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# Chloroselenate(IV) Equilibria in Aqueous Hydrochloric Acid[1]

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"Dichloroselenious acid", formed from a 2:1 $HCl/SeO_2$ mixture (1:1 $SeOCl_2/H_2O$), has been shown by Raman spectroscopy to be a hydrate of seleninyl chloride. Liquid seleninyl chloride and its monohydrate are shown to have significant chloride bridging. The principal Se(IV) species present in solutions of selenium dioxide in concentrated hydrochloric acid (4–12 M) has been confirmed to be seleninyl chloride and not a chloroselenate(IV) ion. The equilibrium constant has been determined by quantitative Raman spectroscopy for the reaction $H_2SeO_3 + 2HCl = SeOCl_2 + 2H_2O$. At higher concentrations of hydrochloric acid (15.18 M) pentachloroselenate(IV) ion is formed according to $SeOCl_2 + 3HCl = H_3O^+ + SeCl_5^-$.

## Introduction

The species formed in solutions of selenium dioxide in hydrochloric acid or seleninyl chloride in water have been the subject of several studies.[2-4] Electrical conductivity and spectrophotometric studies on dilute solutions of selenium dioxide in HCl and HBr suggest that a 4:1 $HX/SeO_2$ species is formed.[2] The preparation of hexachloroselenate(IV) compounds from concentrated hydrochloric acid solutions[5] suggests that $SeCl_6^{2-}$ is present in these solutions. However, Raman spectra of such solutions are not consistent with the presence of just $SeCl_6^{2-}$ nor do they indicate that oxoselenate(IV) species are present.[3] In the standard method of preparation of seleninyl chloride from selenium dioxide and hydrogen chloride,[6] an intermediate, called "dichloroselenious acid" is formed. This intermediate was formulated as $SeOCl_2{\cdot}H_2O$ although no experimental evidence was presented to favor this formulation over that of $Se(OH)_2Cl_2$.[7] The formulation as hydrated seleninyl chloride is favored by a second Raman study of selenium dioxide in hydrochloric acid solutions, which indicates that seleninyl chloride is present.[4] Seleninyl halides have also been shown by Raman spectroscopy to be formed in solutions of selenium dioxide in hydrofluoric[8] and hydrobromic[9] acids.

In view of the differing interpretations as to the species present in aqueous hydrochloric acid solutions of selenium dioxide and in light of recent Raman spectral information on oxochloroselenate(IV) ions,[10,11] it was considered of interest to reexamine these solutions by Raman spectroscopy.

## Experimental Section

**Materials.** Selenium dioxide (Alfa) was dried under vacuum before use. Seleninyl chloride (Fisher) was purified by vacuum distillation. Dichloroselenious acid was prepared by the standard method.[6] Selenium tetrachloride was prepared as described earlier.[10] Acetonitrile and nitromethane were purified by distillation from phosphorus pentoxide. Both hydrochloric and perchloric acids were standardized before use.

**Methods.** The Raman spectra were taken by using a Jobin-Yvon grating monochromator in conjunction with PAR photon counting. The spectra were excited with a Control Laser argon-ion laser operating at 488 nm. Resolution for all spectra was 8.5 cm$^{-1}$. The spectra were taken in 1-cm path length cells designed for fluorescence spectroscopy which were held in a water-jacketed aluminum holder maintained at 25 °C. All spectral intensities were normalized by comparison to perchloric acid solutions which were run after each selenium dioxide–hydrochloric acid solution. The normalization assumption was that the 925-cm$^{-1}$ band of perchloric acid had an area intensity of 1 in.$^2$ (6.45 cm$^2$). A plot of the intensity of the 925-cm$^{-1}$ band against concentration was shown to be linear up to 9 M perchloric acid. Slit width, time constant, laser power, photon counting rate, scan rate, and sample position were held constant for each series of runs. Polarized spectra were obtained by rotating the plane of polarization of the exciting laser beam with a half-wave plate.

## Results and Discussion

**Seleninyl Chloride Solutions.** The Raman spectra of seleninyl chloride, in pure form and in solutions with acetonitrile and water, are listed in Table I and given in Figure 1. The spectrum of the 1:1 $SeOCl_2/H_2O$ mixture, which is called "dichloroselenious acid"[6] has no bands in the Se–O single bond stretching region. This and the similarity in band position and relative intensity in the normal and polarized spectra with those in the spectra for pure seleninyl chloride show that the mixture consists of $SeOCl_2$ units and weakly bound water as suggested in previous work.[4]

$$2HCl + SeO_2 = SeOCl_2{\cdot}H_2O$$

The chloride acceptor[10,11] and electrical conductivity[12] behavior of pure seleninyl chloride, among other properties, suggest that the liquid is strongly associated via chloride bridging. The Raman spectra in Figure 1 and Table I support this interpretation. The SeO stretching vibration of seleninyl chloride is increased by 29 cm$^{-1}$ when the compound is dissolved in acetonitrile to give a 0.8 M solution. Dilution of seleninyl chloride in carbon disulfide results in a similar shift to higher frequency and this has been attributed to an association equilibrium.[13] Moreover, a shift in the frequency of the SeO stretching mode is found between $KSeOCl_3$ (924 cm$^{-1}$), which is polymeric, and $Ph_4AsSeOCl_3$ (954 cm$^{-1}$), which contains discrete $SeOCl_3^-$ units.[10] The downward shift in frequency is unlikely to be due to SeO bridging since this is not found in the structures of oxochloroselenate(IV) compounds.[14,15] The decrease in the frequency of $\nu$(SeO) with increased Cl coordination as a result of bridging would be caused by the greater number of SeCl bond pairs as near neighbors to the Se–O bond and the decrease in the Se–O–Cl bond angle, compared to that in the isolated seleninyl chloride molecule. These increased SeCl bond pair repulsions would result in a weakening of the Se–O bond and lowering of the frequency of $\nu$(SeO).

In the case of trichloroselenate(IV)[10] and pentachlorotellurate(IV) compounds[16,17] chloride bridging is accompanied by a general increase in the frequencies of the chloride stretching modes. On the basis of the increase in the SeCl stretching frequencies upon going from seleninyl chloride dissolved in acetonitrile to pure liquid seleninyl chloride, it appears that liquid seleninyl chloride is chloride bridged. The bridging must, however, be weak inasmuch as the Raman spectrum of liquid seleninyl chloride follows the selection rules expected for a trigonal-bipyramidal molecule with $C_s$ symmetry. The similarity of the spectra of liquid seleninyl chloride and the 1:1 $SeOCl_2/H_2O$ mixture indicates that the chloride-bridged structure remains essentially intact in the mixture. Further addition of water, however, leads to the appearance of a band at 684 cm$^{-1}$ and decreases in the SeO and SeCl stretching frequencies as shown in the spectrum of 1:3 $SeOCl_2/H_2O$ mixture shown in Figure 1. The appearance of a band in the SeO single bond stretching region indicates that hydrolysis is occurring to form either selenious or chloroselenious acid according to

$$SeOCl_2 + H_2O = HCl + HSeO_2Cl \quad (1)$$

$$SeOCl_2 + 2H_2O = 2HCl + H_2SeO_3 \quad (2)$$

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**Table I.** Raman Spectra (cm$^{-1}$) of Oxochloroselenium(IV) Species[a]

| $SeOCl_2$ | $SeOCl_2/H_2O$ (1:1) | $SeOCl_2/H_2O$ (1:3)[b] | $SeOCl_2$ in $CH_3CN$[c] | $SeOCl_3^-$[d] | 1 M $SeO_2$ in 12.17 M HCl |
|---|---|---|---|---|---|
| 143 (3, p) | 152 (3, p) | 154 (1, p) | 146 (3, p) | 139 (1, p) | 152 (1, p?) |
| 232 (2, dp) | 244 (2, dp) | 250 (sh) | 237 (2, dp) | 228 (10, dp?) | |
| 259 (3, p) | 261 (3, p) | 275 (5, p) | 263 (3, p) | 248 (10, p) | 265 (5, p) |
| 337 (3, dp) | 340 (5, dp) | 326 (7, dp) | 334 (3, dp) | 287 (1, p?) | |
| 374 (10, p) | 377 (10, p) | 358 (10, p) | 362 (10, p) | 336 (4, p) | 336 (10, p) |
| 937 (3, p) | 936 (3, p) | 926 (3, p) | 966 (3, p) | 951 (3, p) | 925 (2, p) |

[a] Measured up to 1000 cm$^{-1}$. [b] Additional band due to hydrolysis, 684 cm$^{-1}$. [c] 0.8 M $SeOCl_2$; solvent bands are 375 and 915 cm$^{-1}$. [d] LaHaie, P; Milne, J. *Inorg. Chem.* 1979, *18*, 632.

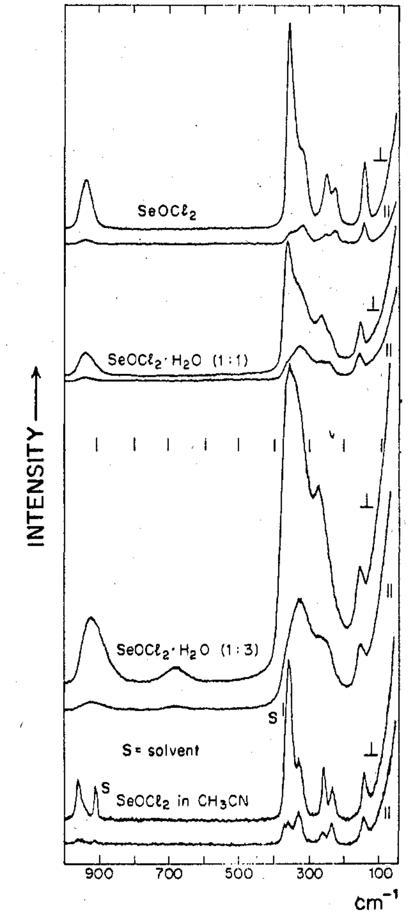

**Figure 1.** Raman spectra of seleninyl chloride as pure liquid and in solution.

The position of the band due to the hydrolysis product corresponds well with that of selenious acid in aqueous hydrochloric acid solution (689 cm$^{-1}$) which suggests that hydrolysis occurs by reaction 2. From the intensities of the SeCl and SeO (single bond) peaks and a knowledge of the molar intensities of these peaks for seleninyl chloride and selenious acid given below, it can be shown that 80% of the seleninyl chloride is still unhydrolyzed in the 3:1 $SeOCl_2/H_2O$ solution. Thus, the spectrum shown in Figure 1 is still largely representative of molecular seleninyl chloride in water. The SeCl stretching frequencies have both shifted to lower frequencies, just as was observed when seleninyl chloride was dissolved in acetonitrile, and this is the result of the breakdown of the chloride-bridged structure. The SeO stretching frequency also decreases relative to that in liquid seleninyl chloride. This shift is the opposite of that observed for seleninyl chloride in acetonitrile and may be the result of hydrogen bonding to the oxygen of seleninyl chloride by water.

**Solutions of Selenious Acid.** For purposes of determining the concentrations of the various Se(IV) species in hydrochloric acid solutions, it was necessary to measure the molar intensities of the SeO double and combined single bond stretching mode peaks (896 and 695 cm$^{-1}$, respectively) and the combined deformation modes (200–400 cm$^{-1}$) of selenious acid. In spite of the complex condensation equilibria known to occur in these solutions,[18] the dependence of intensity on concentration was found to be linear for these peaks within experimental error over the range 0–1.5 M. The molar intensities are listed in Table II.

**Table II.** Molar Intensities of Selenious Acid Bands

| freq, cm$^{-1}$ | mode description | molar intens, cm$^2$ |
|---|---|---|
| 200–400 | deformations | 2.3 ± 0.2 |
| 695 | SeO single bond stretch modes | 6.1 ± 0.2 |
| 896 | SeO double bond stretch modes | 5.0 ± 0.2 |

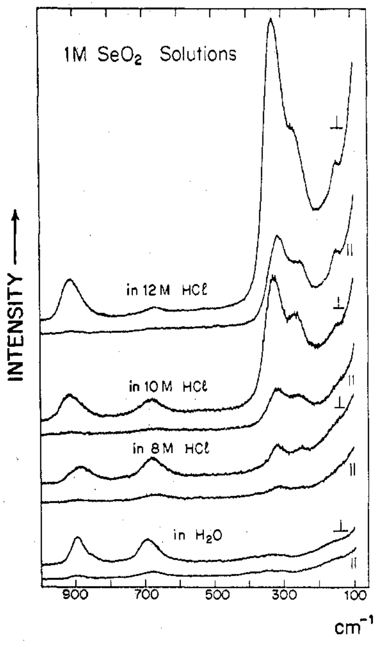

**Figure 2.** Raman spectra of 1 M selenium dioxide solutions in 0, 8, 10, and 12 M hydrochloric acid.

**Solutions of Selenium Dioxide in Hydrochloric Acid (0–12.17 M).** The Raman spectra of 1 M solutions of selenium dioxide in hydrochloric acid over an HCl range of 0–12.17 M are shown in Figure 2 and the bands of the 12.17 M solution are listed in Table I. As the concentration of hydrochloric acid is increased, commencing at about 4 M hydrochloric acid, there is an increase in the intensity of peaks near 330 cm$^{-1}$, the region of SeCl stretching modes. This is accompanied by an initial broadening and shift of the SeO double bond stretching band from 896 to 924 cm$^{-1}$. Before there is any indication of SeCl bond formation, that is over the hydrochloric acid concentration range 0–4.04 M, the form of the peak due to the SeO single bond stretching mode (695 cm$^{-1}$) changes slightly relative to that of the SeO double bond band. Calculation shows that this cannot be the result of repression of the simple selenious acid ionic dissociation.[18] The effect is small and is

**Table III.** Intensities of SeCl Peaks, Concentrations, and Equilibrium Constants for Seleninyl Chloride Formation

| $c_{HCl}$, M | $I_{SeCl}$,[a] cm$^2$ | [$SeOCl_2$], M | [$H_2SeO_3$], M | [HCl], M | $a_w$ | $a_{HCl}$ | $10^6K$,[b] mol$^{-2}$ L$^2$ |
|---|---|---|---|---|---|---|---|
| 7.10 | 3.96 | 0.045 | 0.955 | 7.10 | 0.508 | 57 | 3.7 |
| 8.11 | 12.04 | 0.136 | 0.864 | 7.84 | 0.436 | 89 | 3.8 |
| 9.12 | 25.62 | 0.290 | 0.710 | 8.54 | 0.377 | 133 | 3.3 |
| 10.14 | 40.50 | 0.458 | 0.542 | 9.22 | 0.325 | 192 | 2.4 |
| 11.15 | 60.41 | 0.684 | 0.316 | 9.78 | 0.287 | 253 | 2.8 |
| 12.17 | 77.27 | 0.874 | 0.126 | 10.42 | 0.246 | 349 | 3.5 |

[a] Corrected for $H_2SeO_3$ deformations. [b] Based on a normalized molar intensity of 88.37 cm$^2$ for the SeCl stretching modes of $SeOCl_2$.

probably a result of the selenious acid dimerization equilibrium, which has been shown to occur in selenious acid solutions.[18] At concentrations of hydrochloric acid greater than 4.04 M, the intensity of the SeO single bond peak falls as the SeCl band intensity increases. The new chloro species has an SeO double bond and this species persists as the major component in the more concentrated hydrochloric acid solutions. The presence of $SeCl_5^-$ and $SeCl_6^{2-}$ in significant amounts as suggested by Hendra and Jovic[3] is ruled out on this basis. Comparison of the spectrum of the 12.17 M hydrochloric acid solution with those of known oxochloroselenate(IV) ions[10,11] and that of seleninyl chloride indicates that the equilibrium occurring in solution is

$$H_2SeO_3 + 2HCl = SeOCl_2 + 2H_2O \qquad (3)$$

as suggested by Futekov and Iordanov.[4] The highest SeCl stretching band of the $SeOCl_4^{2-}$ ion comes at 285 cm$^{-1}$ and the most intense at 242 cm$^{-1}$. It is not possible that there would be a shift in frequency to 325 cm$^{-1}$ upon dissolution in aqueous solution, and the presence of a 4:1 $Cl^-$/Se(IV) species as a major component in these solutions, as suggested by other authors,[2] is not supported by the observations. The Raman spectrum of the $SeOCl_3^-$ ion in acetonitrile,[10] Table I, is quite different from that of 1 M selenium dioxide in 12.17 M hydrochloric acid, especially with respect to the relative peak intensities and polarizations of the two spectra. Although the most intense SeCl stretching mode ($\nu_2(A')$) of liquid seleninyl chloride at 374 cm$^{-1}$ is 38 cm$^{-1}$ higher than the most intense peak in the selenium dioxide/hydrochloric acid solution at 336 cm$^{-1}$, the solution spectra are best interpreted in terms of equilibrium 3. In particular the relative peak intensities and their polarization characteristics in the spectra of seleninyl chloride and the selenium dioxide/hydrochloric acid solutions are the same. The SeCl stretching mode ($\nu_2$) of seleninyl chloride decreases in frequency upon dissolution as discussed above and approaches that for the hydrochloric acid solution. The difference in frequency of the SeO double bond stretching mode ($\nu_1(A')$) in the two cases is probably the result of hydrogen bonding. The concentrated hydrochloric acid solution spectrum of selenium dioxide is similar to that of the 1:3 seleninyl chloride/water solution. In a previous Raman spectral study, it was concluded that seleninyl chloride was formed in selenium dioxide/hydrochloric acid solutions but the large shift in the SeCl band and the possibility of other oxochloroselenate(IV) species being present were not considered.[4] Moreover, polarization measurements, which strengthen the interpretation, were not done in the earlier work.

From the measurement of normalized peak intensities and a knowledge of molar peak intensities, the concentrations of the species present may be determined and the equilibrium constant calculated.[19] The equilibrium constant for eq 3 is given by

$$K = \frac{[SeOCl_2]a_w^2}{[H_2SeO_3]a_{HCl}^2}$$

where $a_w$ is the rational activity of water and $a_{HCl}$ is the molar activity of hydrochloric acid. The activity coefficients of seleninyl chloride and selenious acid are assumed to be equal. From a knowledge of the concentration of seleninyl chloride or selenious acid and the solution stoichiometry, the concentration of all other species may be calculated. From the hydrochloric acid concentration both $a_{HCl}$ and $a_w$ may be obtained from tables,[20,21] by using density data for hydrochloric acid solutions. For purposes of this work the effect of Se(IV) species in solution on $a_{HCl}$ and $a_w$ is ignored. The concentration of selenious acid may be determined from the intensity of the band at 695 cm$^{-1}$. Because of the low relative intensity of this peak and the complication which results from the selenious acid dimerization,[18] use of this peak does not yield constant values for $K$. In the case of the most highly concentrated hydrochloric acid solution, where the selenious acid concentration is the lowest in the series of solutions studied and the effects of dimerization the least, [$H_2SeO_3$] was determined to be 0.151 M by using the molar intensity for the 695-cm$^{-1}$ peak, which is listed in Table II. This gives an equilibrium constant of $2.6 \times 10^{-6}$ mol$^{-2}$ L$^2$. Because of the great intensity of the SeCl stretching bands in the spectra, they are better suited for the calculation of $K$. Allowance must, however, be made for the weak peaks due to $H_2SeO_3$ deformation modes, which lie in this region of the spectrum. The corrected and normalized intensities of these combined peaks (152, 265, and 336 cm$^{-1}$) are listed in Table III. The molar intensity of these SeCl peaks for $SeOCl_2$ may be calculated from the intensity in the spectrum for the 12.17 M hydrochloric acid solution and a knowledge of the concentration of selenious acid and the total Se(IV) concentration.

$$c_{\text{total Se(IV)}} = [H_2SeO_3] + [SeOCl_2] \qquad (4)$$

The molar intensity of the SeCl bands of $SeOCl_2$ was found in this way to be 91.03 cm$^2$. For the calculation of $K$, the following procedure was followed. By use of the molar intensity, a preliminary value for the concentration of seleninyl chloride was calculated, the selenious acid concentration was determined with eq 4, and a correction to the intensity of the SeCl envelope could then be made to allow for the selenious acid deformations lying under the SeCl peaks. The molar intensity of the selenious acid deformations is given in Table II. The concentration of hydrochloric acid was then calculated from

$$[HCl] = c_{HCl} - 2[SeOCl_2]$$

From this information $a_{HCl}$ and $a_w$ could be obtained[20,21] and $K$ could be calculated. Peak intensities, concentrations, activities, and equilibrium constants are listed in Table III. The best constancy of $K$ over the range of concentrations studied was calculated when the molar intensity of the SeCl bands was adjusted to 88.37 cm$^2$. The average $K$ value was found to be $3.2 \times 10^{-6}$ mol$^{-2}$ L$^2$ in fair agreement with that calculated from the intensity of the SeO single bond peak in the 12.17 M hydrochloric acid solution.

**Solutions of Selenium Dioxide in Hydrochloric Acid Saturated with Hydrogen Chloride at 0 °C.** A 1 M solution of selenium dioxide in 12 M hydrochloric acid is pale yellow, but if such a solution is cooled to 0 °C and then saturated with

**Table IV.** Raman Spectra (cm$^{-1}$) of Chloroselenate(IV) Species[a]

| $SeCl_4$ in $CH_3NO_2$[b] | $SeCl_5^-$ in $CH_3CN$[c] | $SeCl_6^{2-}$ in $CH_3CN$[c] | 1 M $SeO_2$ in 15.18 M HCl |
|---|---|---|---|
| 150 (1, br) | 150 (2, br, p) | 171 (1, p?) | 153 (0, dp) |
| 206 (2) | | | |
| | 239 (8, dp) | 235 (10, dp) | |
| 264 (1, p) | 260 (8, sh, dp?) | | |
| | 272 (10, p) | 284 (9, p) | 275 (8, br, sh, p?) |
| 310 (0) | | | |
| 356 (10, dp) | 333 (1, p) | | 325 (10, p) |
| 390 (6, dp) | | | |
| | | | 915 (0, p) |

[a] Measured up to 1000 cm$^{-1}$. [b] Solvent bands are 474 (2), 604 (1), 649 (8, p), and 994 (25) cm$^{-1}$. [c] LaHaie, P.; Milne, J. *Inorg. Chem.* 1979, *18*, 632.

hydrogen chloride, it becomes an intense yellow. The hydrogen chloride concentration of an aqueous solution saturated at 0 °C is 15.18 M.[22] The Raman spectra of solutions of several concentrations of selenium dioxide in 15.18 M hydrochloric acid are shown in Figure 3 and the spectrum of the 1 M selenium dioxide solution is listed in Table IV along with those of several species which may give rise to the spectra of the hydrochloric acid solutions. Seleninyl chloride is still present in these solutions as shown by the peak at 915 cm$^{-1}$. Its concentration may be estimated by using the molar intensity for this peak, which has been determined from the spectrum of selenium dioxide in 12.17 M hydrochloric acid shown in Figure 2. This solution contains 0.126 M selenious acid (Table III) and the intensity of the SeO double bond peak must be corrected for this contribution, using the molar intensity for this band listed in Table II. The total normalized intensity of the SeO double bond band in the 12.17 M hydrochloric acid solution is 8.55 cm$^2$ from which the molar intensity of the SeO band for $SeOCl_2$ is calculated to be 9.06 cm$^2$. From this molar intensity, the concentration of seleninyl chloride in the 1 M selenium dioxide solution in 15.18 M hydrochloric acid is found to be 0.310 M.

In the spectra of 1 M selenium dioxide solutions in hydrochloric acid in concentrations from 11.15 M upward, the valley at ca. 287 cm$^{-1}$ is seen to be filled in progressively (Figures 2 and 3). At the same time the concentration of seleninyl chloride decreases on increasing the concentration of hydrochloric acid from 12.17 to 15.18 M. It is clear that a new Se(IV) species is being formed at the higher hydrochloric acid concentrations. This new species may be the reason for the higher value of the seleninyl chloride formation constant for the solution with the highest hydrochloric acid concentration given Table III. Judging from the reduced intensity of the SeO double bond peak, its position, and the position of the new band near 287 cm$^{-1}$, both $SeOCl_3^-$ and $SeOCl_4^{2-}$[11] may be ruled out as the new species. The spectrum of $SeCl_4$ dissolved in nitromethane is also given in Table IV. In this solvent, where it is probably monomeric,[23] it exhibits SeCl stretching bands at much higher frequencies than those observed in 15.18 M hydrochloric acid and seems, therefore, unlikely to be present. However, both the pentachloro- and hexachloroselenate(IV) anions have Raman peaks near 287 cm$^{-1}$ and may be formed in solution. Their spectra are listed in Table IV. Of these two possibilities, the pentachloroselenate(IV) anion appears more likely to be present on the basis of the polarized spectra, which show a band at 254 cm$^{-1}$. Neither $SeOCl_2$ nor $SeCl_6^{2-}$ ion exhibits strong peaks in their polarized spectra at this frequency but the spectrum of the pentachloroselenate ion does, and thus the principal reaction occurring in these solutions is

$$Cl^- + SeOCl_2 + 2HCl = SeCl_5^- + H_2O$$

The possible presence of some hexachloroselenate(IV) ion

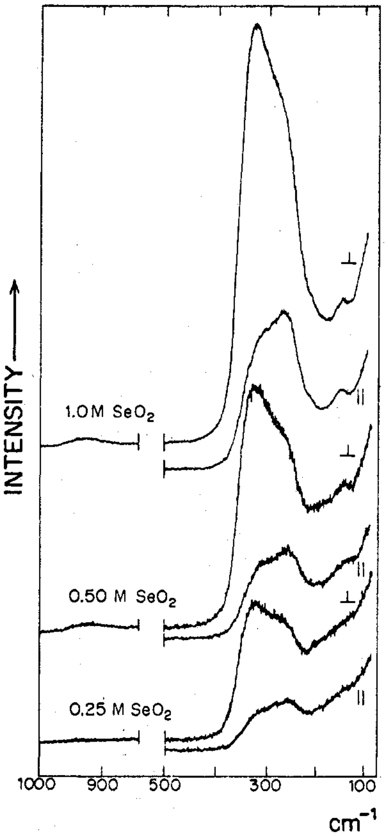

**Figure 3.** Raman spectra of 0.25, 0.50, and 1.00 M selenium dioxide in 15.18 M hydrochloric acid.

cannot be ruled out and, indeed, compounds of this anion are prepared from such solutions.[10] Quantitative treatment of these results, to calculate an equilibrium constant, has been attempted.[24] A plot of total SeCl band intensity against selenium dioxide concentration is not linear, confirming the existence of one or more equilibria but, in the absence of information on hydrochloric acid and water activities, an equilibrium constant could not be determined.

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**Registry No.** $SeOCl_2$, 7791-23-3; $SeO_2$, 7446-08-4; $H_2SeO_3$, 7783-00-8; $SeCl_4$, 10026-03-6.

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