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Spectroscopic Evidence for Selenium Iodides in CS_2 Solution: Se_3I_2, Se_2I_2, and SeI_2

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Analysis of selenium solubility in solutions of iodine in carbon disulfide shows that selenium iodides are formed, according to the equilibrium nSe + I_2 = Se_nI_2. Selenium-77 NMR spectra of these solutions exhibit 4 principal peaks, which are assigned to Se_3I_2 (α-Se and β-Se), Se_2I_2, and SeI_2, as supported by their concentration dependence, chemical shifts, and half-height line widths. The main selenium iodide formed is Se_2I_2, the concentration of which is one-twentieth of that of the total iodine in a solution saturated in selenium. Spectrophotometric methods indicate that some SeI_4 is also formed in the carbon disulfide solutions, but the corresponding NMR signal is not observed due to low signal intensity and exchange broadening. No evidence was found for the formation of Se_nI_2 (n = 1, 2, 3) in carbon tetrachloride, although some selenium iodide or a selenium–iodine complex, perhaps $Se_8{\cdot}I_2$, is formed. The chemical shift and half-height line width of the selenium-77 NMR signal for the Se/I_2 eutectic melt (51 atom % Se) at 65.5 °C indicates that selenium iodides are formed but ^{77}Se MAS NMR spectra and X-ray powder photography give evidence only for crystalline Se and I_2 in the solid formed from the melt.

Introduction

Simple binary selenium iodides are generally regarded as being nonexistent[1] although there is evidence for their formation in aprotic media.[2-5] On the basis of density and surface tension measurements on CS_2 solutions, Se_3I_2, SeI_2, and SeI_4 are claimed to be formed.[3] Several stable species with Se–I bonds have been reported (SeO_2I^-,[6] SeOClI,[7] aryl selenium iodides,[8] SeI_6^{2-},[9] SeI_3^+,[10] $(C_2F_5)SeI_2^+$,[10] $Se_2I_4^{2+}$,[11] $Se_4I_4^{2+}$,[12] and $Se_6I_2^{2+}$ [13]) and molecular adducts of organic selenides with molecular iodine have been characterized.[14-17] The iodoselenium cation work has been recently reviewed.[18] However, vapor pressure measurements[19,20] and phase diagrams[21,22] of Se/I_2 mixtures show no evidence for solid selenium iodide compound formation although recent EXAFS studies indicate the formation of Se–I bonds in Se/I_2 melts.[23]

We have recently reported on the nature of selenium chlorides and bromides in aprotic solvents,[24,25] and in view of the equivocal characterization of binary selenium iodides, we have extended our studies of chalcogen halides to include them.

Experimental Section

Iodine (AnalaR) was sublimed before use and selenium (Baker analyzed and Oak Ridge National Laboratories, 91.77% isotope enriched) was used directly. Carbon disulfide (BDH assured), bromine (Fisher Reagent) and carbon tetrachloride (Fisher certified) were distilled from phosphorus pentoxide before use.

Raman spectra were recorded, using a Spectra Physics Krypton ion laser (647.1 nm) with a Hamamatsu PM tube, Princeton Applied Research photon counter and a Jobin-Yvon monochromator. The average resolution over the range of wavenumbers studied was 7 cm^{-1}.

The ^{77}Se NMR spectra of liquid samples were recorded unlocked, using a Varian XL300 spectrometer operating at 57.28 MHz. The spectra were run with a 2-s pulse delay and 30° tip angle. For good quality spectra, using 91.77% ^{77}Se isotope enriched selenium, up to 74 000 transients were taken. For spectra using natural abundance ^{77}Se (7.58%), no pulse delay was employed. The reference signal used was that of saturated aqueous selenious acid at 21 °C. All chemical shifts are quoted with respect to neat dimethylselenium ($\delta(Me_2Se) = \delta(H_2SeO_3) + 1300.0$ ppm). We were unable to observe the NMR signal of Se_8 in CS_2 by employing the same tip angle and pulse delay as used for the earlier work.[26] The resonance frequency used earlier was 76.1 MHz, and our failure to observe this signal could be due to a difference in the CSA relaxation rate. However, the difference may also be due to the high crystallinity of the isotope-enriched selenium used. Hexagonal Se is known to exhibit very low solubility in CS_2.[27] The MAS ^{77}Se NMR spectra were measured at 57.2 MHz on a Chemmagnetics CMX-300 NMR spectrometer with a 60-s pulse delay and 2-μs pulse width. The magic angle spinning rate was approximately 4 kHz. The chemical shifts were referenced directly to that of pure liquid dimethylselenium.

The UV–visible spectra were recorded on a Perkin-Elmer Lambda 3B spectrophotometer, using 1 mm path length quartz cuvettes.

All solution preparation and sample transfers were done in a drybox. In the case of the CS_2 solutions, it was difficult to avoid some solvent

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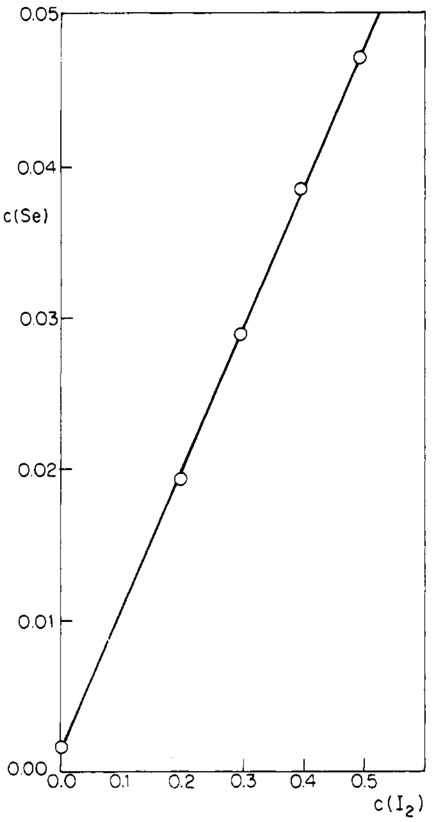

Figure 1. Selenium solubility (c(Se)) in CS_2 solutions of varying iodine concentration ($c(I_2)$).

evaporation (bp 46.25 °C), and this led to considerable scatter in the UV–visible absorbances.

Selenium solubilities were determined at ambient temperature (23 °C) by gravimetry. Finely divided commercial vitreous selenium was used, and the solutions were stirred for 24 h before analysis. The elemental selenium was filtered out, washed with ethanol and diethyl ether, dried at 105 °C, and weighed.

Results

The solubility of selenium in CS_2 varies from 2.5×10^{-4} to 8.2×10^{-3} mol L^{-1} at room temperature,[27] depending on the solid modification of Se used. For the commercial vitreous Se used in this work, the solubility was 0.001 63 (±0.000 02) mol L^{-1} at 23 °C. This solubility is 5 times lower than that of amorphous Se but greater than that of hexagonal Se.[27] Addition of I_2 to the solution increased the Se solubility dramatically as shown in Figure 1. The linear dependence of c(Se) on $c(I_2)$ indicates that the equilibrium involved is of the type

$$n\text{Se} + I_2 = \text{Se}_nI_2 \qquad (1)$$

The linear dependence parallels that observed for Se/I_2 solutions in carbon tetrachloride but the Se is over 4 times more soluble in the CS_2 than in the CCl_4 solutions of the same I_2 molarity. These observations eliminate SeI_4 as a major species in these solutions.

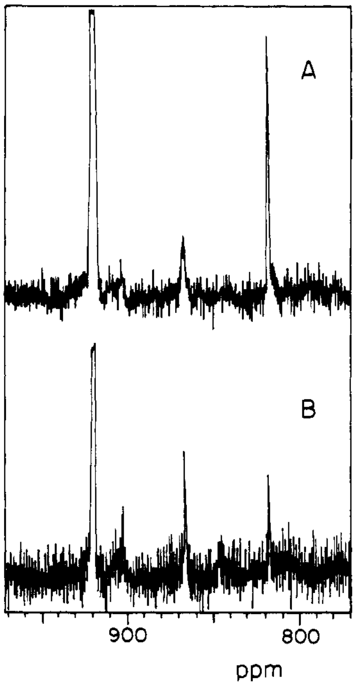

Figure 2. ^{77}Se NMR spectra of Se/I_2 mixtures in CS_2. Trace A: $c(I_2)$ = 0.39 M; c(Se) = 0.022 M, Trace B: $c(I_2)$ = 0.39 M; c(Se) = 0.039 M.

Table I. ^{77}Se NMR Chemical Shifts, Intensities, and Half-Height Line Widths, $w_{1/2}$, of Selenium Iodides

sample	δ (Me_2Se)[a] (ppm)	rel intens	$w_{1/2}$ (Hz)	assignt
	Solution in CS_2			
$c(I_2)$ = 0.70 M	645.3[b]			$Se_8{\cdot}I_2$
c(Se) = 0.080	918.2		54	Se_2I_2
	Solution in CCl_4			
$c(I_2)$ = 0.44 M	651.6		27	$Se_8{\cdot}I_2$
c(Se) = 0.011 M				
	Solution in CS_2			
$c(I_2)$ = 0.39 M	646.5[b]			$Se_8{\cdot}I_2$
c(Se) = 0.022 M	813.2	0.058	53	SeI_2
	862.3	0.024	170	α-Se in Se_3I_2
	899.3	0.014	120	β-Se in Se_3I_2
	915.8	0.901	20	Se_2I_2
	Solution in CS_2			
$c(I_2)$ = 0.39 M	647.8[b]			Se_8I_2
c(Se) = 0.039 M	813.8	0.027	64	SeI_2
	862.8	0.067	90	α-Se in Se_3I_2
	898.9	0.032	80	β-Se in Se_3I_2
	915.6	0.873	22	Se_2I_2
	842/904			Se_4I_2
	Se/I_2 Eutectic (51 atom % Se)			
melt (65.5 °C)	915.7		206	Se_n,Se_nI_2,SeI_4
solid[c,d]	808.0		1028	hexagonal Se
	2:1:1 $Se/I_2/Se_2Br_2$			
liquid (21 °C)	1047.7		2260	Se_2Br_2,Se_nI_2
	Vitreous Se[c,e]			
	865.1		17,200	amorphous Se

[a] Relative to $\delta(Me_2Se)$ = 0.0 ppm. [b] Transient. [c] ^{77}Se MAS/NMR. [d] $\delta_{\text{isotropic}}$. [e] Baker analyzed commercial product.

The ^{77}Se NMR spectrum of Se in CS_2 consists of a strong signal at 614.6 ppm due to Se_8 and two weak signals at 997.6 and 685.1 ppm due to Se_7 and Se_6, respectively.[26] A saturated solution of natural abundance Se and I_2 in CS_2(c(Se) = 0.07 M; $c(I_2)$ = 0.7 M) gives one ^{77}Se NMR signal at 918.2 ppm. In as much as Se_3I_2 and Se_4I_2 are expected to give multiplet signals with 2:1 and 2:2 intensity ratios, respectively, like the corresponding bromides and chlorides,[24,25] and SeI_4 would be present at relatively low concentration, as shown by the gravimetric results, this signal must be due to either SeI_2 or Se_2I_2. The NMR spectrum of a CS_2 solution 0.022 M in isotope-enriched Se and 0.39 M in I_2 exhibits initially a peak at 646.5 ppm, which weakens over a period of minutes and is replaced by the four signals shown in Figure 2, trace A. The chemical shifts, half-height line widths, and intensities are listed in Table I. The NMR spectrum of a 0.44 M I_2 solution in CCl_4, saturated with Se (c(Se) = 0.011 M), exhibits a single peak at 648.4 ppm, which persists over the period of time of the experiment (2 h). This peak near 650 ppm does not correspond to the chemical shift of any known Se_n species[26] but may be caused by an Se_n–I_2 adduct, which is stable in CCl_4 but reacts to form selenium iodides in CS_2. There is evidence for

Table II. Selenium Iodide Concentrations (M) and Equilibrium Constants Calculated from ^{77}Se NMR Signal Intensities

	solution no.	
	1	2
$c(I_2)$	0.39	0.39
c(Se)	0.022	0.039[a]
$[Se_2I_2]$	0.99×10^{-2}	1.7×10^{-2}
$[SeI_2]$	1.2×10^{-3}	1.05×10^{-3}
$[Se_3I_2]$	3.0×10^{-4}	1.30×10^{-3}
$[I_2]$	0.380	0.375
$K_d(SeI_2)$	3×10^3	6×10^3
$K(Se_2I_2)$	3.7×10^{-3}	4.7×10^{-3}

[a] Saturated in Se.

the formation of an $S_8 \cdot I_2$ adduct in CH_2Cl_2 solution[28] and an 8:2 Se/I complex in CH_3I.[29] An analogous $Se_8 \cdot I_2$ complex may be formed in CCl_4. This would be consistent with the linear dependence of c(Se) on $c(I_2)$ in this solvent. Of the four signals which arise in the spectrum of the CS_2 solution (c(Se) = 0.022 M), the most deshielded signal at 915.8 ppm corresponds to the signal observed in the spectrum of the Se/I_2 solution in CS_2 with ^{77}Se at natural abundance. This signal, as shown in Table I, is 10 times more intense than the next strongest signal at 813.2 ppm. The ^{77}Se NMR spectrum of a CS_2 solution with the same $c(I_2)$ (=0.39 M), but with c(Se) = 0.039 M in isotope-enriched Se, is shown in Figure 2, trace B and the chemical shifts, signal intensities and half-height line widths are listed in Table I. With increased c(Se) the relative intensity of the most shielded signal at 813 ppm decreases. The two central signals at 862 and 899 ppm retain a relative intensity with respect to each other of 2:1 even with the change in c(Se) at constant $c(I_2)$, but their relative combined intensity falls with decreasing c(Se). All of these observations are consistent with the assignment of the signal at 915.8 ppm to Se_2I_2, that at 813 ppm to SeI_2, and those for the central two peaks at 862 and 899 ppm to Se_3I_2 for which two signals of intensity ratio 2:1, for the two α-Se's and one β-Se, are expected. All of these compounds are Se_nI_2 species and the stoichiometry of each is known for the corresponding selenium chlorides and bromides.[24,25] This assignment is also supported by the changes in chemical shift with change in halogen for each species, Se_3X_2, Se_2X_2, and SeX_2, through the series X = Cl, Br, I. The Se_2X_2 signal is shifted 101 ppm, from 1290.2 to 1189.1 ppm, on going from Se_2Cl_2 to Se_2Br_2 while the SeX_2 signal is shifted 260 ppm, from 1724 to 1464 ppm, on going from $SeCl_2$ to $SeBr_2$. It is expected that, on going from the bromide to the iodide, the Se_2X_2 signal will experience greater shielding but will be overtaken by the shift in the SeX_2 signal such that the SeI_2 signal will exhibit stronger shielding than the Se_2I_2 signal. The Se_3X_2 signals always lie slightly more shielded (3–30 ppm) than the Se_2X_2 signal for X = Cl and Br.[24,25] Again, the position of the Se_3I_2 signal is consistent with these observations. The half-height line widths, $w_{1/2}$, of the principal signals in these spectra are also listed in Table I. They too are consistent with the assignment given. In general, $w_{1/2}$ values for the SeX_2 species are 3–4 times greater than those of the corresponding Se_2X_2 (X = Cl, Br).[30,31] For instance, in acetonitrile, $w_{1/2}(SeCl_2)$ is 90.7 Hz and $w_{1/2}(Se_2Cl_2)$ is 30.3 Hz[31] and in S_2Cl_2/Se_2Br_2 mixtures $w_{1/2}(SeCl_2)$ is 174 Hz and $w_{1/2}(Se_2Cl_2)$ is 35 Hz.[30] The $w_{1/2}$ of the less shielded peak due to Se_2I_2 in the spectrum of the solution with c(Se) = 0.022 M is 20 Hz while that of the more shielded peak due to SeI_2 is 53 Hz. The large half-height line widths of the signals assigned to Se_3I_2 are a result of a combination of exchange broadening[30] and ^{77}Se–^{77}Se coupling. The two signals for the spectra with isotope-enriched Se are expected to consist of a doublet and a triplet with J_{Se-Se} = 23–56 Hz.[32] The multiplet structure is not observed due to exchange broadening, but exchange broadening and Se-Se coupling lead to line widths greater than those of Se_2I_2 and SeI_2, where only singlets arise. The spectrum of the CS_2 solution with the highest c(Se) (=0.039 M) also shows two weak signals of approximately equal intensity at 842 and 904 ppm, in addition to the signals already discussed. These are assigned to Se_4I_2, the signal of which is expected to lie in this region of the spectrum ($\delta(Se_4Cl_2)$ = 934 ppm; $\delta(Se_4Br_2)$ = 923 ppm[24,25]) and to consist of an equal intensity pair of peaks due to α- and β-Se. The principal equilibria occurring in these solutions are

$$2\mathrm{SeI_2} \overset{K_d(\mathrm{SeI_2})}{=} \mathrm{Se_2I_2} + \mathrm{I_2} \tag{2}$$

and

$$2\,\mathrm{Se_2I_2} \overset{K(\mathrm{Se_2I_2})}{=} \mathrm{SeI_2} + \mathrm{Se_3I_2} \tag{3}$$

From the NMR peak intensities and stoichiometry of the solutions $[Se_3I_2]$, $[Se_2I_2]$, $[SeI_2]$, $[I_2]$, and the equilibrium constants may be calculated. These are listed in Table II.

Elemental Se and I_2 form a eutectic at 51 atom % Se, which has a melting point of 57 °C.[20] The ^{77}Se chemical shift of the eutectic measured at 65.5 °C is 915.7 ppm, as given in Table I. The solid MAS/NMR spectra of commercial Se and of the solid eutectic at 21 °C are also given in Table I. The signal for the eutectic melt is markedly less shielded than the signal for Se_8 in CS_2 (614.6 ppm[26]) and those of commercial (865.1 ppm) and hexagonal (808.8 ppm) Se (Table I) and closer to the chemical shifts for selenium iodides. This is consistent with the conclusions of EXAFS studies that indicate that selenium iodides are formed in these melts.[23] Furthermore, cryoscopic studies of selenium in iodine indicate a molecular mass corresponding to "Se_2", which would not be differentiated from Se_2I_2 in these experiments.[19,29] The half-height line width of the melt signal (206 Hz) is indicative of rapid selenium exchange relative to that of pure Se_2Cl_2 and Se_2Br_2.[24] A 2:1:1 molar mixture of Se, I_2 and Br_2 gave the single broad signal at 1047.7 ppm listed in Table I. This behavior is to be compared with that of Se_2Cl_2/Se_2Br_2 mixtures where distinct signals for Se_2BrCl, Se_2Cl_2, and Se_2Br_2 are observed.[24] The chemical shift lies at the mean of the signals for Se_2Br_2[24] and Se_2I_2. This and the half-height line width indicate rapid Se exchange between Se_2Br_2 and Se_2I_2.

An X-ray powder photograph of the solid produced on freezing the eutectic melt shows the presence of hexagonal selenium and orthorhombic iodine with no additional lines indicative of selenium iodide formation and no broad diffraction expected for amorphous material. Iodine is known to act as a catalyst for the crystallization of selenium.[33] The ^{77}Se MAS/NMR spectrum of the solid exhibits, after 248 scans, 10 lines with $\delta_{isotropic}$ at 808.8 ppm. The reported isotropic shift for hexagonal Se from single crystal work[34] is 794.2 ppm. The difference in shift may arise from differences in sample temperature and selenious acid reference concentration, which was unspecified for the single crystal work. The chemical shift of aqueous selenious acid is known to change with concentration.[35] The method of Herzfeld and Berger[36] was used to calculate the ^{77}Se chemical shift tensors from the relative sideband intensities and gave $\sigma_{11} = -247$ (±16), $\sigma_{22} = -26$ (±5) and $\sigma_{33} = 273$ (±20). These values compare well with the values determined for hexagonal Se.[34] The ^{77}Se MAS/NMR spectrum of commercial vitreous Se gave a broad resonance ($w_{1/2}$ = 17 200

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Hz) centered at 865.1 ppm. The absence of structure in the spectrum indicates that the substance is largely amorphous.

Raman spectroscopy has been used to characterize selenium halides with good success,[24,37] because of the strong scattering by these molecules. However, where samples absorb the exciting frequency strongly, often the spectra are of poor quality. This is the case for the selenium iodides and with the increased possibility of band overlap for low vibrational frequencies, little information can be obtained by this technique. The Raman spectrum of a solution of I_2 in CS_2 (0.20 M I_2) saturated with Se (0.02 M Se) is virtually identical with that of the solution with I_2 alone except for a very weak peak at 275 cm^{-1} (0.05 intensity relative to unit intensity for the strong iodine peak at 208 cm^{-1}). This peak lies at the frequency expected for the Se-Se stretching mode in Se_2I_2 ($\nu_{SeSe}(Se_2Cl_2)$ = 292 cm^{-1}; $\nu_{SeSe}(Se_2Br_2)$ = 286 cm^{-1} [38]). The SeI stretching modes are masked by the strong I_2 peak at 208 cm^{-1}.

The Raman spectrum of the 51 atom % Se/I_2 eutectic as a solid is essentially the sum of the spectra of I_2 (95 w, 190 s cm^{-1}) and vitreous Se (95 s, 115 sh, 175 w, 210 sh, 235 s, 275 w cm^{-1}) and there is no indication of additional bands arising from selenium iodide formation. The single strong additional band at 235 cm^{-1} in the spectrum of the solid eutectic arises from hexagonal selenium.[20] The spectrum of the melt exhibits the same bands as those of the solid but the peak at 275 cm^{-1} is stronger relative to that in the solid spectrum. This peak coincides with that observed in the spectrum of the Se/I_2 mixture in CS_2 and indicates the formation of some Se_2I_2 in the melt.

It has been demonstrated previously by spectrophotometry, that some selenium iodide of unknown stoichiometry, is formed in a mixture of Se and I_2 in solution in CS_2.[2] The UV–visible spectra of Se and I_2 mixtures in CS_2 exhibit a strong absorbance at 510 nm due to I_2 as well as a band at 400 nm due to some selenium iodide, which is formed. Elemental Se shows no absorbance in this region. A Job plot[38] at constant total concentration of Se and I_2 equal to 0.00163 M is given in Figure 3. The maximum for this plot lies near the Se mole fraction, X_{Se}, of 0.30, which corresponds to a Se/I stoichiometry of 1:4.7. Precise location of the maximum in this plot is difficult due to the weak absorbance of the shoulder at 400 nm lying on the strong I_2 peak but the data suggest that the peak at 400 nm is due to SeI_4, which could be a molecular adduct such as $SeI_2 \cdot I_2$ or a true selenium(IV) iodide. The absorbances due to SeI_2, Se_2I_2, and Se_3I_2 are not observed and lie under the strong I_2 peak at 510 nm, the absorbance of which varies linearly with $c(I_2)$, and to shorter wavelengths unaccessible due to solvent absorbance. The absence of a signal from SeI_4 in the ^{77}Se NMR spectra parallels the absence of the $SeCl_4$ signal in solutions of $SeCl_4$ in acetonitrile and pyridine, reported earlier[25] and is probably a result of signal breadth, due to inter and intramolecular exchange, and low signal strength.

Conclusion

The strong interatomic bonding in solid Se and I_2 relative to SeI bond strengths prevent the formation of stable solid selenium iodides but in Se/I_2 melts and solutions of Se and I_2 in CS_2, molecular selenium iodides exhibit limited stability. The stoichiometry of the iodides formed, parallel those of the corresponding chlorides and bromides formed in aprotic solvents.[24,25] Se_3X_2, Se_2X_2, SeX_2, and SeX_4 are all known except for $SeBr_4$, which is unknown in solution.[39] The iodoselenium(IV) ions SeI_3^+ [10] and SeI_6^{2-} [9] are known, and it is apparent that the Se(IV)–I bond does not undergo autoredox decomposition in these cases. Both surface tension and density measurements on Se/I_2 mixtures in CS_2 have shown that Se_3I_2, SeI_2, and SeI_4 are formed in these solutions.[3] While these methods can be used to support the presence of some selenium iodides, they cannot be used to exclude the formation of others, such as Se_2I_2. The dissociation of SeX_2 to Se_2X_2 and X_2, equilibrium 2, is more extensive, the less strongly oxidizing the halogen. Free chlorine is not detected even in solutions with Se/Cl mole ratios of 1:4, where $SeCl_4$ formation is complete.[25] Ignoring solvent effects, which are small for weakly donating solvents,[25], $K_d(SeX_2)$ increases in aprotic solvents in the order

$$\underset{(=0.0\ (\mathrm{MeCN,\ MeNO_2})^{24,40})}{K_d(\mathrm{SeCl_2})} < \underset{(\approx 0.025\ (\mathrm{CCl_4})^{24})}{K_d(\mathrm{SeBr_2})} < \underset{(4\times 10^3\ (\mathrm{CS_2}))}{K_d(\mathrm{SeI_2})}$$

On the other hand, the disproportionation of Se_2X_2 to Se_3X_2 and SeX_2, equilibrium 3, increases with lower oxidizing power of the halogen but the differences are small compared to those for $K_d(SeX_2)$ (Se_2Cl_2 in CH_2Cl_2, 1.3 × 10^{-3}; Se_2Br_2 in CH_2Cl_2, 2.2 × 10^{-3} [24]; Se_2I_2 in CS_2, 4.2 × 10^{-3}).

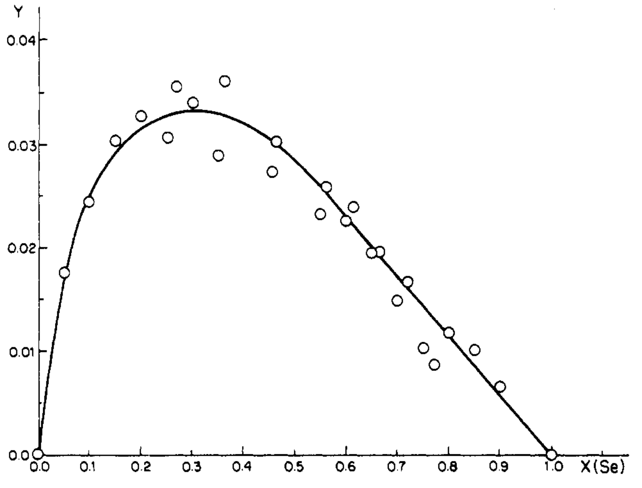

Figure 3. Job plot for Se/I_2 solutions in CS_2 at 400 nm with total solute concentration = 0.001 63 M. X(Se) = Se mole fraction; $Y = A_{1\,\mathrm{mm}} - 0.105X(\mathrm{Se}) - 0.0066X(\mathrm{I_2})$, where 0.105 and 0.0066 are the $A_{1\,\mathrm{mm}}$ of 0.00163 M solutions of Se and I_2, respectively.

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