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## Polarography of Some p-Block Elements in Anhydrous Hydrogen Fluoride

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The polarography of the p-block elements In(III), Tl(I), Pb(II), Cd(II), As(III), Sb(III), Bi(III), and the halides in anhydrous hydrogen fluoride has been investigated using a Teflon dropping mercury electrode and an all Kel-F vacuum line. Data obtained are compared with those reported previously for Sn(II) in HF and with corresponding values for aqueous solution systems and the differing roles of the two solvents are discussed, hydrogen fluoride appearing the simpler solvent. The effects of simple solvation and fluoro complexation on the reversibility of reduction processes in HF are also discussed.

### Introduction

Anhydrous hydrogen fluoride (AHF) undergoes self-ionization to give very simple and mobile anionic and cationic species.<sup>2</sup> Having a large dielectric constant the solvent is potentially very useful for effecting dissolution of ionic compounds, particularly fluorides. Because of its volatility and its corrosive and toxic properties, specialized vacuum systems have been used for its manipulation. The majority of physical studies in AHF have been largely confined to conductivity,<sup>3</sup> spectroscopy,<sup>4,5</sup> and, more recently, cryoscopic measurements.<sup>6,7</sup> Prior to the last few years, electrochemical studies were few in number and mainly limited to poten-

tiometry.<sup>8,9</sup> The earliest reports of polarographic investigations in hydrogen fluoride gave details of work which was essentially exploratory since the solvent was not truly anhydrous and the polarograms were not reproducible.<sup>10</sup>

Although polarographic measurements have yielded much information about aqueous solution chemistry and the nature of electrode processes, the conventional use of this technique in fluoride media was largely precluded because of the dissolution of the glass capillaries by the strongly acidic solvent. However, with the use of an all Kel-F vacuum system in conjunction with a Teflon dropping mercury electrode (DME), reliable polarographic parameters may be obtained for metal

ions and complexes in AHF.<sup>11,12</sup> Polarography has one advantage over many solid electrodes in that mercury has a large hydrogen overpotential in AHF enabling a wide range of cathodic processes to be observed. Recently, voltammetric reductions at solid electrodes in anhydrous hydrogen fluoride have been reported.<sup>13</sup>

This paper reports the polarographic behavior of several p-block elements in AHF and discusses trends observed in the redox reactivity of the various oxidation states. Elements of main groups 1 and 2 and early members of main groups 3 and 4 were not included in the survey because their very electropositive nature precludes the observation of reduction processes at the DME in AHF. Other simple fluorides, for example, of sulfur and phosphorus were not studied because of their lack of solubility in hydrogen fluoride. Many of the p-block elements in higher oxidation state oxidize mercury. It was therefore not possible to study reduction of or formation of compounds of Tl(III), Pb(IV), As(V), Sb(V), or Bi(V). Oxidation of tin(II) to tin(IV) was observed and has previously been reported.<sup>12</sup> Oxidation of mercury in AHF solutions containing chloride, bromide, and iodide was studied and is herein reported. Although cadmium is often termed a transition metal it is included in this work because of its similar behavior to that of the p-block metal ions in hydrogen fluoride. For the systems studied fluoride complexation often resulted in significant changes in the reversibility of the electrode process and such trends can be rationalized in terms of simple solvation-complexation models. The results indicate that the nature of many solvated and complexed ions in AHF is much simpler than the behavior of the corresponding oxo and hydroxo species in water.

### Experimental Section

**Apparatus and Procedures.** The polarographic cell, Teflon DME, and the all Kel-F vacuum system were essentially as described previously.<sup>12</sup> Polarograms were obtained with a Metrohm Polarecord E261 using a three-electrode system with a platinum wire as the auxiliary electrode. Both dc and ac polarograms were compensated for ohmic loss with a Metrohm IR Compensator E446 after simple modification.<sup>14</sup> All ac polarography was carried out with a Metrohm ac Modulator E393 with a superimposed ac voltage of 10 mV rms at 50 Hz. To minimize cell impedance the modulating ac voltage was applied through the auxiliary electrode.

For observations requiring variation in the fluoride concentration an external  $\text{CuF}_2/\text{Cu}$  (1 M NaF) reference electrode was used, separated from the polarographic cell by a disk of Teflon filter medium (Millipore Filter Corp.). The mercury pool was also used as an internal reference electrode, the potential of which relative to the external reference electrode was measured to facilitate comparisons of polarograms. All ac peak potentials ( $E_p$ ) were reproducible within  $\pm 1$  mV while the dc half-wave potentials ( $E_{1/2}$ ) had a reproducibility of  $\pm 2$  mV. Degassing of the solutions was not necessary since the use of vacuum techniques had eliminated the possible presence of oxygen in solution. All polarograms were recorded at ambient temperature (15–25 °C) but for any one run the temperature was constant to within 1°, the very poor heat transfer properties of Kel-F being an advantage in this respect.

**Reagents.** Bismuth(III) fluoride was prepared by dissolving the carbonate in aqueous hydrofluoric acid and evaporating to dryness, followed by recrystallization from hydrofluoric acid. Lead tetrafluoroborate resulted from the reaction in aqueous solution of the metal nitrate and sodium tetrafluoroborate. Addition of excess sulfuric acid to an equimolar mixture of calcium fluoride and arsenic trioxide gave arsenic trifluoride. The product was distilled at 60 °C and stored in Kel-F tubes. Antimony trifluoride was purified by sublimation of the commercial reagent at 180 °C. Indium trifluoride was prepared by a halogen exchange reaction of the anhydrous chloride with liquid AHF at 70 °C. Commercial samples of sodium fluoride (analytical reagent) and potassium tetrafluoroborate (Alfa Inorganics) were used. Commercial hydrogen fluoride (Matheson) was pumped at –196 °C to remove hydrogen, distilled twice from trap to trap, and then fractionated in a Teflon column packed with Teflon rings, based on a modification of the design of Shamir and Netzer.<sup>15</sup> The specific

conductance of the AHF was routinely about  $10^{-5} \Omega^{-1} \text{cm}^{-1}$  at 0 °C.

Standard solutions were prepared by condensing HF onto weighed amounts of dried solids in calibrated Kel-F tubes. Potassium tetrafluoroborate and sodium fluoride were used as supporting electrolytes, the former being used to maintain constant ionic strength during runs in which the fluoride concentration was varied. All potentials reported are the average of at least three measurements and are relative to the  $\text{CuF}_2/\text{Cu}$  (1 M NaF) reference electrode.

### Results

In describing electrode characteristics in AHF solutions, the solvent can be regarded as neutral when the fluoride ion activity is that of the pure solvent and basic when there is an increase in fluoride concentration above that level. Solutions of the alkali metal tetrafluoroborate may therefore be regarded as being neutral since dissociation of the tetrafluoroborate ion is negligible. For the following discussion neutral HF refers to solutions with the tetrafluoroborate as the supporting electrolyte and basic HF to those where sodium fluoride is used.

**Indium.** Indium(III) fluoride in 0.1 M sodium fluoride gave one reduction wave apparently due to the electrode process



Logarithmic analysis of the dc wave gave linear plots of slope 31 mV and a half-wave ( $E_{1/2}$ ) potential of –0.841 V, while the corresponding ac wave was also irreversible with a half-width of 56 mV, and  $E_{1/2} - E_p$  was 48 mV. The high ratio of  $i_{dc}/I_p$  of 12 indicates that the electrode process is irreversible. The simple three-electron reduction (eq 1) process observed in AHF is also observed in aqueous media. In neutral HF the dc parameters of the single wave are unchanged but the ac half-width increased from 56 to 65 mV. Addition of sodium fluoride restored the half-width to its former value and increased the solubility by a factor of 5. This change in solubility reflects some Lewis acidity of indium trifluoride; however, complex formation cannot be particularly significant since the half-wave potential did not change appreciably.

**Thallium.** In both neutral and basic solution the wave for reduction of thallium(I) to thallium(0) was well defined. In 0.5 M tetrafluoroborate solutions the half-wave potential was –0.572 V and the electrode process was fully reversible in both dc and ac modes. The half-wave potential was independent of fluoride concentration and, allowing for a maximum error of 4 mV, an upper estimate of  $K_{\text{stab}} < 1.07$  can be made using the modified DeFord–Hume equation.<sup>16</sup> Data from potentiometric measurements under similar conditions<sup>17</sup> show that  $K_{\text{stab}} < 0.7$  for thallium(I) fluoride in AHF.

**Cadmium.** Cadmium fluoride in 0.1 M sodium fluoride solution gave rise to ill-defined dc and ac polarograms for the overall electrode process



The dc wave was irreversible and of slope 84 mV with a half-wave potential of –0.498 V. The irreversibility was reflected in a high value of the ratio  $i_{dc}/I_p$  and the ac half-width of 140 mV. The behavior in 0.1 M tetrafluoroborate was identical with that in sodium fluoride. In neutral and basic HF the dc wave height for saturated solutions was the same which shows cadmium fluoride has no appreciable Lewis acidity or basicity.

**Lead.** Solutions of lead tetrafluoroborate in 0.1 M tetrafluoroborate gave a well-defined reversible dc wave corresponding to the electrode process



with a half-wave potential at –0.729 V. The corresponding ac wave was quasi-reversible with a half-width of 62 mV, and the separation of peak and half-wave potentials was 22 mV. Addition of fluoride, at constant ionic strength, caused the rate of the electrode process to decrease since the dc wave became

quasi-reversible at a fluoride concentration of  $4.4 \times 10^{-3}$  M. A concomitant increase in the half-width occurred. Increasing the fluoride concentration to 0.1 M caused the reversible half-wave potential (extrapolated from the  $\log i/(i_d - i)$  vs.  $E$  plots)<sup>18</sup> to shift by 14 mV to more cathodic potentials and the ac half-width increased to 88 mV. As the fluoride concentration was increased to 1.7 M the ac polarogram broadened into two overlapping waves of total half-width 152 mV but only one dc wave was observed.

**Arsenic.** In 0.1 M fluoride the reduction wave may be assigned to the electrode process



The irreversible reduction was characterized by a dc wave of slope 99 mV with a half-wave potential of -0.594 V and an ac wave with peak potential -0.653 V and a half-width of 137 mV. The irreversibility of the electrode process was further reflected in the small peak current, the ratio  $i_{dc}/I_{peak}$  being 15:1. Although the ac wave was broad it was symmetrical about the peak potential, indicating the absence of adsorption phenomena. In neutral media, the dc wave slope was the same as in 0.1 M fluoride but the ac half-width had increased to 172 mV. This change is reversible since addition of fluoride to the neutral solution restored the ac parameters to their former values. The fact that there is little difference in the rate of reduction of arsenic(III) in neutral and basic hydrogen fluoride probably indicates that arsenic(III) is anionic under both sets of solution conditions. Arsenic trifluoride has been reported to be a fairly strong Lewis acid.<sup>19</sup>

**Antimony.** Solutions of antimony(III) fluoride in AHF provided two reduction waves whose relative heights were dependent on both antimony and fluoride concentrations. The following electrode process is proposed for the first reduction wave



while the second (at more cathodic potentials) is considered to arise from reduction of oxo-antimony(III) species. The first electrode process was characterized by a dc reduction wave of slope 64 mV at -0.743 V, and the ac wave had a half-width of 84 mV with peak potential at -0.770 V in neutral media. Addition of fluoride decreased the dc slope to 39 mV and the half-wave potential to -0.776 V in 0.1 M fluoride solutions, while the ac half-width decreased to 71 mV. The second electrode process was characterized by a dc wave of slope 62 mV and a half-wave potential of -0.901 V; the corresponding ac half-width was 76 mV with peak potential at -0.915 V in neutral HF. Addition of fluoride changed the dc slope to 71 mV in 0.1 M fluoride and the half-wave potential to -0.946 V, and the ac half-width increased to 120 mV.

**Bismuth.** Saturated solutions of bismuth(III) fluoride gave one well-defined irreversible reduction wave in 0.1 M fluoride to which the following electrode process is assigned



The half-wave potential was -1.129 V and the dc wave slope was 47 mV; the corresponding ac half-width was 82 mV while the peak potential was -1.182 V. As expected for such an irreversible process the ac peak current was greatly diminished, the ratio of  $i_{dc}/I_p$  being 40:1. Saturated solutions of bismuth trifluoride in neutral media gave a single reduction wave with parameters the same as those observed in fluoride media.

**Chloride, Bromide, and Iodide.** Solutions of hydrogen chloride, hydrogen bromide, and hydrogen iodide were prepared by adding HF to the appropriate sodium halides and gave, in 0.1 M sodium fluoride solutions, well-defined ac and dc anodic waves which may be represented by the general equation



Table I. Half-Wave Potentials (Volts)

System	HF (basic) <sup>a</sup>	H <sub>2</sub> O (acidic) <sup>b</sup>	H <sub>2</sub> O (neu- tral) <sup>b</sup>	H <sub>2</sub> O (basic) <sup>b</sup>
In(III) → In(0)	-0.84	-0.57	-0.71	-1.09
Tl(I) → Tl(0)	-0.53	-0.48	-0.47	-0.48
Sn(II) → Sn(0)	-0.44	-0.43	-0.62	-1.22
Pb(II) → Pb(0)	-0.73	-0.38	-0.50	-0.78
Cd(II) → Cd(0)	-0.50	-0.59	-0.65	-0.78
As(III) → As(0)	-0.59	-0.70	-0.92	-1.04
Sb(III) → Sb(0)	-0.80	-0.30	-0.50	-1.30
Bi(III) → Bi(0)	-1.11	-0.01	-0.25	-0.60
2Hg + 2Cl <sup>-</sup> → Hg <sub>2</sub> Cl <sub>2</sub>	-0.13 <sup>c</sup>		+0.25	
2Hg + 2Br <sup>-</sup> → Hg <sub>2</sub> Br <sub>2</sub>	-0.20 <sup>c</sup>		+0.12	
2Hg + 2I <sup>-</sup> → Hg <sub>2</sub> I <sub>2</sub>	-0.28 <sup>c</sup>		-0.03	

<sup>a</sup> Relative to CuF<sub>2</sub>/Cu (1 M NaF/HF). <sup>b</sup> Values, relative to SCE, from L. Meites, "Polarographic Techniques", 2nd ed, Interscience, New York, N.Y., 1965. For aqueous values, acidic = 1 M H<sub>2</sub>O<sup>+</sup>, neutral = pH 5, basic = 1 M OH<sup>-</sup>. <sup>c</sup>  $E_{1/2}$  values dependent on [HX]; values given for [HX] =  $10^{-3}$  M.

Both the dc and ac waves were markedly asymmetric with the initial increase in the anodic current at the foot of the wave being much greater than that normally associated with a simple faradaic process. For a millimolar hydrogen chloride solution the initial slope of the dc wave was 16.5 mV while the final portion of the polarogram had a slope of 32 mV. The ac half-width was only 36 mV compared with 45 mV expected for a reversible two-electron process and the peak current was approximately six times as great as that expected for a reversible electrode process. Such behavior is characteristic of specific adsorption of the electroactive species at the DME.<sup>20</sup> At low bromide concentrations,  $8 \times 10^{-4}$  M, the characteristics of the electrode process were similar to those observed for chloride but the ac half-width was 94 mV. As the concentration of bromide was increased the wave broadened and became irreversible and the ac peak height tended toward a limiting value. The behavior of iodide was similar to that of bromide with a half-wave potential at -0.280 for a millimolar solution and an ac half-width of 96 mV. At more positive potentials, +0.083 V, a very sharp ac wave was observed with no corresponding dc wave which indicated that the wave was "tensammetric" in origin, that is, it probably arises from an adsorption-desorption process of a film of mercurous iodide.<sup>21</sup> The half-wave potentials for all the halides were dependent on halide concentration and for convenience they are compared at a given hydrogen halide concentration in HF,  $10^{-3}$  M, and are -0.130, -0.201, and -0.280 V respectively for chloride, bromide, and iodide.

Solutions of arsenic trifluoride in 0.1 M sodium fluoride gave rise to an anodic wave very similar to those observed with the above solutions of the hydrogen halides. The half-wave potential was -0.154 V with an ac half-width of 60 mV. The electrode characteristics of this process were essentially the same when measured in neutral HF solutions.

## Discussion

The results given above are summarized in Table I to provide a basis for discussion of relative values. Earlier, it has been suggested<sup>22</sup> on the basis of a very small number of potentiometric data that, while the reduction potentials for several corresponding redox systems in water and anhydrous hydrogen fluoride differ somewhat in absolute values for each system, the order of potentials in each solvent is the same. The present work indicates that, while this generalization may be valid for cations which may undergo simple solvation in each solvent, it does not hold where the solution processes are more complex. Further, recent spectroscopic observations<sup>23</sup> have shown that cations, particularly in relatively low oxidation

states, are solvated very simply by HF to give species of the type  $M(FH)_x^{n+}$ . It will be suggested that complex solvolysis is more likely in water than in HF, because in addition to aquation there is complexation, first by hydroxo ligands which correspond to fluoro ligands and then, after further deprotonation, by oxo ligands, for which no counterpart is possible in HF.

It was observed in the present work that there was a high degree of irreversibility for many of the systems in neutral HF and that some of these systems became much more reversible as the concentration of the base fluoride was increased. Therefore, comparisons of values from Table I are usually made for acidic water and basic HF. In addition to the fact that the values of  $E_{1/2}$  in each solvent are numerically closer for basic HF and acidic water, it is under these conditions that reversibility is usually greatest in each solvent for the species studied and therefore comparisons, which ideally should be related to  $E^\circ$  values, are most valuable.

It should be noted that  $E_{1/2}$  values do not shift as much in HF as in water as the basicity of the medium is changed. In HF, the change in half-wave potential was not more than about 40 mV in going from neutral solution to one which was 0.1 M in fluoride. Much greater changes are evident in passing from neutral to basic aqueous solution. No polarographic studies can be made in acidic HF. It is open to question whether any solutes demonstrate Brønsted acidity in anhydrous HF. Those which are strong Lewis acids, such as the pentafluorides of arsenic and antimony, are strong oxidants and could not be used with a dropping mercury electrode.

An inspection of Table I shows that the species least susceptible to complex solvolysis is thallium(I) because of its low charge. Values of  $E_{1/2}$  for thallium(I) are seen to be virtually identical in acidic, neutral, and basic aqueous solutions and to be close for basic HF and for acidic water. Thallium(III) could not be studied because it oxidizes mercury.

In principle a two-electron reduction of indium(III) to indium(I) might be expected to be observed; however, the three-electron reduction in HF is consistent with the fact that a stable monofluoride cannot be prepared and that the normal electrode process observed in aqueous media is also a simple three-electron reduction. The reduction potentials of indium(III) in neutral and basic HF are essentially the same ( $\pm 4$  mV), indicating that there is no significant fluoride complexing. This behavior is contrasted with that in water where changes in basicity cause large shifts in the reduction potential due to formation of hydroxo and oxo complexes.

A detailed study of the oxidation and reduction of tin(II) in neutral and basic HF and in the presence of water has been reported previously.<sup>12</sup> When the reduction of tin(II) is considered with its group 4 congener lead(II) and the formally analogous cadmium(II), the values of  $E_{1/2}$  are roughly comparable for each system in basic HF and in acidic water, although it should be noted that the aqueous value for lead(II) is subject to the same sort of discussion in terms of significant hydrolysis as is given for the group 5 elements immediately below.

Values of  $E_{1/2}$  for the reduction in HF to the element of the three group 5 elements in oxidation state three become progressively more negative with increase in atomic number, a trend which is consistent with the values for tin(II) and lead(II) reductions. No comparison is possible for the group III elements because of the lack of stability of indium(I) and because thallium(III) could not be studied at the mercury electrode.

A complete inversion of the order of  $E_{1/2}$  values for reduction of As(III), Sb(III), and Bi(III) occurs in aqueous solution, both acidic and basic. The aqueous species for As(III) is  $As(OH)_3$  or anionic in acid and neutral solution and

anionic forms exist in basic solutions. Antimony(III) is cationic in acid and anionic in base and so gives the largest shift in potentials, while Bi(III) occurs as cations only, with polymeric oxo-cation formation increasing with increasing basicity. It is postulated that the aqueous values might run parallel to those in HF if interaction of the ions with water were restricted to solvation or formation of hydroxo cations, but that the superimposition of oxo complexing leads to the formation of polymeric species, cationic or anionic, in solution and, largely as a result of this, the solution and electrode processes are far less simple than in HF.

In the Sb(III)-HF system a second reduction wave was observed at about 160 mV more negative than that assigned to reduction of a simple antimony(III) species. Anionic antimony(III) species would be expected to be more susceptible to hydrolysis by traces of water present as impurities than arsenic(III) fluoro anions. This shift, attributed to reduction of a fluorooxoantimonate(III), can be compared with the observed shift of 106 mV<sup>24</sup> in the oxidation of tin(II) to tin(IV) when water is added to the system. Since the electrochemistry indicates that Bi(III) probably exists as cations solvated by HF, formation of a second wave due to the presence of adventitious water would be expected to be less likely than in the antimony case.

The above metals are likely to exist as simply solvated ions in neutral HF solutions because of their low charge and the ionizing ability of the solvent. Recent spectroscopic evidence suggests very strongly that di- and tripositive metal cations exist in anhydrous HF as simple solvated entities.<sup>23</sup> Also it is now well established that similar highly acidic solvents such as fluorosulfuric acid stabilize cations even for nonmetals such as the halogens and the group 6 elements.<sup>25</sup>

If the rate of solvent exchange is the slow step in the overall reduction process, then in any one group the larger the ion the more reversible should be the electrode process for ions of the same charge because of the smaller electrostatic attraction.<sup>26</sup> The reduction of tin(II) is quasi-reversible while that of the larger lead(II) is reversible and this may be a reflection of the above argument. A similar trend is observed in the main group 5 elements where the slopes of the dc waves are 99, 64, and 47 mV respectively for reduction of arsenic(III), antimony(III), and bismuth(III). In the isoelectronic series of thallium(I), lead(II), and bismuth(III) the progressive decrease in ionic radius and the increase in positive charge would be expected to cause the ions to become increasingly solvated by the highly polar solvent molecules. This is reflected in the rates of the reduction processes since the ac waves are reversible for thallium, quasi-reversible for lead, and irreversible for bismuth. Similarly, reduction of tin(II) is quasi-reversible while that of the isoelectronic antimony(III) is irreversible. It would appear that the interaction of the metal ions and HF solvent molecules is essentially electrostatic in origin and that the rate of exchange of solvent molecules is the rate-determining step in the overall reduction processes.

The behavior of the hydrogen halides in AHF is seen to follow essentially the same pattern as that of the halides in aqueous media.<sup>21,27,28</sup> Although the differences in half-wave potentials in AHF are not the same as in water, the order of the  $E_{1/2}$  values for the halides is preserved. This order is a measure of the relative solubilities in that mercurous iodide is less soluble than mercurous bromide which is less soluble than mercurous chloride in AHF. Given that the halides exist essentially as HX in hydrogen fluoride, it is not surprising that there are differences in behavior from the aqueous cases. For example, the prestep associated with adsorption of the anions prior to electron transfer in water does not occur in AHF. The decrease in the rates of the electrode process in passing from chloride to iodide in aqueous solution is also observed in HF

and the nature of the overall electrode process is seen to be the same. Differences in behavior are essentially due to differences in the solvation of the "ions" and in the nature of the double layer in AHF compared with water.

**Registry No.** In, 7440-74-6; Tl, 7440-28-0; Sn, 7440-31-5; Pb, 7439-92-1; Cd, 7440-43-9; As, 7440-38-2; Sb, 7440-36-0; Bi, 7440-69-9; Hg, 7439-97-6;  $\text{Hg}_2\text{Cl}_2$ , 10112-91-1;  $\text{Hg}_2\text{Br}_2$ , 15385-58-7;  $\text{Hg}_2\text{I}_2$ , 15385-57-6.

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