The Hydrogen Fluoride Solvent System. Part V. Solutions of SeF_4 and SeF_4,BF_3

By **Morley Brownstein** and **R. J. Gillespie**,* Department of Chemistry, McMaster University, Hamilton, Ontario, Canada

Conductimetric measurements show that selenium tetrafluoride is a weak base in liquid hydrogen fluoride having an ionization constant of 4×10^{-4}. The adduct SeF_4,BF_3 ionizes in hydrogen fluoride but the solutions have a considerably lower conductivity than those of $SF_3^+BF_4^-$; it is concluded that SeF_4,BF_3 is both polymeric and incompletely ionized in solution in HF. The ^{19}F n.m.r. chemical shift of SeF_4,BF_3 in solution in HF, the ^{77}Se–^{19}F coupling constant and the isotopic shift of the ^{19}F resonance in $^{77}SeF_4,BF_3$ have been determined and are discussed.

THE adducts of selenium tetrafluoride with Lewis acids are considered to be ionic compounds containing the SeF_3^+ cation. Raman spectra of the molten complexes SeF_4,AsF_5 and SeF_4,SbF_5 have been assigned in terms of the ionic structures $SeF_3^+AsF_6^-$ and SeF_3^+-SbF_6^-.[1] Crystal structure determinations of SeF_4,NbF_5 and $SeF_4,2NbF_5$ show that they are composed of the SeF_3^+ and NbF_6^- or $Nb_2F_{11}^-$ ions respectively although there is considerable interaction between the ions through fluorine bridging.[2,3] In the case of SeF_3^+-NbF_6^-, four formula units are linked to give Se and Nb atoms at alternate corners of a distorted cube, while for $SeF_3^+Nb_2F_{11}^-$ the ions interact to form endless chains. Recent Raman spectral studies of the solid adducts of SeF_4 with a number of pentafluorides showed that they contain SeF_3^+ and MF_6^- ions, but their symmetry is lower than that of the free ions, presumably because of fluorine bridging.[4] The Raman spectra of a number of solid SF_4 adducts with pentafluorides have also been interpreted in the same way.[5] In addition it has been found that association between the ions in the SeF_4 adducts persists in the molten state and to some extent in solution in nitrobenzene.[4]

In this paper we report the results of studies of solutions of SeF_4 and SeF_4,BF_3 in the strongly ionizing solvent, anhydrous hydrogen fluoride.

EXPERIMENTAL

Hydrogen fluoride was purified as previously described.[6] Boron trifluoride (C. P. grade, Matheson) was used without further purification. Selenium tetrafluoride was prepared by the fluorination of selenium (AnalaR) at 0 °C. The product was stored in liquid air in glass containers with break seals until used. SeF_4,BF_3 was prepared in a Kel-F trap on a Monel vacuum line by adding BF_3 to a solution of SeF_4 in HF cooled to $-78°$. White crystals precipitated from the solution. When no more BF_3 would dissolve the solution was kept cold for several hours under an excess BF_3 pressure. Then the excess BF_3 and HF were slowly pumped off while allowing the trap to warm up to room temperature. When all the HF had apparently been removed the trap was transferred to a glass vacuum line and further evacuated. The SeF_4,BF_3 was then purified by vacuum sublimation before use; m.p. 53·5—55·3 °C (lit.[7] 50 °C). This m.p. indicates that our material was purer than that prepared previously by Bartlett and Robinson [7] who reacted SeF_4 with an excess of BF_3 without the use of HF as a solvent.

Conductivity measurements were made at $0{\cdot}00 \pm 0{\cdot}01$ °C in a ' test tube ' type conductivity cell.[8]

^{19}F N.m.r. spectra were measured using a Varian DA-60IL spectrometer operating at 56·4 MHz. The 2500 Hz audio modulation side bands forming part of the base line stabilization circuitry of the instrument sometimes overlapped part of the centreband spectrum and the ' lock box ' was therefore modified to take an external manual oscillator frequency from a Muirhead D-890-A audio frequency oscillator. Spectra were then measured using the first upper sideband in the field sweep unlock mode. Low temperature spectra were obtained using a Varian V4540 temperature controller with the variable temperature probe. Solutions were contained in thin wall Kel-F tubes which were inserted into precision glass n.m.r. tubes. The reference liquid, $CFCl_3$, was contained in the annular space. Accurate measurements of the coupling constant and isotope shift for F on ^{77}Se were made in frequency-sweep lock-mode operation. In order to check the values

---

[1] J. A. Evans and D. A. Long, *J. Chem. Soc.* (*A*), 1968, 1688.

[2] A. J. Edwards and G. R. Jones, *J. Chem. Soc.* (*A*), 1970, 1491.

[3] A. J. Edwards and G. R. Jones, *J. Chem. Soc.* (*A*), 1970, 1891.

[4] R. J. Gillespie and A. Whitla, *Canad. J. Chem.*, 1970, **48**, 657.

[5] M. Azeem, M. Brownstein, and R. J. Gillespie, *Canad. J. Chem.*, 1969, **47**, 4159.

[6] R. J. Gillespie and K. C. Moss, *J. Chem. Soc.* (*A*), 1966, 1170.

[7] N. Bartlett and P. L. Robinson, *J. Chem. Soc.*, 1961, 3417.

[8] M. Brownstein and R. J. Gillespie, unpublished results.

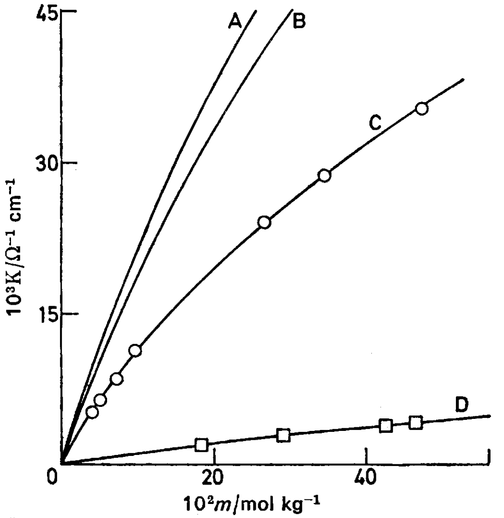
obtained they were also measured on a Varian HA-100 n.m.r. spectrometer operating at 94·1 MHz in the frequency-sweep lock mode.

RESULTS AND DISCUSSION

Selenium tetrafluoride dissolves in hydrogen fluoride to give weakly conducting solutions (Table 1 and Figure) and it presumably ionizes as a weak base:

$$SeF_4 + HF \rightleftharpoons SeF_3^+ + HF_2^- \qquad (1)$$

By assuming that the mobility of the SeF_3^+ ion is equal to that of the potassium ion, the concentration of SeF_3^+ and HF_2^- ions was found by comparison with the conductivity curve for KF in HF.[8] Hence values for the degree of dissociation and the equilibrium constant $K_b = [SeF_3^+][HF_2^-]/[SeF_4]$ were obtained (Table 1).



Conductivities of some solutions in HF, A, KBF_4; B, SF_4,BF_3; C, SeF_4,BF_3; D, SeF_4

TABLE 1

Electrical conductivities of solutions of SeF_4 and SeF_4,BF_3 in HF

SeF$_4$			SeF$_4$,BF$_3$		
Molality mol kg^{-1}	$10^2\kappa$ Ω^{-1} cm^{-1}	10^4K_b* mol l^{-1}	Molality mol kg^{-1}	$10^2\kappa$ Ω^{-1} cm^{-1}	K_2† mol l^{-1}
0·184	0·20	2·0	0·039	0·52	0·019
0·289	0·29	3·6	0·049	0·64	0·023
0·425	0·38	2·9	0·069	0·86	0·036
0·466	0·40	3·2	0·096	1·12	0·048
0·620	0·52	4·2	0·265	2·40	0·10
1·119	0·80	5·7	0·344	2·85	0·10
			0·472	3·52	0·12

* $K_b = [SeF_3^+][HF_2^-]/[SeF_4]$. † $K_2 = [SeF_3^+][BF_4^-]/[SeF_4,BF_3]$. Calculated assuming that ionization occurs according to equation 2 and that the mobility of SeF_3^+ is equal to that of K^+.

SeF_4 is a weaker base in HF than SF_4 ($K_b = 4 \pm 2 \times 10^{-2}$ mol l^{-1}) by two orders of magnitude.[5]

The ^{19}F n.m.r. spectrum of a solution of SeF_4 in HF is a single broad line at all temperatures. The chemical shift was found to be intermediate between that for pure HF and that for pure SeF_4 and was at approximately the position expected for a weighted average of the relative number of fluorines in SeF_4 and in HF (Table 2). Rapid exchange of fluorine between SeF_4 and HF presumably occurs through the SeF_3^+ ion. The ^{19}F chemical shift of pure liquid SeF_4 has been previously reported as −141 p.p.m. from CF_3CO_2H (*i.e.*, −61 p.p.m. from $CFCl_3$).[9] This value differs markedly from the value that we have found (Table 2) but we are unable to explain this discrepancy.

TABLE 2

^{19}F Chemical shifts for SeF_4 and its complexes

	t/°C	δ_{CFCl_3}/p.p.m.
SeF_4		−24·8
SeF_4,SbF_5 molten [a]	150	−15·8
SeF_4,SO_3 molten [b]	70	−4·3
SeF_4,SO_3 in HSO_3F [b]	−85	−3·9
SeF_4,BF_3 in HF (5·5 m)	−82	−6·0
SeF_4 in HF	−80	+128
HF	−90	+194

[a] Ref. 4. [b] Ref. 10.

SeF_4,BF_3 gives conducting solutions in HF but the conductivity is only about half as great as that of the fully ionized KBF_4 or $SF_3^+BF_4^-$ (Table 1, Figure). Thus it might at first sight appear to be reasonable to assume that the ionization of the adduct is incomplete particularly since it is very probable that there is strong fluorine bridging in the solid state, *i.e.*

$$SeF_4,BF_3 \rightleftharpoons SeF_3^+ + BF_4^- \qquad (2)$$

By comparison of the conductivity curve with that of the fully ionized $SF_3^+BF_4^-$ [5] or KBF_4 [8] the degree of dissociation and the ionization constant $K_2 = [SeF_3^+][BF_4^-]/[SeF_4,BF_3]$ can be calculated (Table 1). The dissociation 'constant', K_2 was found to increase markedly with increasing concentration and consequently we conclude that SeF_4,BF_3 is not behaving simply as a weak binary electrolyte ionizing according to equation (2).* This is perhaps not surprising in view of the fact that both SeF_4 and BF_3 are weak electrolytes in HF and consequently appreciable fluoride ion transfer between SeF_3^+ and BF_4^- according to equation (3) may be expected.

$$SeF_3^+ + BF_4^- \rightleftharpoons SeF_4 + BF_3 \qquad (3)$$

Further evidence can be obtained from the ^{19}F n.m.r. spectrum of solutions of SeF_4,BF_3 in HF which show at temperatures below −40° a single peak due to BF_4^- at +152 p.p.m. from $CFCl_3$. On addition of an excess of BF_3 this peak due to BF_4^- disappears and a new peak appears at −6·0 p.p.m. from $CFCl_3$. This new peak may be assigned to a selenium species since it is accompanied by the characteristic satellite peaks arising from ^{19}F coupled to ^{77}Se ($I = 1/2$) which has

---

* The choice of a fully ionized comparison electrolyte affects the calculated value of K_2 to some extent but whatever comparison electrolyte is used, *e.g.*, $SF_3^+BF_4^-$, KBF_4, or $CsBF_4$ there is a marked variation in K_2 with concentration.

[9] E. L. Muetterties and W. D. Phillips, *J. Amer. Chem. Soc.*, 1959, **81**, 1084.

[10] T. Birchall, R. J. Gillespie, and S. L. Vekris, *Canad. J. Chem.*, 1965, **43**, 1672.

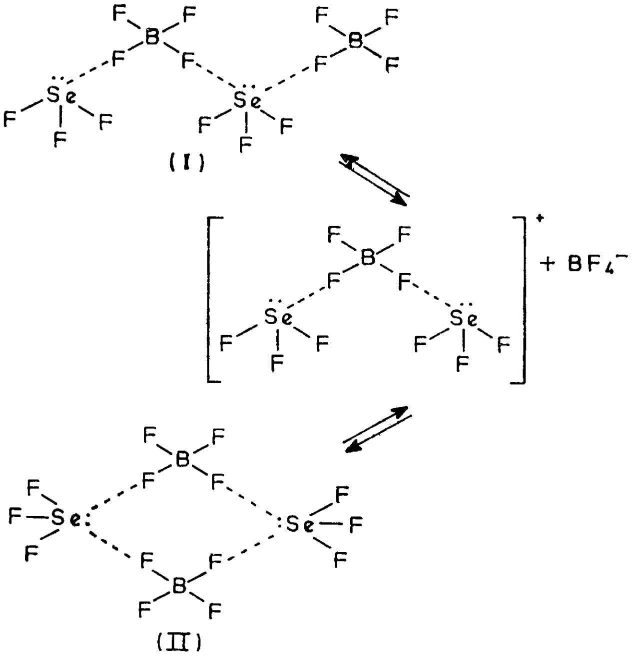
7·5% natural abundance but this cannot be SeF_4 as this has a chemical shift of −24·8 p.p.m. from $CFCl_3$ and it may therefore reasonably be assigned to SeF_3^+.

In order to account for the conductivity of the solutions according to equation (3) there would have to be comparable concentrations of BF_4^-, BF_3, SeF_4, and SeF_3^+, but it has previously been found that HF solutions containing both BF_3 and BF_4^- exchange fluorine rapidly with the solvent and only a single ^{19}F peak arising from BF_3, BF_4^-, and HF is observed. Consequently the observation of the BF_4^- signal is not in accord with the presence of BF_3 in the solution and is therefore not in agreement with equation (3).

Since it is very probable that SeF_4,BF_3 has a fluorine bridged structure such as has been found for SeF_4,NbF_5 and $SeF_4,2NbF_5$ [2,3] it is reasonable to assume that the fluorine bridges are not completely disrupted in solution and that polymeric molecules and ions may be present. The simplest equilibrium of this type that could be envisaged would be that involving the dimer $(SeF_4,BF_3)_2$, *i.e.*

$$(SeF_4,BF_3)_2 \rightleftharpoons (SeF_3)_2BF_4^+ + BF_4^- \qquad (4)$$

Assuming that $(SeF_4,BF_3)_2$ has either a linear structure (I) or a cyclic structure (II) this equilibrium can be written out in more detail as follows:



If ionization according to equation (4) is almost complete, the conductivity of the solutions would be accounted for. A similar equilibrium has been proposed to account for the conductivities of solutions of SeF_3,SO_3F in HSO_3F.[11] However the fact that a peak due to F on Se is not observed in the n.m.r. spectrum, except on addition of an excess of BF_3, means that the F on Se must be exchanging with the solvent presumably by formation of SeF_3^+ according to the equation

$$(SeF_3)_2BF_4^+ \rightleftharpoons SeF{,}_3BF_4 + SeF_3^+$$

which then exchanges with the solvent in the following manner

$$SeF_3^+ + F^- \rightleftharpoons SeF_4$$

the F^- arising from the solvent self-ionization or from a small initial impurity which is almost invariably present in HF due to the difficulty of completely removing all the water. Addition of BF_3 then serves to remove this fluoride ion thus preventing the exchange of SeF_3^+ with the solvent while at the same time promoting the exchange of fluorine between BF_4^- and the solvent:

$$BF_3 + F^- \rightleftharpoons BF_4^-$$

The fluorine-on-selenium signal that is observed after the addition of BF_3 to the solution must be considered to be due to the equilibrium mixture of $(SeF_3)_2BF_4^+$, SeF_3,BF_4, and SeF_3^+. In the exchange between these species no Se–F bonds are broken and consequently ^{77}Se satellites are observed in the ^{19}F spectrum.

The coupling constant $J(^{77}Se-^{19}F)$ in ‘ SeF_3^+ ’ [*i.e.*, the equilibrium mixture of $(SeF_3)_2BF_4^+$, SeF_3,BF_4, and SeF_3^+] was found to be 1212·6 ± 0·2 Hz which, it is interesting to note, is significantly larger than the Se–F coupling constant found in other Se^{IV} compounds and it approaches that found in several Se^{VI} compounds (Table 3).[10] The value of the coupling constant $J(^{127}I-^{19}F)$ in IF_6^+ shows a similar increase over that in the parent IF_7, going from *ca.* 2100 Hz to 2700 Hz.[12] The isotope shift from F on ^{77}Se to F on ^{80}Se was found to be +0·012 ± 0·004 p.p.m. for ‘ SeF_3^+ ’. This is of similar magnitude to the selenium isotope effect on the fluorine chemical shift observed previously for several compounds (Table 3).[13]

TABLE 3

Coupling constants and isotope shifts selenium-fluorine compounds [a]

	$J(^{77}SeF)$/Hz	$\Delta\delta(^{77}Se-^{80}Se)$ / p.p.m.
$SeOFCl$	647	
$SeOF_2$	837	0·009 ± 0·005
‘ SeF_3^+ ’ $(SeF_4,SO_3$ in $HSO_3F)$ [b]	1088	
‘ SeF_3^+ ’ $(SeF_4,BF_3$ in $HF)$ [c]	1212·6	0·012 ± 0·004
SeF_6	1421	0·021 ± 0·004
$HSeO_3F$	1453	0·016 ± 0·005
SeO_2F_2	1584	0·020 ± 0·005

[a] Refs 11 and 13. [b] Ref. 11. [c] This work.

The +18·8 p.p.m. change in ^{19}F chemical shift on going from SeF_4 (−24·8 p.p.m. from $CFCl_3$) to ‘ SeF_3^+ ’ is in the same direction though somewhat smaller than the shifts for F on S on going from SF_4 to SF_3^+ (*ca.* +65 p.p.m.) [5,9] and from SOF_4 to SOF_3^+ (+43 p.p.m.).[14] Similar results have been obtained for the

---

[11] R. J. Gillespie and W. A. Whitla, *Canad. J. Chem.*, 1969, **47**, 4153.

[12] M. Brownstein and H. Selig, *Inorg. Chem.*, 1972, **11**, 656.

[13] T. Birchall, S. L. Crossley, and R. J. Gillespie, *J. Chem. Phys.*, 1964, **41**, 2760.

[14] M. Brownstein, P. A. W. Dean, and R. J. Gillespie, *Chem. Comm.*, 1970, 9.

BrF_2^+ and ClF_2^+ cations,[15] the upfield shift on going from BrF_3 to BrF_2^+ being smaller than the upfield shift on going from ClF_3 to ClF_2^+. The chemical shift for 'SeF_3^+' is similar to those found previously for molten SeF_3,SO_3F and for a solution of SeF_3,SO_3F in HSO_3F[10] (Table 2). The coupling constant for SeF_3^+ in SeF_3,BF_4 is however appreciably larger than that found in the earlier work on SeF_3,SO_3F.

Several molten SeF_4,MF_5 adducts (M = As, Nb, or Ta) have been found to have only a single line in their n.m.r. spectra.[4] Only for M = Sb was the exchange between SeF_3^+ and MF_6^- slow enough in the molten state (150°) to allow the observation of a separate F-on-Se peak. In this case the 'SeF_3^+' peak has a chemical shift considerably closer to that of SeF_4 than does the 'SeF_3^+' peak in a solution of SeF_4,BF_3 in HF. This is perhaps surprising but the measurements on the two systems were made at very different temperatures and as one system is a molten salt while the other is a solution in excess HF comparison between the two may hardly be valid.

We thank the N.R.C. of Canada for financial support of this work, and for the award of a scholarship (to M. B.), and Mr. J. I. A. Thompson for technical assistance in the operation of the n.m.r. spectrometers.

[2/1458 *Received*, 22*nd June*, 1972]

---

[15] M. Brownstein and J. Shamir, 6th International Symposium on Fluorine Chemistry, Durham, July 1971.