

Separation of astatine and bismuth upon extraction into conventional solvents

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Astatine is one of the least chemically studied elements of the periodic table. Chemical knowledge about fundamental properties of this element is limited due to absence of any stable astatine isotopes. The longest half-lives are 8.3 h and 7.2 h for ^{210}At and ^{211}At , respectively. It should be mentioned that ^{211}At also attracts attention of chemical and medical communities because of its convenient decay mode for α -emitting therapy. The main route to produce medically relevant amounts of astatine-211 activity is the $^{209}\text{Bi}(\alpha, 2n)^{211}\text{At}$ reaction [1]. The energy of the α -beam must be carefully controlled near 28 MeV, leading to 0.9 barn of ^{211}At cross section, to avoid production of radiotoxic ^{210}At [2].

Here we focus on the astatine behavior of the nitric media. Usually, Bi target dissolution is performed at $\sim 10\text{ M HNO}_3$. Based on current understanding of astatine behavior in this solution, there is a mixture of at least two cationic species, monovalent At^+ and trivalent AtO^+ [3, 4]. The vast majority of organic molecules have been applied to extract astatine like alkanes (including chloro-derivatives) and oxygen containing solvents (ether, alcohol, and ketone) [5-8]. The goal of this work is to study fundamental behavior of both astatine and bismuth upon transfer from nitric acid media to conventional solvents, 1-octanol and methyl anthranilate.

The bismuth extraction from nitric acid media to 1-octanol has been studied in experiments utilizing liquid-liquid extraction technique. Fig. 1 shows dependency of Bi distribution ratio values on the aqueous equilibrium concentration of nitric acid. It can be seen that despite the fact that all D-values are below 0.1, there is a clear increasing trend with increase of acidity. To understand the mechanism of Bi

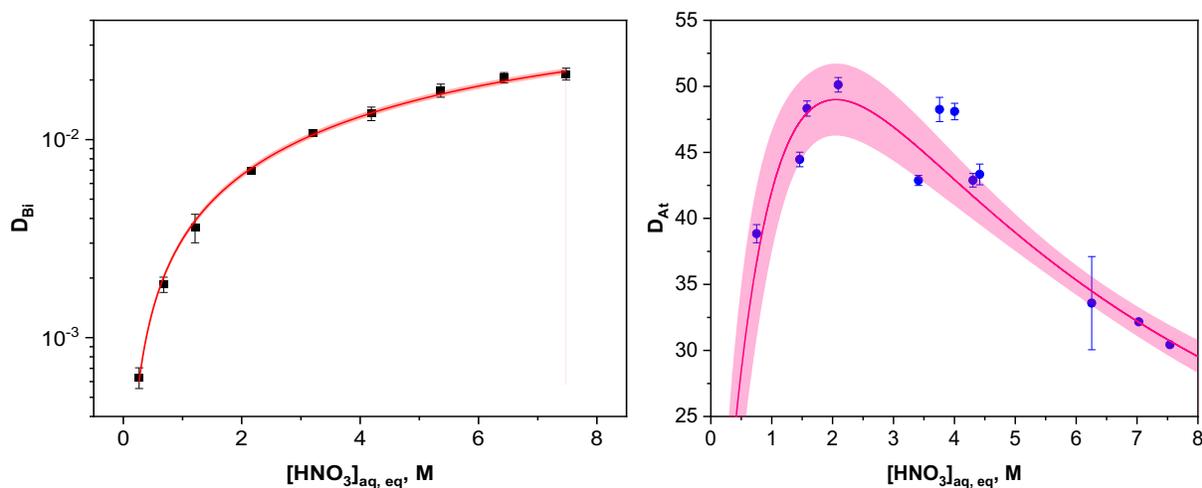


Fig. 1. Distribution ratio values of Bi (left) and At (right) as a function of aqueous equilibrium nitric acid concentration upon extraction into 1-octanol. Lines are fit according to a distribution ratio definition. Shade represents 95% confidence interval.

extraction and as a result to fit experimental data in Fig.1, a mathematical model must be developed. This model is based on a definition of distribution ratio value and Bi speciation in the nitric acid media.

Only one species in the aqueous, namely $\text{Bi}(\text{NO}_3)_3$, can be extracted into 1-octanol in order to maintain the charge balance of the system. The function $D_{\text{Bi}} = f([\text{NO}_3^-])$ based on the distribution ratio definition contains some parameters, namely Bi extraction and stability constants. The latter can be found in the literature and the former one can be estimated by fitting experimental data in Fig. 1 resulting in $K_{\text{ext_Bi}} = 0.234 \pm 0.003$.

The extraction behavior of astatine from nitric acid media into 1-octanol was then studied. In contrast to bismuth, the astatine D-values are much higher, >30 over the HNO_3 range studied. Also, the astatine data trend is significantly different. The treatment previously discussed for bismuth is used to model the At behavior. In this particular case the $D_{\text{At}} = f([\text{NO}_3^-])$ function contains three unknown thermodynamic constants (extraction of At, complex formation with NO_3^- , and potentially reduction of At) and they can be estimated by means of mathematical treatment of experimental data. The corresponding parameters are found to be $K_{\text{ext_At}} = 126 \pm 32$, $K_I = 0.62 \pm 0.27$, and $K_{\text{redox}} = 0.237 \pm 0.033$. The value K_I was previously estimated [9] at a level of 1.35 (no uncertainty provided) and is in agreement with the current findings.

Bismuth extraction into methyl anthranilate was studied by analogy with its extraction into 1-octanol. It can be seen in the left panel of Fig. 2, as with 1-octanol, the extraction efficiency also increases with an increase of acidity; however, the distribution ratio values are much greater with methyl anthranilate, almost reaching 1 at 2.5 M HNO_3 . The methyl anthranilate solubility in the aqueous phase increases with increased nitric acid concentration and this limits the studied acidity range. More importantly, the rise in extraction as a function of acidity is much steeper for methyl anthranilate compared to 1-octanol (D_{Bi} at 2.5 M HNO_3 upon extraction to 1-octanol is ~ 0.01). This, along with high D-values, indicates a stronger interaction between Bi and methyl anthranilate compared to Bi and 1-octanol, resulting in the higher extractability of the metal. Analysis of experimental data indicates bismuth

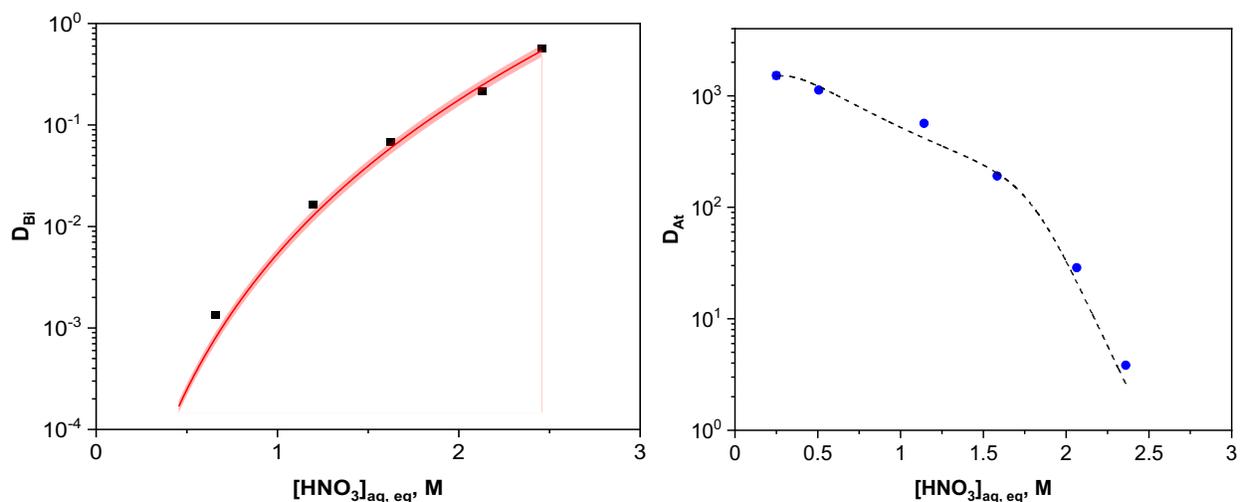


Fig. 2. Bi (left) and At (right) extraction into methyl anthranilate from nitric acid solutions. Solid line is calculated based on a definition of a distribution ratio. Shade represents 95 % confidence interval. D value uncertainties are less than the symbols shown.

is extracted in the form of $Bi(NO_3)_3 \cdot 4RNH_2$ with the extraction constant $K_{ext_{Bi_MA}} = 0.94 \pm 0.05$.

The astatine distribution ratio values at low acidity, ≤ 0.5 M HNO_3 , (shown on the right of Fig. 2) deserve attention due to very high numbers exceeding 1,000. This makes methyl anthranilate one of the most efficient astatine extractants. There is a slight decrease in extraction as the acidity is increased to 1.5 M, after which point there is a sharp decline leading to a very small D-value of 4 at 2.4 M HNO_3 . This is most likely a result of the protonation of the amine group on the methyl anthranilate, preventing the strong interaction between the AtO^+ species and the ligand. It is unclear at this point what the exact source of this diminished interaction is. Overall, this trend indicates that there is also an interaction between the At and methyl anthranilate. However, contrary to Bi behavior this interaction does not facilitate astatine extraction because the D_{At} values monotonically decrease with an increase of acidity.

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