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CHEMICAL PROPERTIES OF POSITIVE SINGLY CHARGED ASTATINE ION IN AQUEOUS SOLUTION

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The mobility of oxidized astatine in solutions $H(Na)ClO_4$ (μ = 0.4 M) – $1 \cdot 10^{-4}$ M $K_2Cr_2O_7$ has been measured at 25 °C in the interval $0.63 \leq pH \leq 1.68$. Under these conditions astatine migrates to the cathode only. The speed of the migration depends upon the concentration of hydrogen ions in solution:

pH 1.68 $U_c = 1.17 \cdot 10^{-4}\ cm^2\ V^{-1}\ s^{-1}$
pH 0.63 $U_c = 2.67 \cdot 10^{-4}\ cm^2\ V^{-1}\ s^{-1}$

The effect agrees with the opinion that the singly charged cation of astatine formed in acidic solutions is a strong aquacomplex $[(H_2O)_xAt]^+$ (x = 1–2) (protonated hypoastatic acid). Deprotonation constant of this cation is $K_{dp} = 0.032 \pm 0.005$. Specific properties of the astatine cation are given. They can be explained, probably, through the peculiarities of its structure.

Introduction

Unlike other halogens, dichromate oxidized astatine is stabilized in acidic solutions in the form of a positive singly charged ion.[1,2] The investigations of its properties showed that it should be a composite ion. It was proposed to denote it $(At\ \Theta)^+$.[3] In some cases the behaviour of $(At\ \Theta)^+$ could not be predicted and explained by the known properties of other singly charged cations under similar conditions. For example, during the absorption of $(At\ \Theta)^+$ by a cation exchanger from solutions of constant ionic strength the cation distribution coefficients are not constant, as expected, but decrease when the acid concentration increases (Fig. 1). Obviously, hydrogen ion is the main competing counterion in this case. Increasing temperature influences negatively the coefficient of $(At\ \Theta)^+$ distribution between Dowex 50X8 resin and $HClO_4$. In the 10–50 °C interval it changes by a factor of 2.

The influence of temperature on $(At\ \Theta)^+$ sorption by cesium phosphotungstate was even greater: distribution coefficients decrease from many hundreds at

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$T \leqslant 30$ °C to nearly zero at $T > 90$ °C (Fig. 2). But at constant temperatures, relatively high concentrations of acid, multiply charged ions and cesium ion do not influence the distribution coefficients. Ammonium phosphotungstate and potassium phosphotungstate do not adsorb $(\mathrm{At}\,\Theta)^+$.^{4,5}

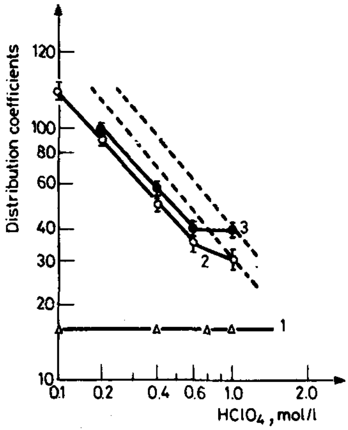

Fig. 1. Dependence of distribution coefficients for $(\mathrm{At}\,\Theta)^+$ and Tl^+ between 50X8 cation exchanger resin and solutions of $H(Na)ClO_4$ ($\mu = 1$) upon the acid concentration. Dashed lines show sorption from pure solutions of $HClO_4$. Curves: 1 – Tl^+, 20 °C; 2 – $(\mathrm{At}\,\Theta)^+$, 20 °C; 3 – $(\mathrm{At}\,\Theta)^+$, 35 °C

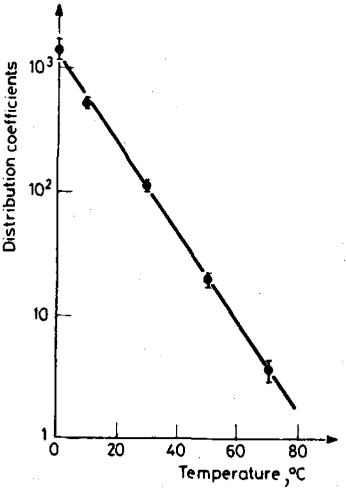

Fig. 2. Dependence of distribution coefficients for $(\mathrm{At}\,\Theta)^+$ between $Cs_3PW_{12}O_{40}$ and 3M HNO_3 $2 \cdot 10^{-2}$ M $CsNO_3$ solution upon temperature

Low sorption of astatine at higher temperatures is not always the case. We observed the opposite for $(At\ \Theta)^+$ on oxidized platinum from nitric acid solutions. Adsorption was more rapid and complete at 80 °C than at 23 °C.[6] Adsorption by platinum under these conditions seems to be characteristic of $(At\ \Theta)^+$ only. We did not find in the literature any information about the yield of other cation traces as effective as $(At\ \Theta)^+$.

The character of $(At\ \Theta)^+$ ion sorption by titanium hydroxide characterizes the chemical properties of $(At\ \Theta)^+$. If the sorption of other cations, e.g. Tl^+, by $Ti(OH)_4$ increases with decreasing acidity,[7] the adsorption of $(at\ \Theta)^+$ reaches its maximum at $pH < 3$ (Fig 4).

It follows from the above mentioned and other properties of $(At\ \Theta)^+$ [8] that a positive ion of the fifth halogen has little in common with singly charged cations of metals. We assume that the peculiarities of $(At\ \Theta)^+$ behaviour are connected with the fact that in acid solutions At^+ forms a stable aquacomplex $(At\ OH_2)^+$ or diaquacomplex $(H_2OAtOH_2)^+$ with a centrosymmetrical structure, which is attributed sometimes to hydroxonium ion[9] and might be found probably in the well-known diaquacomplex of silver.[10] Aquacomplex of the monovalent astatine can be regarded as a protonated hypoastatic acid. In the literature there is information about the possible existence of the similar iodine compound.[11,12] The formation constant for $(H_2OI)^+$ in I_2 hydrolysis is $K_{(H_2OI)^+} \cong 10^{-10}$; and the deprotonation constant for this cation is $K_{dp} \cong 3 \cdot 10^{-2}$.[11] If At_2 existed in aqueous solutions, $K_{(H_2OAt)^+}$ would be about 10^{-4} according to our estimation, and the deprotonation constant in the reaction

$$(H_2OAt)^+ + H_2O \rightleftarrows HOAt + H_3O^+ \qquad (1)$$

would probably be, lower than that of $(H_2OI)^+$ because the first ionization potential of the astatine atom is lower than for iodine. Stabilization of astatine in aqueous solutions of acids as $(H_2OAt)^+$ must be favoured greatly by its extremely low concentration, which prevents the formation of higher oxidation states of the element in disproportionation reactions. If the astatine-bearing ion is a true aquacomplex of monovalent astatine, it might react in some cases, like a hydroxonium ion, without splitting off water, owing to a strong covalent bond At – 0. Moreover, the polarizing influence of At^+ must decrease the force constants of 0 – H interaction thus strengthening donor properties of hydroxy groups in water molecules combined with astatine. They can probably take part in the formation of astatine compounds, where hydrogen bonds dominate over the electrostatic ones. The cases when the reaction requires dehydration of $(At\ H_2O)^+$ should not be excluded either. In one way or another, the observed "strangeness" of the cation can be positively explained

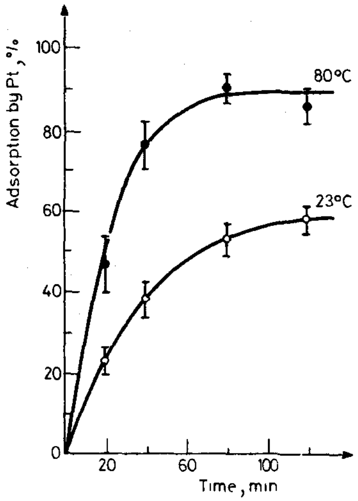

Fig. 3. Adsorption of (At Θ)$^+$ by metallic platinum (4 cm^2) from 5M HNO_3 (10 ml)

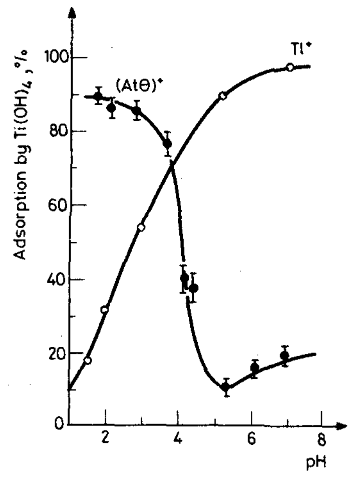

Fig. 4. Dependence of (At Θ)$^+$ and Tl^+ adsorption by $Ti(OH)_4$ from 0.1M $NaNO_3$ (20 °C) upon the pH. Quantity of sorbent in solution is 0.12 and 0.48 mg/ml, respectively

if we assume that (At Θ)$^+$ is a strong aquacomplex or a protonated hypoastatic acid, which is practically the same.

One of the possible ways to prove practically the hypothesis of (At Θ)$^+$ structure is to measure the mobility of the ion in solutions at varying acidity and constant ionic strength. If our assumptions are correct, we should expect slowing down of astatine mobility in an electric field with increasing pH, because the balance in reaction (1) shifts to the right. We have made these measurements and the results are included in this paper.

Experimental

Astatine was synthesized in the reaction between bismuth and α-particles of 36 MeV. The irradiation was done by the external ion beam in U–200 accelerator (Laboratory of Nuclear Reactions, JINR). Technique of astatine separation from the target, purification and concentration procedure were described in our previous paper.[13] The technique allowed us to get compounds of high specific (volumetric) activity: 0.2–0.4 GBc were dissolved in 100–150 microlitres of 0.5M $HClO_4$ – $1 \cdot 10^{-3}$M $H_2Cr_2O_7$. Before being used, the compounds were heated in a hot water bath for about an hour. We determined the mobility of astatine ions according to our methods of measuring ion migration rate in free electrolytes.[14] Astatine distribution in the electromigration tube was detected by means of polonium X-rays (81.2 keV). The experiments with $(\mathrm{At}\,\Theta)^+$ were carried out in solutions of (0.4–x)M $HClO_4$ – xM $NaClO_4$ – $1 \cdot 10^{-4}$M $K_2Cr_2O_7$, where $0.1 \leqslant x \leqslant 0.375$. Solutions of analytically pure reagents were prepared in doubly distilled water. Values of pH > 1 were measured with the help of a glass electrode with a reproducibility of ±0.05 pH. In more acidic solutions the hydrogen ion activity was calculated on the basis of the known $HClO_4$ concentration.

Results and discussion

Experiments on astatine electrophoresis in dichromate-containing solutions of $H(Na)ClO_4$ proved perhaps most significantly the existence of a positive ion of the fifth halogen. In all the experiments we observed the migration of astatine to the cathode only (Fig. 5). At the entry of activity into the electromigration tube, there was immobile astatine in balance with mobile astatine. Most likely it was $(\mathrm{At}\,\Theta)^+$, adsorbed by colloidal particles of silicic acid. Its microquantities are always present in the original solution as a result of radiation destruction of glass surface of the ampoule containing the highly active astatine compound by α-particles of ^{211}At (5.86 MeV) and ^{211}Po (7.48 MeV). Desorption of astatine from gel particles reduce the relative activity of the immobile zone and lead to a pronounced asymmetry of the migrating zone, the rear limit of which was impossible to

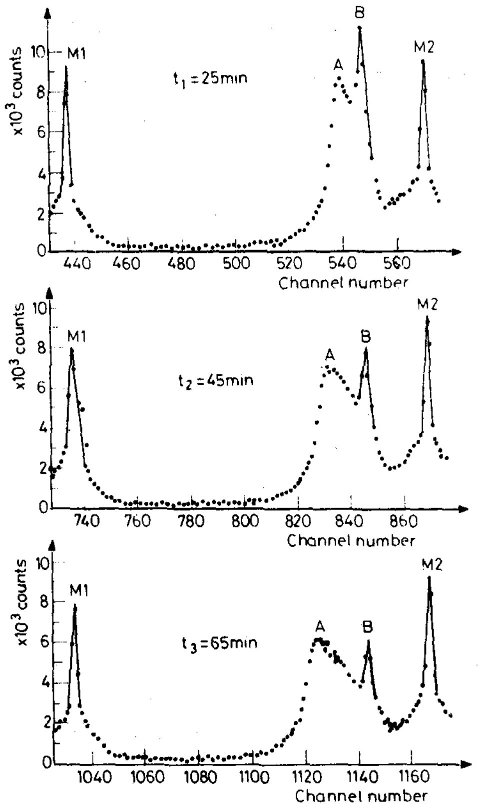

Fig. 5. Distribution of astatine along the electromigration tube t min after the experiment started. A – mobile zone, B – immobile zone at the entry. M1 and M2 – radioactive markers limiting the measuring base 190 mm long

determine. This fact did not allow us to calculate gravity centers of the mobile zones and we had to use another characteristic, viz. maximal activity, to measure the electrophoretic velocity of $(At\ \Theta)^+$.

The measurements in the acidity intervals available to our technique proved our expectations that the $(At\ \Theta)^+$ cation mobility is not constant but increases with decreasing of pH (Table 1). That means that, firstly, the effect agrees with our idea that $(At\ \Theta)^+$ is a protonated hypoastatic acid, and, secondly, it shows that neither AtO^+ nor AtO_2^+ can be the migrating ions, because the hydrogen ions concentration does not influence them.

If the observed dependence of astatine migration to the cathode upon the pH indicates actually deprotonation of $(At\ \Theta)^+$ according to reaction (1), the data

Table 1
Mobility of astatine in 0.4M H(Na)ClO_4 –
$1 \cdot 10^{-4}$M $K_2Cr_2O_7$ at 25 °C

pH	$U_C \cdot 10^{-4}$ * $cm^2\ V^{-1}\ s^{-1}$	pH	$U_C \cdot 10^{-4}$ * $cm^2\ V^{-1}\ s^{-1}$
1.68	1.17	0.93	2.43
1.56	1.34	0.81	2.45
1.42	1.67	0.71	2.64
1.21	2.38	0.63	2.67
1.09	2.41		

*Value of U_C was determined only once.

allow us to estimate the value of the deprotonation constant (K_{dp}) for the astatine-bearing cation

$$K_{dp} = \frac{c_{AtOH}}{c_{(At\ \ominus)^+}}\, c_{H^+} \cdot \frac{f_{AtOH}}{f_{(At\ \ominus)^+}}\, f_{H^+} \qquad (2)$$

where c_i and f_i are concentrations and activity coefficients respectively. As the activity coefficients for ultramicroconcentrations of astatine compounds are the same,

$$K_{dp} = \frac{c_{AtOH}}{c_{(At\ \ominus)^+}}\, a_{H^+} \qquad (2')$$

Obviously, the concentration mobility of astatine (U_c) must be proportional to the mobility of an astatine cation ($U_{(At\ \ominus)^+}$) and its relative concentration in solution:

$$U_c = U_{(At\ \ominus)^+} \cdot \frac{c_{(At\ \ominus)^+}}{c_{(At\ \ominus)^+} + c_{AtOH}} = U_{(At\ \ominus)^+} \cdot \frac{a_{H^+}}{a_{H^+} + K_{dp}} \qquad (3)$$

Transforming Eq. (3) we get

$$\frac{U_c}{U_{(At\ \ominus)^+} - U_c} = \frac{a_{H^+}}{K_{dp}} \quad \text{or} \qquad (4)$$

$$\lg \frac{U_c}{U_{(At\,\ominus)^+} - U_c} = \lg \frac{1}{K_{dp}} - pH \qquad (5)$$

It follows from Eq. (5) that the straight line which shows the dependence of its left part upon pH has a slope of $\alpha = 45°$. Therefore, for the straight line drawn through the points calculated by the least squares method tg α must equal 1. The solution of Eq. (5) with $U_{(At\,\ominus)^+}$ as a fitting parameter shows that the difference $|\mathrm{tg}\,\alpha - 1|$ is *minimal when* $U_{(At\,\ominus)^+} = 3.08 \cdot 10^{-4}$ cm^2 V^{-1} s^{-1} (Fig. 6). The calculated deprotonation constant $K_{dp} = 0.032 \pm 0.005$. It is higher than expected and the same as for IOH_2^+.[11] The order of magnitude seems to be correct, but more experimental data are required to make the value more precise. We think that our result is valuable because it proves, along with other data, the hypothesis on the structure of the astatine-bearing cation in aqueous solution.

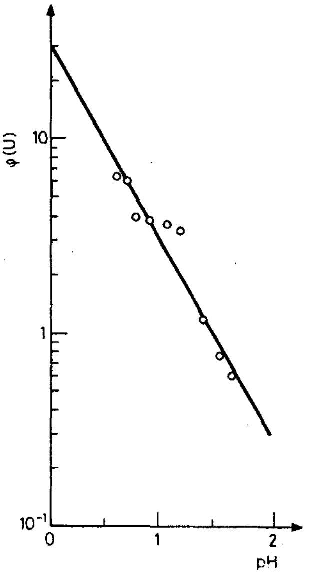

Fig. 6. Dependence of $\varphi(U) = \lg \frac{U_c}{U_{(At\,\ominus)^+} - U_c}$, for $U_{(At\,\ominus)^+} = 3.08 \cdot 10^{-4}$ cm^2 V^{-1} s^{-1} upon the pH of the electrolyte

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