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HYDROGEN FLUORIDE - A SIMPLER SOLVENT THAN WATER?

T.A. O'DONNELL

Department of Inorganic Chemistry, University of Melbourne,
Parkville, Victoria 3052, Australia

SUMMARY

Recent solution chemistry of inorganic species in anhydrous hydrogen fluoride is reviewed, covering investigations involving dme polarography and solid electrode voltammetry, measurement of conductance and colligative properties and spectroscopy, both electronic and esr. Using the data from these studies it is postulated that speciation of solutes, particularly cationic entities, is simpler in hydrogen fluoride than in water. This is interpreted in terms of the small number of potential ligands derived from anhydrous hydrogen fluoride, namely the hydrogen fluoride molecule itself and the fluoride ion; on the other hand, species in aqueous solution can be aquo-, hydroxo- and oxo-complexes, the latter frequently being very complex polymeric species. Also few, if any, anions exist in anhydrous hydrogen fluoride which are not related to the solvent, so that complexation by extraneous species does not occur to the extent that it does in water.

INTRODUCTION

Over the last decade refinements in the design of vacuum-tight apparatus constructed from Teflon, Kel-F and similar polymeric materials coupled with the ready availability of synthetic sapphire as windows and in other shapes have led to a deepening and diversification in the application of physico-

chemical techniques to the study of solution processes in anhydrous hydrogen fluoride (AHF). Whereas, previously, investigations were restricted to conductance and fairly simple spectral measurements, there have been recent reports of studies in this solvent using potentiometry, polarography and voltammetry, electronic, Raman and nmr spectroscopy and colligative properties.

Given suitable manipulative techniques, the AHF solvent system is not a difficult one to study. Being extensively associated through hydrogen-bonding, AHF has a conveniently high boiling point, so that extremes of temperature or pressure are not encountered in investigations - an experimental complication in the study of the other hydrogen halides. It is extremely acidic and dissolves a wide range of organic compounds, usually by protonating a functional group. However, this review will be restricted to systems involving inorganic solutes, where interest in the solvent's high acidity, specifically, is limited largely to a consideration of whether Bronsted acids can exist in solution.

By comparison with other solvents it has a very high dielectric constant and therefore is, potentially, a very good solvent for ionic compounds; but the range of ionic solids that can be studied is somewhat limited. Few anions dissolve as such, the other halides being protonated and expelled from solution as molecular gases while the common oxo-anions are either protonated or solvolysed with decomposition. The only anions which appear to have separate existence are fluoride, the base of this solvent system, and those derived from this base and Lewis acids of the system, e.g. BF_3 , GeF_4 , AsF_5 , SbF_5 , TaF_5 , WOF_4 , etc.

Until very recently, relatively few cationic species were amenable to study in AHF and those that were provided little of spectroscopic, magnetic or other inorganic chemical interest. Except in highest oxidation states (usually d^0 configurations), when they dissolve as molecular entities, transition metal, actinide and lanthanide ions could not be studied because of the very low solubility of their fluorides [1]. AcF , TlF and the Group I fluorides are very soluble. Main Group difluorides, e.g. SnF_2 , PbF_2 and

those of Group II, give low cationic concentrations in AHF. A wide range of heavy metal cations can now be studied since it has been shown [2,3] that the addition of a Lewis acid such as BF_3 or AsF_5 to suspensions of metal fluorides in AHF produces appreciable concentrations of cations and of fluoro-anions of the Lewis acid, these anions being formed at the expense of fluoride, causing dissolution of the solid fluoride.

In addition to the few heavy metal fluorides which dissolve because of their relatively strong Lewis acidity, fluorides of several heavy metals in highest oxidation state are soluble in AHF as stated above. The hexafluorides of transition metals and of actinides [4] as well as VF_5 [5] and ReF_7 [6] are soluble in AHF at room temperature to the extent of 0.5 to 3.3 M, without dissociating or without accepting fluoride ions. Xenon fluorides dissolve, the hexafluoride with dissociation into XeF_5^+ and F^- [4,7]. HSO_3F provides another example of a non-dissociating solute; cryoscopy gives a value of unity for ν for HSO_3F [8], an indication of the great acidity of AHF as a solvent.

If solvent-solute interaction is considered in greater depth than in the descriptive introduction to this review and then compared with solvent-solute interaction in water, simpler species can be expected in HF than in H_2O . Potential ligands derived from water are OH_2 itself, OH^- and O^{2-} . In general, aquo-species are relatively simple as are entities in water in which the only other ligand is OH^- . However, oxo-complexation frequently leads to bridged polymeric species, particularly for cationic species, as indicated by the complex aqueous chemistry of Fe(III), Ti(IV), Ce(IV), U(IV), etc. In many instances, formation of stable oxo-species is the driving force in disproportionation reactions in aqueous media. Thus U(V) disproportionates readily to the soluble UO_2^{2+} ion and U(IV) while Mn(III) gives insoluble MnO_2 and Mn^{2+} .

Against this situation, ligands derived from HF are the solvent molecule itself and F^- , each of which would be expected to be involved in simple soluble species. There is no equivalent of oxo-complexation. It is noteworthy that U(V) [9] and Mn(III) [1,2] are both stable in AHF. In passing, it

is worth comment that, for the other "water-like" solvent, NH_3 , the possible ligands are NH_3 , NH_2^- , NH^{2-} and N^{3-} . Ammonolysis of BiCl_3 and TiCl_4 is reported to yield BiN and TiNCl , the solvolysis equivalents of BiOCl and TiOCl_2 . So, on the grounds proposed here, ammonia would be expected to give a much wider range of solvolysis products than H_2O and HF in turn.

VOLTAMMETRY OF HEXAFLUORIDES AND RELATED COMPOUNDS

Polarography and voltammetry can provide very simple evidence as to whether changes in stereochemistry of species in solution occur with changes in oxidation state. If an electroactive species retains its stereochemical environment during oxidation or reduction the observed electrode process is usually reversible whereas structural change, particularly from a simple to a complex species (or vice versa), leads to electrochemical irreversibility. An example relevant to this discussion is reduction of Te(VI) in aqueous solution. Data for polarographic reduction [10] show that the observed reduction from Te(VI) to Te(-II) is irreversible, hardly surprising when the parent species is Te(OH)_6 , the reduced product is Te^{2-} and the intermediate Te(IV) can exist as species such as TeO(OH)^+ or HTeO_3^- depending on the pH of the solution.

For the transition metal tungsten, the formal equivalent of Te(OH)_6 in water would be W(OH)_6 . However, it is well-known that tungstic acids are much more complex than this and tabulation and discussion of the polarographic data [11] for reduction of tungstic acids show very high degrees of irreversibility, even for $\text{W(VI)} \rightarrow \text{W(V)}$.

Voltammetric reduction in AHF of WF_6 [12], the analogue of W(OH)_6 , showed perfect reversibility at both mercury and platinum electrodes as indicated by the fact that the peak-to-peak separation in the cyclic voltammogram (Fig. 1) was 60 mV for each electrode. The value of $E_{1/2}$, corresponding with E^0 in the case of a reversible system, was -0.10 volt (relative to

the Cu/CuF₂, 1.0M F⁻ reference electrode). The same voltammetric parameters were reproduced for oxidation of NaWF₆.

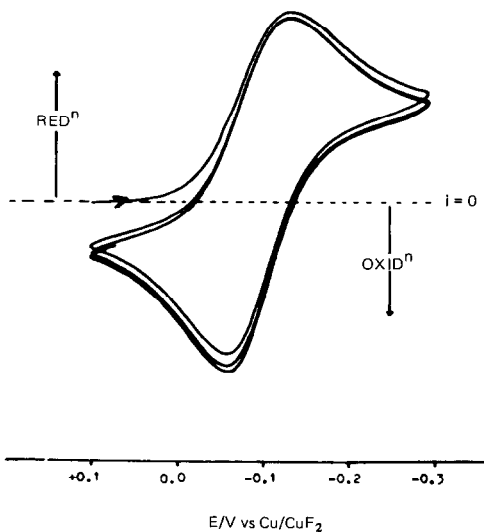
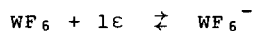


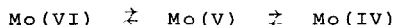
Fig. 1 Cyclic voltammogram for the reduction $WF_6 + 1e \rightleftharpoons WF_6^-$ in neutral AHF at a Pt electrode.

There was no change in reduction or oxidation parameters when neutral AHF (containing BF_4^- as the supporting electrolyte) was replaced by progressively more basic solutions (those in which F^- was added to replace BF_4^-). All of these observations indicate the presence of simple species in a redox reaction:

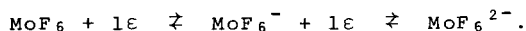


Shift in $E_{1/2}$ value on addition of F^- would have indicated that species such as WF_7^- or WF_8^{2-} were significant in the redox processes. This voltammetric work supports the postulation by Frlec and Hyman [4], based on conductance measurements and simple Raman spectroscopy, that WF_6 exists as such in AHF.

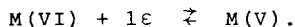
For the corresponding molybdenum system, the story is essentially the same. In aqueous solution the voltammetric reduction:



is very complex [13]. However, MoF_6 in neutral and in basic AHF showed reversible reduction to Mo(V) at +0.91 volt and to Mo(IV) at +0.31 volt [14]. This was checked by recording the voltammogram for both oxidation and reduction of NaMoF_6 in neutral and basic AHF. So again the evidence, supporting Frlec and Hyman's observations on MoF_6 alone [4], is that the redox reactions are those in which simple species of unchanging stereochemistry participate:



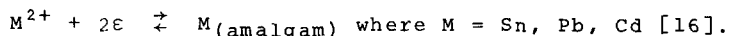
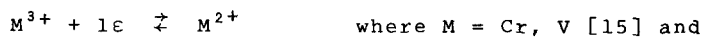
Because the oxidized and reduced species have identical stereochemistry in both the Mo and W systems, E° values for both systems are directly and validly comparable for the general reaction:



No such reliable basis exists for comparison of the aqueous redox reactions for both systems. The magnitude of the difference in E° for the fluorides, namely 1 volt, is of particular interest because not many years ago MoF_6 and WF_6 were thought to be virtually identical chemically. It should be noted that both WOF_4 [12] and MoOF_4 [14] also proved amenable to voltammetric study in AHF, indicating retention of relatively simple stereochemistry in each case.

POLAROGRAPHY OF CATIONIC SPECIES

Voltammetry of heavy metal hexafluorides in AHF has been discussed initially because in that work the component species are demonstrably simpler than in the formally corresponding aqueous solutions. However, many systems have been investigated which, superficially, conform more faithfully to conventional polarographic and voltammetric systems, for example:



Polarographic oxidation and reduction of Sn(II) were studied in considerable depth [17] and typical dc and ac polarograms are shown in Fig. 2. In that work, electrode processes were interpreted in terms of reduction and oxidation in neutral solution of the species $\text{Sn}(\text{FH})_x^{2+}$ with very weak fluoro-complexation occurring with increasing basicity of the of the solution. The question of fluoro-complexation will be taken up later in this review.

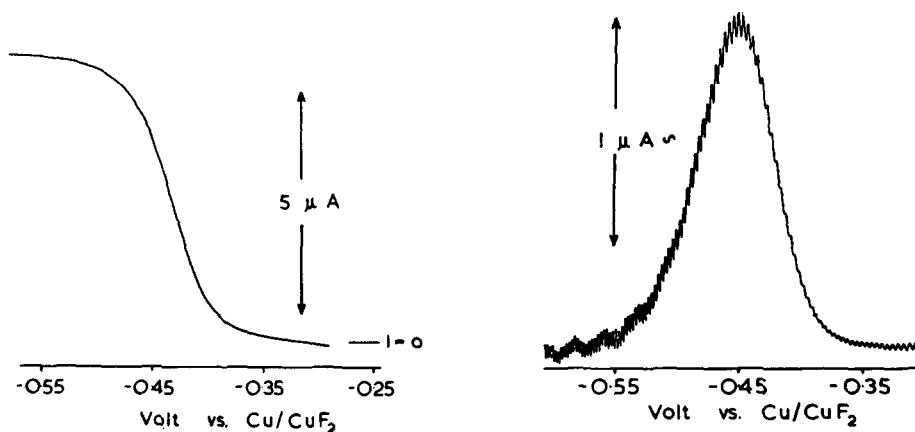


Fig. 2 Dc and ac polarograms for the reduction $\text{Sn}^{2+} + 2e \rightleftharpoons \text{Sn}$ in basic AHF.

SPECTROSCOPY AND SOLVATION

There is now a considerable body of evidence from spectroscopy, electronic and more recently esr, about the precise nature of HF-solvation of metal cations in solution. As stated earlier, BF_3 has been used as a Lewis acid in AHF - even though a weak one - to produce solutions of cations such as Ni^{2+} , Co^{2+} , Pr^{3+} and Nd^{3+} . Reliable quantitative UV-visible spectra of these solutions were recorded using Kel-F spectral cells with sapphire windows [3]. The observed spectra were quite extraordinarily similar to the corresponding aqueous ones, as exemplified in Fig. 3.

These spectra are interpreted as indicating that Ni(II) and Co(II) must be in solution as $\text{Ni}(\text{FH})_6^{2+}$ and $\text{Co}(\text{FH})_6^{2+}$ by comparison with the established entities $\text{Ni}(\text{OH}_2)_6^{2+}$ and $\text{Co}(\text{OH}_2)_6^{2+}$ as they exist in strongly acidic, non-complexing aqueous solution. Similarly, the evidence is that Pr^{3+} and Nd^{3+} cations in AHF are the counterparts of the hydrated ions.

When a pressure of BF_3 is applied to a suspension of MnF_2 in AHF a solution is obtained, the UV-visible spectrum of which shows both similarities to and differences in intensity

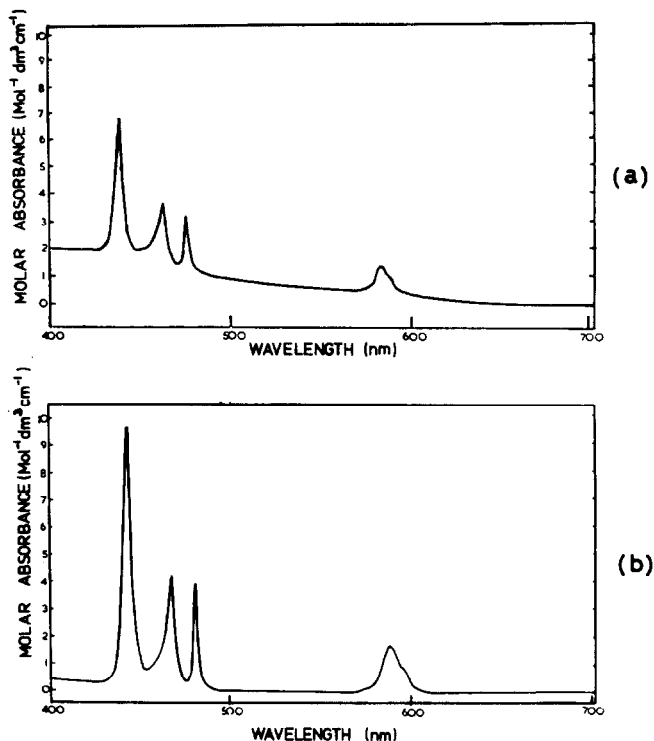


Fig. 3 Electronic spectra for Pr^{3+} in (a) AHF; (b) aqueous HClO_4 .

from the aqueous spectrum for $\text{Mn}(\text{OH}_2)_6^{2+}$. Furthermore, esr spectroscopy gives a six-line spectrum consistent with an octahedral environment of HF molecules around the cation [18].

Treatment of metallic vanadium in AHF with BF_3 yields a solution of V^{2+} , the spectrum of which is given in Fig. 4 [19].

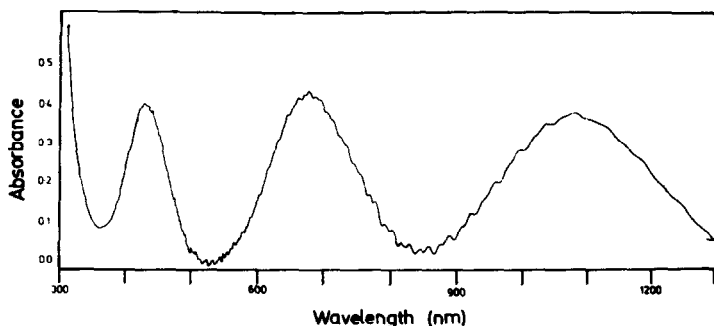


Fig. 4 Electronic spectrum for V^{2+} in AHF.

This work has particular interest in two respects. Firstly, the spectrum is very similar to reflectance spectra of crystalline solids containing the $V(OH_2)_6^{2+}$ cation, indicating that the solution contains $V(FH)_6^{2+}$. Secondly, the spectra for Ni^{2+} , Co^{2+} , Pr^{3+} , Nd^{3+} and Mn^{2+} are for the elements in their normal oxidation states, whereas in this instance we have a stable solution of V(II). Several AHF solutions have now been prepared, and their spectra recorded, with metals in oxidation states which are difficult or impossible to maintain in aqueous solution. Such systems include Ti(II) [19], U(III) [9], Ni(IV) [20] and Ag(II) [21]. AHF is proving a valuable solvent for solutes in unusual oxidation states because stronger reductants are needed to reduce HF to H_2 than for H_2O and none but the strongest oxidants will liberate F_2 .

CONDUCTANCES, COLLIGATIVE PROPERTIES AND SOLVATION

Unpublished conductance data from McMaster University for AHF solutions of Group I fluorides [22] suggest that HF-solvation of cations may be somewhat easier to interpret than the corresponding hydration processes. Fig. 5(a) gives the variation in specific conductance with change in concentration for Group I chlorides in water. This observed behaviour is usually interpreted in terms of differing extent of hydration of the cations. Fig. 5(a) suggests that there is no simple relationship between hydration number and atomic number,

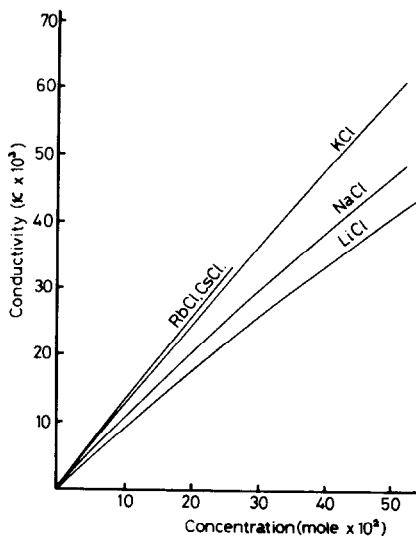


Fig. 5(a)

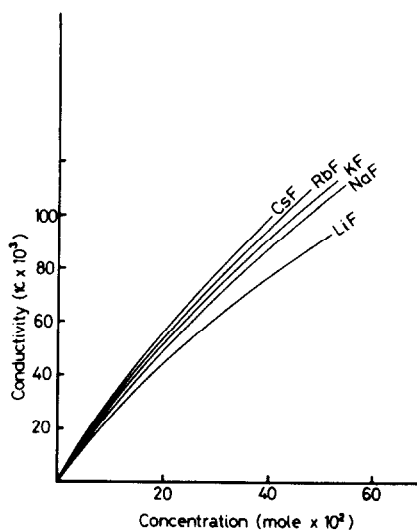


Fig. 5(b)

Fig. 5 Conductivity vs. concentration for:
 (a) Group I chlorides in H_2O ;
 (b) Group I fluorides in AHF .

particularly for the lighter alkali cations. On the other hand, for the same solvated cations in AHF the conductances in Fig. 5(b) indicate a much more direct dependence of solvation number, and therefore of mobility, on ionic radius. Li^+ , expectedly, is somewhat anomalous; but thereafter conductances and mobilities appear to be much more directly related to ionic radius.

With its high dielectric constant, AHF could be a fruitful medium in comparison with water in which to study attractions between solvated ions. In their cryoscopic work at about $-84^\circ C$, Gillespie and Humphreys [8] showed ideal relationship between lowering of freezing point and molality of Group I fluorides until solutions were at least 0.1 molal. Measuring vapour pressure lowering at much higher temperature ($0^\circ C$), O'Donnell and Peel [23] found ideality of solution behaviour at molalities approaching 2.

FLUORO-COMPLEXATION

Spectroscopic data have been presented above to establish that, even in weakly acidic AHF solutions, cations are solvated simply by HF molecules, the coordination numbers being identical with or similar to those which occur for coordinated water molecules for the same cations in highly acidic, non-complexing aqueous solutions, e.g. in strong HClO₄ solutions. It should be noted that virtually all of the anions which can exist in AHF are closely related to the solvent itself, i.e. there is no equivalent of the enormous range of complexation that can occur in water by ligands such as halide ions, sulphate, carboxylates and the many other ions and molecules with oxygen, nitrogen or other donor atoms. Recent spectroscopy of AHF solutions acidified with different Lewis acids has shown that, for species such as uranium and neptunium in oxidation states (III) and (IV), solution spectra are unchanged regardless of whether the Lewis acid of the system is BF₃, AsF₅ or SbF₅ [9]. This shows that the anions BF₄⁻, AsF₆⁻ and SbF₆⁻ have no significant coordinating effect on the cation in solution.

The only ligand other than the HF molecule which can be derived from the solvent is the fluoride ion. There is a relatively small amount of polarographic information now available to suggest that fluoro-complexing leading to species soluble in AHF is fairly weak. When fluoride is added to neutral AHF containing Sn²⁺ and BF₄⁻ ions, the shift in the observed value of E_{1/2} in passing from neutral solution to one 0.5M in fluoride is only 25 mv, indicating very weak fluoro-complexation. Similarly, for the Cr(III) + 1e ⇌ Cr(II) system, a shift in E_{1/2} of only 40 mv occurs in passing from neutral AHF to a solution 0.1M in fluoride.

MacLeod and O'Donnell [16] have tabulated differences in values of E_{1/2} for many metallic species in neutral aqueous solution and in basic solutions 1M in OH⁻. Admittedly, the concentrations of base in the aqueous and AHF solutions are not identical; but the comparison is stark. The shift for the aqueous Sn(II) system is 600 mv, 380 for In(III), 280 for Pb(II) and 130 for Cd(II). It is significant that in neutral

and basic solutions of Tl(I), for which OH^- complexing would be expected to be very weak, the difference in $E_{\frac{1}{2}}$ between neutral and basic solution is very small.

In some preliminary investigational potentiometry in AHF, Hefter [24] examined the change in potential (relative to the Cu/CuF₂, 1M F⁻ reference electrode) of a Ni/NiF₂ electrode with change in F⁻ concentration. Amongst other studies, he showed by direct potentiometry that β_1 for $\text{Tl}^+ + \text{F}^- \rightleftharpoons \text{TlF}$ was not greater than 0.4 l mol⁻¹ and for $\text{Sn}^{2+} + \text{F}^- \rightleftharpoons \text{SnF}^+$ was 10 ± 10 l mol⁻¹. These early potentiometric measurements support the polarographic evidence for weak complexation of cations by F⁻ in AHF and suggest that further direct potentiometric investigation could be very rewarding.

Lattice energies of solid fluorides are very high. So, as stated in the Introduction, many cations complex with fluoride in AHF to give very insoluble precipitates. While many of these are now known to be soluble in acidic AHF solutions, it appears that re-dissolution of these solids in strongly basic AHF does not occur readily. CrF₃ dissolves in AHF containing fluoride [19] but AlF₃ does not to any appreciable extent. One rather peculiar feature is that the fluorides which do dissolve readily in base are frequently those of metals in unusually high oxidation states, e.g. Ni(IV) [20], Mn(III) and Mn(IV) [21] and Co(III) [2].

CONCLUSION

Whereas there is a very restricted range of anions which can exist in AHF, whether as simple anions or as fluoro-anions derived from the Lewis acids of the system, a feature of AHF solution chemistry, as developed in this review, is that a wide range of simple uncharged and cationic species does exist, for many of which there are no aqueous counterparts. The list is not exhaustive. For example, Gillespie and co-workers have used conductance measurements as well as Raman, infra-red and nmr spectroscopy to demonstrate the existence in AHF solution of simple fluoro-cations such as SF₃⁺ [25] and SeF₃⁺ [26]. Several other simple fluoro-cations

for which there are no aqueous counterparts have been shown to have separate existence in AHF, e.g. XeF^+ , XeF_3^+ , XeF_5^+ , ClF_2^+ and BrF_2^+ .

It has been recognized throughout this review that in its own right as a liquid, HF is no less complex than H_2O . Hydrogen-bonding is two-dimensional rather than three-dimensional as in water and HF vapour is complex and polymeric whereas water vapour is not. However, a considerable body of evidence is emerging that speciation is frequently simpler in HF than in H_2O .

HF provides a smaller range of ligands to participate in solvation and solvolysis reactions than does water. More importantly, in aqueous solutions much of the complexity of hydrolysis products results from the occurrence of oxo-bridging. Even if hydroxo- and fluoro-complexation are regarded as formally analogous, polarographic data indicate that fluoro-complexes in AHF are considerably less stable than hydroxo-complexes in water. Much work needs to be done to establish this point reliably; but this review may help to focus the discussion from existing or new investigations of solution processes in AHF on the comparison between this interesting solvent and water.

If it is ultimately confirmed that speciation is significantly simpler in AHF than in H_2O , it may be possible to use studies of solution processes in AHF to throw light on complex reactions in H_2O and to obtain more fundamental information than is now available on the nature of aqueous solutions which are the ones of prime importance in the environment in which we live.

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