Haloselenate(IV) formation and selenous acid dissociation equilibria in hydrochloric and hydrofluoric acids

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Introduction

While there is a considerable body of quantitative information concerning complexation equilibria involving metal ions in aqueous solution, little work has been done on semimetal complexation. The present work deals with Se(IV) complexation in hydrofluoric and hydrochloric acid and represents an extension of earlier studies on SeO₂ on HF (1), HCl (2), and HBr (3). The reasons for the extension of previous work are threefold. Firstly, it was reported without complete explanation in earlier work (2) that the relative intensities of the SeO double and single bond stretching bands in the Raman spectra of SeO₂ solutions changed with increasing HCl concentration (0.0 to 5.0 M), a range where only H₂SeO₃ was considered to be present, and it was felt that some rationalization of this change was necessary. Secondly, the activities of hydrochloric acid were applied erroneously in earlier work (2) and, while the equilibria occurring at high HCl concentrations (8.0–12.0 M HCl) were correctly identified, the formation constants calculated were incorrect. A reinterpretation of the quantitative Raman intensities with more detailed measurements over the entire HCl concentration range was called for. Finally, while the monohaloselenate(IV) anions, SeO₂X⁻ (X = F, Cl, Br) (4, 5) are familiar, only in the case of the SeO₂–HBr system (3) has one of the parent acids, HSeO₂Br, been observed. It seems likely that the analogous acids would be present in SeO₂–HF and SeO₂–HCl systems also.

Experimental section

Solutions were made up from SeO₂ (Alfa), which was found by permanganometric analysis (6) to be partially converted to H₂SeO₃. The SeO₂ used was found to be 95% pure. Hydrofluoric and hydrochloric acids (Baker) were analyzed by titration before use. The methods for obtaining quantitative Raman spectra have been described elsewhere (2). The spectra of the hydrofluoric acid solutions were recorded at 488 nm using a sapphire cell and those of the hydrochloric acid solutions were recorded at 514.5 nm. The normalization assumption for calibration of band intensities was that the 925 cm⁻¹ band in the spectrum of 1 M perchloric acid solution, used as an external standard, had an area intensity of 6.45 cm² (1 in.²). This

Raman spectroscopy has shown that the initial stages of haloselenate(IV) formation equilibria are the same in HF and HCl solutions.

\[ \text{H}_2\text{SeO}_3 + \text{H}^+ + \text{X}^- \rightleftharpoons \text{HSeO}_2\text{X} + \text{H}_2\text{O} \quad (X = \text{F}, \text{Cl}) \]
\[ \text{HSeO}_2\text{X} + \text{H}^+ + \text{X}^- \rightleftharpoons \text{SeOX}_2 + \text{H}_2\text{O} \]

The constants \( K_4 \) and \( K_5 \), evaluated by quantitative Raman measurements, for HCl solutions are 0.015 (± 0.001) L² mol⁻² and 0.9 (± 0.1) × 10⁻⁵ L² mol⁻², respectively. These constants yield the minimum average deviation in normalized molar scattering intensity for the species formed in three regions of the spectra, 690 and 890 cm⁻¹ (SeO stretching) and 100–450 cm⁻¹ (deformation and SeCl stretching). Before the onset of haloselenate(IV) formation, changes in the SeO stretching band intensities with HX concentration occur due to repression of ionic dissociation of selenious acid

\[ \text{H}_2\text{SeO}_3 = \text{H}^+ + \text{HSeO}_3^- \]

Quantitative Raman measurements yield \( K_1 = 9.8 (± 0.3) \times 10^{-3} \) mol L⁻¹. Reasons for the high value of this constant, compared to reported values, are discussed.

Il a été montré par la spectroscopie Raman que les équilibres initiaux de la formation des halosélénate(IV)s sont les mêmes dans les solutions de HF et HCl.

\[ \text{H}_2\text{SeO}_3 + \text{H}^+ + \text{X}^- \rightleftharpoons \text{HSeO}_2\text{X} + \text{H}_2\text{O} \quad (X = \text{F}, \text{Cl}) \]
\[ \text{HSeO}_2\text{X} + \text{H}^+ + \text{X}^- \rightleftharpoons \text{SeOX}_2 + \text{H}_2\text{O} \]

Les constantes \( K_4 \) et \( K_5 \), évaluées à l'aide de mesures quantitatives Raman, pour les solutions d'HCl, sont respectivement 0.015 (± 0.001) L² mol⁻² et 0.9 (± 0.1) × 10⁻⁵ L² mol⁻². Ces constantes donnent les écarts moyens minimums dans l'intensité molaire normalisée de la lumière diffusée à trois régions des spectres, 690 et 890 cm⁻¹ (SeO allongements) et 100–450 cm⁻¹ (déformations et SeCl allongements). Avant la formation de halosélénate(IV)s, les changements d'intensité des bandes de SeO allongement avec des changements de la concentration d'HCl ont lieu à cause de la repression de la dissociation ionique de l'acide sélénieux,

\[ \text{H}_2\text{SeO}_3 = \text{H}^+ + \text{HSeO}_3^- \]

Les mesures quantitatives Raman donnent \( K_1 = 9.8 (± 0.3) \times 10^{-3} \) mol L⁻¹. Des causes de la haute valeur de cette constante en comparaison aux valeurs dans les literatures, sont discutées.
shown in Fig. 1, it is apparent that the near 300 s stretching mode at 690 cm⁻¹ increases in intensity relative to the 890 cm⁻¹ peak to the 890 cm⁻¹ peak decreases with increasing concentration in accordance with equilibrium (1). It should also be noted at this time that the intensity of the 850 cm⁻¹ peak to the 890 cm⁻¹ peak decreases with increasing concentration in accordance with equilibrium (1).

Results and discussion

From consideration of the Raman spectra of 0.95 M SeO₂ in solutions with HCl concentration in the range 0.0 to 4.0 M, shown in Fig. 1, it is apparent that the SeO single bond stretching mode at 690 cm⁻¹ increases in intensity relative to the SeO double bond mode at 890 cm⁻¹. Normalized intensities given in Table 1 for these bands show that there is an absolute increase in intensity of the 690 cm⁻¹ band and a decrease in intensity of the 890 cm⁻¹ band. These changes are not accompanied by the appearance of an Se—Cl stretching band near 300 cm⁻¹ and must involve changes in selenous acid dissociation equilibria connected with changes in proton activity accompanying the increase in HCl concentration. An understanding of these changes requires first of all a consideration of the equilibria governing selenious acid and the various other non-chloro-coordinated Se(IV) species in solution. It should be noted that the changes in peak intensity and frequency for a single species due to changes in ionic strength as a result of differing solvation effects are normally small relative the effects discussed here. For instance, the position of the 925 cm⁻¹ band of the perchlorate ion in solutions of perchloric acid over the concentration range 0.3 to 9 M increases by 5 cm⁻¹ and the intensity varies directly as the concentration.

Cesium hydrogen selenate(IV) solutions

Plots of normalized intensity of peaks at 850 and 610 cm⁻¹, the double and single bond stretches for HSeO₃⁻, for solutions of CsHSeO₃ (0.38, 0.57, 0.78, and 0.95 M) yield straight lines with molar intensities I₀₅₀ (HSeO₃⁻) = 8.10 (±0.25) cm² and I₀₆₀ (HSeO₃⁻) = 2.40 (±0.30) cm². These solutions apparently contain HSeO₃⁻ ion as the only Se(IV) species. This is expected in view of the magnitude of the dissociation and hydrolysis constants for HSeO₃⁻, K₂ = 7.9 × 10⁻⁹ mol L⁻¹ and K₈ = 3.1 × 10⁻¹² mol L⁻¹, respectively (7). A single measurement of the bands in the deformation region (100–450 cm⁻¹) at c(CsSeO₃) = 0.76 M gave a molar intensity l₀₁₀–₄₅₀ (HSeO₃⁻) = 3.0 cm².

Selenous acid solutions

At low selenous acid concentrations and ambient temperatures the equilibria,

1. H₂SeO₃ → H⁺ + HSeO₃⁻
2. HSeO₃⁻ → H⁺ + SeO₂⁻

Table 1. Interpolated intensities for 0.95 M SeO₂ in 0.0–12.0 M HCl solutions

<table>
<thead>
<tr>
<th>c(HCl) (mol L⁻¹)</th>
<th>i₁₀₀–₄₅₀ (cm²)</th>
<th>i₆₅₀ (cm²)</th>
<th>i₈₉₀ (cm²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0</td>
<td>2.26</td>
<td>6.05</td>
<td>5.33</td>
</tr>
<tr>
<td>1.0</td>
<td>3.09</td>
<td>6.20</td>
<td>5.01</td>
</tr>
<tr>
<td>2.0</td>
<td>4.17</td>
<td>6.46</td>
<td>4.94</td>
</tr>
<tr>
<td>3.0</td>
<td>4.95</td>
<td>6.66</td>
<td>4.88</td>
</tr>
<tr>
<td>4.0</td>
<td>5.23</td>
<td>6.80</td>
<td>4.87</td>
</tr>
<tr>
<td>5.0</td>
<td>5.37</td>
<td>6.98</td>
<td>4.75</td>
</tr>
<tr>
<td>6.0</td>
<td>5.53</td>
<td>7.01</td>
<td>4.70</td>
</tr>
<tr>
<td>7.0</td>
<td>6.56</td>
<td>6.93</td>
<td>4.77</td>
</tr>
<tr>
<td>8.0</td>
<td>12.80</td>
<td>6.52</td>
<td>5.13</td>
</tr>
<tr>
<td>9.0</td>
<td>28.60</td>
<td>6.38</td>
<td>6.03</td>
</tr>
<tr>
<td>10.0</td>
<td>42.70</td>
<td>4.08</td>
<td>7.18</td>
</tr>
<tr>
<td>11.0</td>
<td>65.40</td>
<td>2.74</td>
<td>8.55</td>
</tr>
<tr>
<td>12.0</td>
<td>77.00</td>
<td>1.42</td>
<td>10.00</td>
</tr>
</tbody>
</table>

*Intensity of total band envelope (850 and 890 cm⁻¹).*

Fig. 1. Raman spectra of solutions of SeO₂ (0.95 M) in HCl (0.0–12.0 M).

standard was run before and after each SeO₂ solution spectrum with all spectrometer and laser conditions held constant.

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then calculated from stoichiometry. In the absence of measured ionic activity coefficients, those calculated from Debye–Hückel theory were used (10). In the range of ionic strength for these solutions (ca. 0.1 M), DH coefficients for strong acids with oxoanions are usually within 10% (lower) of measured values (ref. 10, p. 491) and this should apply for $H^+$ and HSeO$_3^-$ ions. The first dissociation constant, $K_1$, is given by

\[ K_1 = \frac{[H^+][HSeO_3^-]}{[H_2SeO_5]} \]

where $y_\pm$ is the molar activity coefficient, was determined to be $9.3 \times 10^{-3}$ mol L$^{-1}$. The agreement between the values of $K_1$, as well as the reasonably constant value of the molar intensities calculated for $H_2SeO_5$ from the concentrations and molar intensities for the HSeO$_3^-$ ion given above, for the five solutions studied supports the interpretation and calculations. The data and calculated values are shown in Table 2. The value calculated for $K_1$ is higher than that reported in the literature (7).

The large apparent concentration of hydrogen selenate(IV) ion may be due to the equilibrium,

\[ H_2SeO_5 + HSeO_3^- \rightleftharpoons K_3 \ H(HSeO_3)_2^- \]

for which there is evidence from pH studies (7). However, calculations which include eq. [4] and which use as criteria of acceptability, the constancy of $K_1$ and $K_3$, lead to little change in $K_1$ (10% lower). Another possible reason for the relatively high value of $K_1$ is ion-pair formation. This is the case for moderately strong acids where the dissociation constant, measured by infinite dilution methods or by methods which can be used in the millimolar range where $y_\pm = 1$ is a good approximation, is lower than that measured by high concentration methods such as nmr or Raman spectroscopy (11, 12). It has been proposed that the high dissociation constants at high concentration are due to the formation of the “hydronium ion – acid anion” ion pair, which would contribute to the high apparent anion concentration (12) and dissociation constant. Finally another possible reason for the difference may be the simplicity of the equilibria model chosen. Barcza and Sillen (7) have found evidence for the dimerization of $H_2SeO_5$ and HSeO$_3^-$ in solutions of moderately low selenous acid concentration (0.02–3.00 M). However, Raman studies show evidence for the formation of $(H_2SeO_3)_2^-$ only at much higher concentrations (8.07 M) (8) than those studied here and it is claimed in other potentiometric and spectrophotometric work (13) that anion dimerization does not occur under the acid conditions which exist in this work. At present the discrepancy between low and high concentration dissociation constants, $K_1$, is best accounted for in terms of ion-pair formation. The trend towards higher values of $K_1$ with increasing concentration shown in Table 2 might also be accounted for by ion-pair formation although H(HSeO$_3$)$_2^-$ formation would also cause the same change in the apparent $K_1$.

**Solutions of selenium dioxide in hydrochloric acid**

The changes in intensity of the 690 and 890 cm$^{-1}$ bands in the spectra of 0.95 M SeO$_2$ in 0.0 to 4.0 M HCl solutions, which are in the opposite direction (Fig. 1), can be readily accounted for in terms of the repression of equilibrium (1). The 690 cm$^{-1}$ band increases with increasing $c_{HCl}$ because this band is more intense for $H_2SeO_5$ ($I_{690}(H_2SeO_5) = 7.4$ cm$^{-1}$) than for HSeO$_3^-$ ($I_{690}(HSeO_3^-) = 2.4$ cm$^{-1}$) while the 890 cm$^{-1}$ band decreases since $I_{890}(H_2SeO_3) = 5.45$ cm$^{-1}$ is lower than $I_{890}(H_2SeO_3^-)$ (8.1 cm$^{-1}$). Quantitative treatment of this region of HCl concentration is difficult, since there is no clear way to deal with the ionic activities. Debye–Hückel activities are unrealistic in this range of ionic strength especially for acid electrolytes (except at $c_{HCl} = 0$). The measured molar ionic activities for HCl ($H^+$, Cl$^-$) probably represent a closer description of these activities for $H^+$ and HSeO$_3^-$ in these solutions than do Debye–Hückel activities. In view of these uncertainties as well as the relatively small changes in intensity of the 690 and...
Table 2. Band intensities and apparent $[\text{HSeO}_3^-]$ for solutions of $\text{SeO}_2$ in water and $K_1$ for simple dissociation

<table>
<thead>
<tr>
<th>$c_{\text{SeO}_2}$ (M)</th>
<th>$i_{890}$ (cm$^2$)</th>
<th>$[\text{HSeO}_3^-]$ (M)</th>
<th>$[\text{H}_2\text{SeO}_3]$ (M)</th>
<th>$10^4 K_1$ (M)</th>
<th>$i_{890}$ (cm$^2$)</th>
<th>$i_{690}$ (cm$^2$)</th>
<th>$i_{100-450}$ (cm$^2$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.048</td>
<td>0.143</td>
<td>0.0176</td>
<td>0.00299</td>
<td>0.59</td>
<td>0.19</td>
<td>0.29</td>
<td></td>
</tr>
<tr>
<td>0.190</td>
<td>0.386</td>
<td>0.00477</td>
<td>0.01423</td>
<td>0.073</td>
<td>0.56</td>
<td>0.82</td>
<td>1.24</td>
</tr>
<tr>
<td>0.475</td>
<td>0.706</td>
<td>0.00872</td>
<td>0.00387</td>
<td>0.076</td>
<td>0.98</td>
<td>1.87</td>
<td>2.95</td>
</tr>
<tr>
<td>0.950</td>
<td>1.104</td>
<td>0.01363</td>
<td>0.01817</td>
<td>0.6474</td>
<td>9.57</td>
<td>4.27</td>
<td>6.02</td>
</tr>
<tr>
<td>1.423</td>
<td>1.513</td>
<td>0.1868</td>
<td>1.2380</td>
<td>0.6011</td>
<td>10.18</td>
<td>6.49</td>
<td>9.17</td>
</tr>
</tbody>
</table>

*a*Apparent concentration, see text.
*b*Debye–Hückel molar activity coefficient.

Table 3. Calculated molar intensities for $\text{HSeO}_2\text{Cl}$ and $\text{SeOCl}_2$ and concentrations of $\text{Se}(\text{IV})$ species for solutions of $\text{SeO}_2$ in 5.0–12.0 M HCl solutions for $K_4 = 0.015$ L$^2$ mol$^{-2}$ and $K_5 = 9 \times 10^{-6}$ L$^2$ mol$^{-2}$

<table>
<thead>
<tr>
<th>$c_{\text{HCl}}$ (M)</th>
<th>$i_{690}$ (cm$^2$)</th>
<th>$[\text{H}_2\text{SeO}_3]$ (M)</th>
<th>$[\text{HSeO}_2\text{Cl}]$ (M)</th>
<th>$[\text{SeOCl}_2]$ (M)</th>
<th>$[\text{Cl}^-]$ (M)</th>
<th>$a_{\text{HCl}}$ (M)</th>
<th>$i_{690}$ (cm$^2$ L$^{-1}$)</th>
<th>$i_{100-450}$ (cm$^2$ L$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>5.0</td>
<td>7.3</td>
<td>0.276</td>
<td>0.673</td>
<td>—</td>
<td>4.33</td>
<td>0.743</td>
<td>11.2</td>
<td>—</td>
</tr>
<tr>
<td>6.0</td>
<td>7.4</td>
<td>0.112</td>
<td>0.835</td>
<td>—</td>
<td>5.16</td>
<td>0.677</td>
<td>18.4</td>
<td>—</td>
</tr>
<tr>
<td>7.0</td>
<td>7.4</td>
<td>0.035</td>
<td>0.901</td>
<td>—</td>
<td>6.07</td>
<td>0.596</td>
<td>32.4</td>
<td>—</td>
</tr>
<tr>
<td>8.0</td>
<td>7.2</td>
<td>—</td>
<td>0.892</td>
<td>—</td>
<td>7.01</td>
<td>0.509</td>
<td>56.0</td>
<td>14.9</td>
</tr>
<tr>
<td>9.0</td>
<td>6.7</td>
<td>—</td>
<td>0.801</td>
<td>0.146</td>
<td>7.91</td>
<td>0.430</td>
<td>93.1</td>
<td>14.4</td>
</tr>
<tr>
<td>10/0</td>
<td>6.6</td>
<td>—</td>
<td>0.616</td>
<td>0.334</td>
<td>8.72</td>
<td>0.363</td>
<td>148</td>
<td>12.4</td>
</tr>
<tr>
<td>11/0</td>
<td>7.2</td>
<td>—</td>
<td>0.380</td>
<td>0.573</td>
<td>9.47</td>
<td>0.310</td>
<td>228</td>
<td>11.7</td>
</tr>
<tr>
<td>12.0</td>
<td>8.3</td>
<td>—</td>
<td>0.172</td>
<td>0.768</td>
<td>10.29</td>
<td>0.254</td>
<td>355</td>
<td>11.9</td>
</tr>
</tbody>
</table>

Values calculated by choosing $i_{690}(\text{HSeO}_2\text{Cl}) = 4.92$ cm$^2$ M$^{-1}$, which gave the lowest average deviation from the mean of $i_{100-450}(\text{SeOCl}_2) = 89 \pm 2$ cm$^2$ M$^{-1}$.

890 cm$^{-1}$ bands (Table 1), it was not considered worthwhile to fit these data to $K_1$.

890 cm$^{-1}$ bands (Table 1), it was not considered worthwhile to fit these data to $K_1$.

As HCl concentration is increased above 4.0 M, a band is seen to grow in intensity at 330 cm$^{-1}$ in the SeCl stretching region of the spectrum. This peak is 50 cm$^{-1}$ higher than that of the $\text{SeO}_2\text{Cl}^-$ anion (5) in acetonitrile and is, therefore, unlikely to be due to this species. Moreover, the growth of this peak is accompanied by a growth in the intensity of the $\text{SeOCl}_2$ stretching peak (690 cm$^{-1}$) over the range 4.0 to 6.0 M HCl where $[\text{H}_2\text{SeO}_3]$ is virtually constant if not decreasing. For these reasons it appears likely that $\text{HSeO}_2\text{Cl}$ is formed in these solutions. At even higher concentrations, $\text{SeOCl}_2$ is formed (2) and its spectrum is apparent in Fig. 1.

In the range 4.0–12.0 M HCl the $\text{Se}(\text{IV})$ equilibria which occur are,

$$K_4 = \frac{[\text{H}_2\text{SeO}_3] a_{\text{HCl}}}{[\text{H}_2\text{SeO}_3] a_{\text{HCl}}}$$

$$K_5 = \frac{[\text{SeOCl}_2] a_{\text{HCl}}}{[\text{HSeO}_2\text{Cl}] a_{\text{HCl}}}$$

where $a_{\text{HCl}}$ is the activity of water, $a_{\text{HCl}}$ is the molar activity of HCl, and $a_{\text{HCl}}$, $a_{\text{HCl}}$ and $a_{\text{HCl}}$ are the stoichiometric concentrations of Se(IV) and HCl, respectively. Various values of $K_4$ and $K_5$ were chosen in increments of $10^{-3}$ and $10^{-6}$, respectively, to yield a minimum in the average deviation in $i_{690}(\text{HSeO}_2\text{Cl})$ for the eight highest...
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since the minimum in the deviation on average deviation as well as the concentrations of all species HCl (100%).
gave an average became very shallow. The best results were given by choosing the analogous values for incremental changes in K4 and K5, because of the low intensity of the bands, at low background contribution to the 100-450 cm⁻¹ region and the changes are consistent with the equilibrium K4 = K5 = K6 > CHClBr-

INTENSITY

1000 600 400 200

100% HF
85% HF
48% HF
0% HF

100-450 cm⁻¹

Fig. 3. Raman spectra of solutions of SeO₂ (3 M) in HF (0.0–100%).

HCl concentrations measured (5.0–12.0 M HCl). Smaller incremental changes in K4 and K5 were not felt to be useful since the minimum in the deviation on I₉₉₀(HSeO₂Cl) then became very shallow. The best results were given by K₄ = 1.5 × 10⁻² L² mol⁻² and K₅ = 9 × 10⁻⁶ L² mol⁻² which gave an average I₉₉₀(HSeO₂Cl) = 7.25 cm². The individual values of I₉₉₀(HSeO₂Cl) at each cHCl and mean value with average deviation as well as the concentrations of all species are given in Table 3. It is possible to calculate the molar intensities of SeOCl₂, I₉₉₀(SeOCl₂) and I₈₅₀–₄₅₀(SeOCl₂), by choosing the analogous values for HSeO₂Cl, I₈₅₀(SeOCl₂) and I₈₅₀–₄₅₀(HSeO₂Cl), which yield the minimum variation in the I(SeOCl₂) values via the equations,

[12] I₈₅₀ = I₈₅₀(SeOCl₂)[HSeO₂Cl] + I₈₅₀(SeOCl₂)[SeOCl₂] + 5.45[H₂SeO₃]

[13] I₈₅₀–₄₅₀ = I₈₅₀–₄₅₀(HSeO₂Cl)[HSeO₂Cl] + I₈₅₀–₄₅₀(SeOCl₂)[SeOCl₂] + 2.18[H₂SeO₃]

because of the low [SeOCl₂], and thus the small influence on the intensity of the bands, at low cHCl, these calculations were only carried out for solutions with cHCl > 7 M. The molar intensities for H₂SeO₂ are taken from Table 2 and the concentrations from Table 3. The least variation, as judged by average deviation, in SeOCl₂ molar intensities was given by choosing I₉₉₀(HSeO₂Cl) = 4.9 cm² and I₈₅₀–₄₅₀(HSeO₂Cl) = 18 cm². The individual I(SeOCl₂) for each cHCl and mean value with average deviation are given in Table 3. Because of the uncertainty in the background contribution to the 100–450 cm⁻¹ envelope at low peak intensities and the uncertainty in I₁₀₀–₄₅₀(H₂SeO₃), the I₁₀₀–₄₅₀(SeOCl₂) calculated at cHCl < 9.0 M are unreliable.
The excellent agreement between I₁₀₀–₄₅₀(SeOCl₂) calculated for the range cHCl = 9.0 to 12.0 M, when I₁₀₀–₄₅₀ changes three-fold in intensity, is strong support for the interpretation in terms of equilibria [5] and [6] as well as the calculated values of K₄ and K₅.

Solutions of SeO₂ in hydrofluoric acid

The Raman spectra of solutions of SeO₂ in hydrofluoric acid shown in Fig. 3 exhibit the same changes at low HF concentrations as those of the corresponding solutions in hydrochloric acid. The changing intensities of the 690 and 890 cm⁻¹ peaks reflect the repression of the dissociation equilibria of H₂SeO₃. When the HF concentration of the solvent used reaches 28.0 M the spectrum of a 3 M SeO₂ solution exhibits new peaks in addition to those of H₂SeO₃. A new peak appears at 930 cm⁻¹ corresponding to an SeO double bond stretch, another peak appears at 600 cm⁻¹ in the SeF stretching region and the SeO single bond peak at 890 cm⁻¹ increases in intensity relative to that at 890 cm⁻¹ indicating that the new species being formed has an SeO single bond. The spectral changes are consistent with the equilibrium

[14] H₂SeO₃ + HF = HSeO₂F + H₂O

With 52.0 M HF as solvent the spectrum due to H₂SeO₃ has completely disappeared, the three principal peaks of HSeO₂F are clearly evident but, in addition, peaks corresponding to those of SeOF₂ at 1008 and 650 cm⁻¹ are apparent. The formation of SeOF₂ from SeO₂ and 100% HF has been demonstrated earlier (1). With 100% HF as solvent the spectrum of SeOF₂ is even more pronounced relative to that of HSeO₂F. In the absence of activity data for HF at the concentrations at which HSeO₂F and SeOF₂ are formed, it is not possible to calculate formation constants.

Conclusions

In solutions of SeO₂ in HX (X = F, Cl, Br), as the concentration of HX is increased, there is first of all a repression of the ionic dissociation of H₂SeO₃ which then undergoes a stepwise substitution of OH groups by halogen X yielding the monohaloselenenic acid shown in Fig. 3 exhibit the same changes at

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