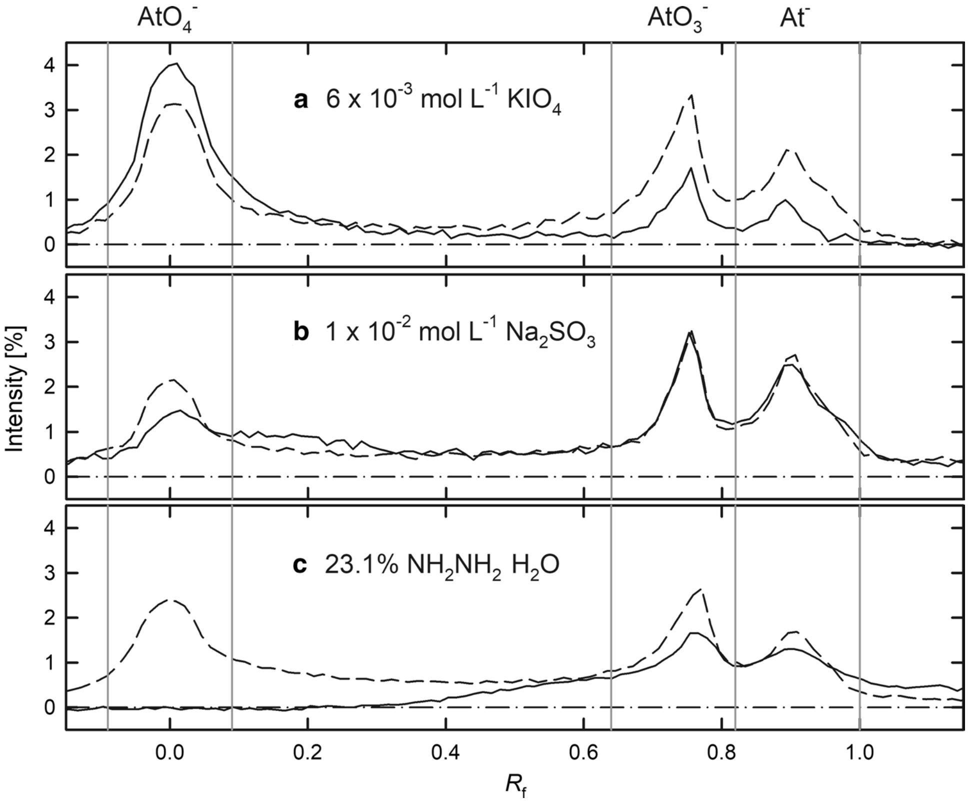

Fig. 4 Typical chromatograms: intensity distributions of astatine activity as a function of R_f for **a** 6×10^{-3} mol L^{-1} KIO_4, **b** 1×10^{-2} mol L^{-1} Na_2SO_3, **c** 23.1% hydrazine, compared with that for aqueous solutions (dashed-line)

Table 1 The results of the component analysis for KIO_4

BAS image	Solution	Relative amount* (%)/R_f			Missing amount[a] (%)
		At^-	AtO_3^-	AtO_4^-	
Figure 1a	H_2O	18/0.91	25/0.74	26/0.00	0
Figure 1b	6×10^{-6} mol L^{-1} KIO_4	19/0.90	21/0.74	22/0.00	6
Figure 1c	6×10^{-5} mol L^{-1} KIO_4	21/0.90	19/0.75	25/0.00	6
Figure 1d	6×10^{-4} mol L^{-1} KIO_4	19/0.90	24/0.74	33/0.00	−18
Figure 1e	6×10^{-3} mol L^{-1} KIO_4	6/0.90	10/0.74	37/0.00	20

*The proportion of intensity to the total intensity for the astatine aqueous solution integrated in the region of $R_f = -0.25$–1.25

[a] Missing amounts obtained from the total intensity integrated in the region of $R_f = -0.25$–1.25 under the assumption of no missing amount for astatine aqueous solution

Table 2 The results of the component analysis for Na_2SO_3

BAS image	Solution	Relative amount* (%)/R_f			Missing amount[a] (%)
		At^-	AtO_3^-	AtO_4^-	
Figure 2a	H_2O	23/0.91	22/0.74	18/0.00	0
Figure 2b	1×10^{-4} mol L^{-1} Na_2SO_3	25/0.91	26/0.74	19/0.01	− 13
Figure 2c	1×10^{-3} mol L^{-1} Na_2SO_3	23/0.90	21/0.75	15/0.01	18
Figure 2d	1×10^{-2} mol L^{-1} Na_2SO_3	24/0.91	23/0.74	14/0.01	0
Figure 2e	1×10^{-1} mol L^{-1} Na_2SO_3	28/0.91	26/0.73	13/0.01	− 11

*The proportion of intensity to the total intensity for the astatine aqueous solution integrated in the region of $R_f = -0.25$–1.25

[a] Missing amounts obtained from the total intensity integrated in the region of $R_f = -0.25$–1.25 under the assumption of no missing amount for astatine aqueous solution

Table 3 The results of the component analysis for hydrazine

BAS image	Solution	Relative amount* (%)/R_f			
		At^-	AtO_3^-	AtO_4^-	At^0 (Missing amount[a])
Figure 3a	H_2O	16/0.90	21/0.74	23/0.00	0
Figure 3b	9.1% $NH_2NH_2{\cdot}H_2O$	21/0.91	24/0.74	3/0.00	24
Figure 3c	16.7% $NH_2NH_2{\cdot}H_2O$	21/0.91	24/0.74	0/0.00	29
Figure 3d	23.1% $NH_2NH_2{\cdot}H_2O$	19/0.91	22/0.74	0/0.00	37
Figure 3e	28.6% $NH_2NH_2{\cdot}H_2O$	15/0.90	15/0.73	0/0.00	50

*The proportion of intensity to the total intensity for the astatine aqueous solution integrated in the region of $R_f = -0.25$–1.25

[a] Missing amounts obtained from the total intensity integrated in the region of $R_f = -0.25$–1.25 under the assumption of no missing amount for astatine aqueous solution

KIO_4, Na_2SO_3 and hydrazine were listed in Tables 1, 2, 3, respectively. The relative amounts for hydrazine were also corrected for the radioactivity concentrations in the solutions. Errors of relative amounts not shown in the Tables 1, 2, 3 were estimated to be the sensitivity for non-uniformity of BAS images (~ 7%).

Finally, it should be noted that the aqueous solutions show rather different composition profiles of the relative amounts of At^-, AtO_3^- and AtO_4^- among trials. The composition range of 16–26% in this work is slightly small compared with that of 18–48% for an aqueous solution in Ref. [14]. The reason of the composition variation for aqueous solutions is not clear but this means that astatine is easily oxidized and reduced in water due to the more electropositive character of astatine than iodine [14]. This implys that such composition variation of At^-, AtO_3^- and AtO_4^- in no-carrier added astatine solution prepared by dry-distillation would conduct problematic results [16] in the repeatability of yields in the chemical and radiolabeling reactions.

Missing amounts

The loss of astatine activity was clearly observed in the component analysis. In order to investigate the loss of astatine activity from TLC plate, missing amount was defined and obtained as difference of the total intensity for the chromatograms between the astatine solutions with and without the oxidizing or the reducing reagent. The results are listed in the column of the missing amount in Tables 1, 2, 3.

The missing amounts assume that At^0 characterized by high volatility [3] is not released from TLC plates for aqueous solutions without the oxidizing or the reducing reagent. This assumption makes a simple consideration of the loss of astatine activity as $At^0(0)$ forms via the oxidation–reduction reaction between At^- (−I) and AtO_3^-(V) in dynamic equilibria and volatilizes from TLC plates as pointed out in our previous study [14]. From the results of the missing amounts, not only the volatilization of At^0 but also validity and ambiguity of such asummption of no release for astatine solution without the oxidizing or the reducing reagent will be discussed as follows.

In Tables 1 and 2 for KIO_4 and Na_2SO_3, the missing amounts range from − 18 to 20% and seem to have no correlation with the reagent concentrations. Thus, the range of these irregulary fluctuated missing amounts (~ 20%) can be regarded as a systematic error in this work. The systematic error originates from experimental and analytical conditions; non-uniformity of BAS images (~ 7%) will be a contributing factor for the systematic error. In addition, one of the other possible factors is volatilization of astatine At^0 from TLC plates not only for KIO_4 and Na_2SO_3 solutions but also for aqueous solutions. At^0 strictly have a chance to form and volatilize from TLC plates even for aqueous solutions. Because the presence of tailing in the region of $R_f = 0.08$–0.64 in Fig. 4 clearly shows that oxidation–reduction reactions between astatine species in dynamic equilibria will occur in the development. Thus, the contribution of At^0 can not be negligible but can be estimated within the systematic error range of approximately 20%.

In Table 3, in contrast to that, the missing amount for hydrazine significantly increases with the volume ratio over the systematic error range (~ 20%) estimated for KIO_4 and Na_2SO_3. This indicates that these large missing amounts come from the formation of At^0 due to the presence of the reducing reagent of hydrazine, therefore the missing amounts are assigned to the relative amounts of At^0 in Table 3. This aspect will be discussed in more detail later.

Dependence of astatine anion yields on concentration of reagents

Figures 5, 6, 7 display that the relation between relative amounts of astatine species with concentrations of KIO_4, Na_2SO_3 and hydrazine listed in Tables 1, 2, 3, respectively.

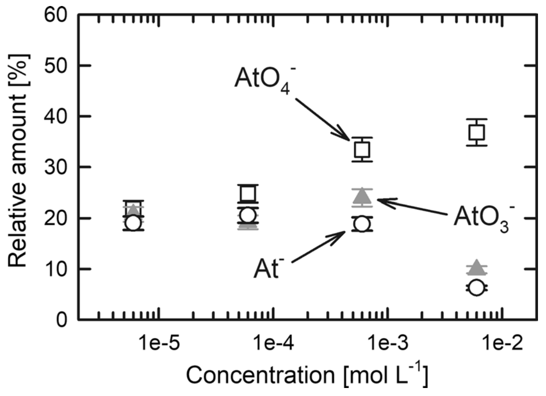

Fig. 5 Dependence of astatine species amounts on concentration of KIO_4

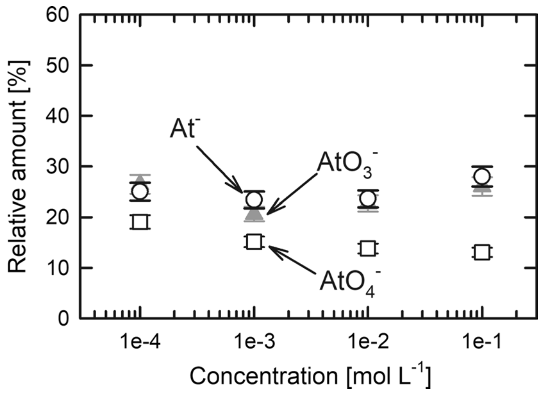

Fig. 6 Dependence of astatine species amounts on concentration of Na_2SO_3

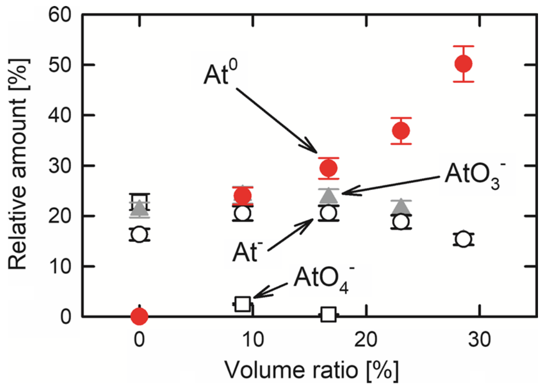

Fig. 7 Dependence of astatine species amounts on volume ratio of $NH_2NH_2{\cdot}H_2O$

As shown in Fig. 5, an increase in KIO_4 concentration enhances relative amounts of AtO_4^- up to more than 30%. In contrast, relative amouts of At^- and AtO_3^- both stay around 20% at low concentrations and largely drop below 10% at the highest concentration of 6×10^{-3} mol L^{-1}. The order of relative amounts is consistent with that of the oxidation number, $AtO_4^-(VII) > AtO_3^-(V) > At^-(-I)$. This dependence of the astatine anion amounts on concentration of KIO_4 obviously indicates the oxidation of astatine and the reliability of the speciation of astatine [13].

Figure 6 shows that the reducing reagent of Na_2SO_3 decreases the relative amounts of AtO_4^- down to less than 20% while yields of At^- and AtO_3^- stay between 20 and 30%. The order of the amounts is roughly good agreement with the inverse order of the oxidation number, $At^-(-I) \geq AtO_3^-(V) > AtO_4^-(VII)$. However, no increasing behavior of missing amounts with concentration was observed. This concentration dependence shows that Na_2SO_3 seems to act as a weak reducing reagent.

In the case of hydrazine, the concentration is presented in volume ratio (Fig. 7). Data for the astatine aquesous solution are plotted at the origin for horizontal axes. The amounts listed in the coloum of At^0 (missing amount) in Table 3 are shown by solid circle. The presence of hydrazine rapidly suppresses the relative amount of AtO_4^-. The AtO_4^- species is vanished and completely reduced to the lower oxidation states of AtO_3^- and At^- over 23.1% in volume ratio. In contrast, the relative amounts of AtO_3^- and At^- slightly increase with the volume ratio of hydrazine at lower concentrations, and then appearently decrease over 16.7% in volume ratio, and finally become less than 20% at 28.6% in volume ratio. Such decreases in the relative amounts of not only AtO_4^- but also AtO_3^- and At^- with hydrazine concentration connect to a large increase of At^0.

The observed concentration dependence of the relative amounts of not only AtO_4^-, AtO_3^- and At^- but also At^0 visibly supports the interpretation in the previous study [14]; The reduction of $AtO_4^-(VII)$ with hydrazine concentration enhances the relative amounts of $AtO_3^-(V)$ and $At^-(-I)$. This facilitates the formation of $At^0(0)$ through the oxidation–reduction reaction between $AtO_3^-(V)$ and $At^-(-I)$ in dynamical equilibria due to both effects of the oxidation on silica gels and the reduction with hydrazine, leading to the volatilization of At^0 from TLC plates. The volatilization of At^0 subsequentially leads to a decrease in the amounts of $AtO_3^-(V)$ and $At^-(-I)$ on the TLC plates in dynamical equilibria.

Such formation mechanism of volatile astatine species $At^0(0)$ through the oxidation–reduction reaction between $AtO_3^-(V)$ and $At^-(-I)$ in dynamical equilibria could provide an account of distillation of astatine solutions under reduction conditions (0.05 M $FeSO_4$ in 0.5 M H_2SO_4 [2] and 0.75 M $FeSO_4$ in 1.5 M H_2SO_4 [13]).

Conclusions

The astatine radionuclides ^{209,210,211}At produced in the ^{7}Li induced reaction of ^{209}Bi were used to fundamental experimental studies on chemical properties of astatine by TLC: oxidation–reduction between the dissolved astatine species, AtO_4^-, AtO_3^- and At^-, as well as formation of the volatile species of At^0.

The component analysis of relative amounts of the astatine species was carried out for astatine aqueous solutions of 6×10^{-6}–6×10^{-3} mol L^{-1} KIO_4, 1×10^{-4}–1×10^{-1} mol L^{-1} Na_2SO_3 and 9.1–28.6% $NH_2NH_2 \cdot H_2O$. The oxidizing and reducing reagents varied the composition profiles of relative amounts of the astatine species. The loss of astatine activities from TLC plates for aqueous solutions with/without KIO_4 or Na_2SO_3 was estimated to be less than approximately 20% of the total activities used to TLC plates. In contrast, the presence of hydrazine causes the remarkable loss of astatine activities, 24–50%.

This work confirmed that At^0(0) characterized high volatility formed in the oxidation–reduction reaction between At^-(−I) and AtO_3^-(V) in dynamic equilibria and volatilized from TLC plates in the development as suggested in our previous study in Ref. [14]. The TLC analysis on a silica gel should not be conducted without adequate ventilation. The volatile species At^0 involves risk regarding radiation safety.

The formation of At^0 provides not only greater risk but also decided uncertainty in TLC analysis for astatine solutions including strong reducing reagents. The studies on high performance liquid chromatography (HPLC) are required to establish a sophisticated analytical method of the astatine anions in solutions as a complementary method of TLC. However, it should be noted that TLC is a simple and conventional analytical method of the astatine anions.

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