Speciation of Main-Group Metal Ions by Electrospray Mass Spectrometry. 1. Investigation of Aqueous Polyselenide Species and Effects of Cations and pH

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Received November 6, 1996[⊗]

Polyselenide anion speciation in aqueous solution has been investigated by electrospray mass spectrometry (ESMS). Two methods of control over this speciation are reported: countercation substitutions and pH adjustments. The countercation has been found to affect the degree of disproportionation or comproportionation. Solutions of sodium tetraselenide displayed numerous Se_n^{2-} and HSe_n^- species in neutral and basic soluions. In potassium solutions, the dominant species was $Se_4^{2-}\cdot H_2O$. Solutions of cesium pentaselenide also showed preference for higher-order polyselenides. The pH dependence has been analyzed in terms of the percent Se_n ($n = 2-5$) present. Di-, tri-, tetra-, and pentaselenide species were present over the entire pH range investigated, and trends in selenide species versus pH were developed. For example, at pH > 9, tetraselenide species were dominant.

Introduction

Some of the earliest speciation studies of polychalcogenides in solution were performed by Zintl during potentiometric titrations of main group elements in liquid ammonia with alkali metals.[1] These studies indicated that numerous polyselenides, for example Se_4^{2-}, existed in solution and could perhaps be isolated in the solid state.[2−4] These essential polychalcogenide building blocks have been used to prepare many new metal polychalcogenide compounds by solvatothermal and other solution methods;[5−11] indeed, some of these compounds contain different polychalcogenide ligand building blocks within the same structural unit.[12−17] These different polychalcogenide ligands are likely the result of disporportionation and comproportionation of the starting polychalcogenides in solution, as well as the redox activity of the reagents. In order to design and develop new materials based on polychalcogenide building blocks through rational synthetic methods, an understanding of the behavior of these building blocks in solvatothermal reactions is required, and consequently detailed studies of the speciation of polychalcogenides in solution are essential. We report here polyselenide speciation investigations in aqueous solutions by electrospray mass spectrometry, wherein we describe the behavior of the polychalcogenide building blocks as a function of pH and countercations.

Polysulfide speciation in solution has been extensively investigated,[18−27] while there have been relatively few polyselenide speciation studies.[28−34] These investigations have used UV−visible spectroscopy, NMR, or electrochemical techniques to identify the species present. Spectroscopic studies of polychalcogenide speciation have required the deconvolution of up to 6 overlapping spectral bands[31] or numerical iterative procedures to fit a proposed model.[30] Several groups have attempted to use electrochemical techniques to identify polychalcogenides in solution with little success, due to the similar reduction−oxidation potentials of the different species.[33,34] For polyselenides, ^{77}Se NMR spectroscopy has provided some information concerning speciation in aqueous solutions but only at low temperatures (<250 K).[35]

The previous speciation studies cited above have encountered problems due to similarities in the property measured, namely the reduction−oxidation potential or the electronic absorption energies. In mass spectrometry the property measured, the mass

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[⊗] Abstract published in *Advance ACS Abstracts,* May 15, 1997.

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S0020-1669(96)01336-5 CCC: $14.00

to charge ratio (*m*/*e*), is significantly different for all polychalcogenide species concerned. Because of this fact, electrospray mass spectrometry (ESMS) was chosen to investigate polychalcogenide solutions. This technique has proven useful for studying delicate solution species, as electrospray provides a soft ionization source.[36] ESMS has been utilized to investigate the acidities of diols,[37] the stability of gas phase ions,[38] and identification of organometallic and inorganic ions.[39−41] Most recently, the speciation of sulfates and sulfites in solution has been accomplished,[38] and Horlick et al. used the variations in collision-induced dissociation to validate the species identified.[42] Overall, the ESMS technique is a proven technology that has only recently begun to demonstrate its remarkable versatility in identifying complex solution species. For us, this technique also allows a range of temperatures to be explored, from 25 °C to greater than 70 °C, that was not accessable in the previously reported ^{77}Se-NMR study and that more closely resembles our metal−polyselenide synthesis conditions.[43,44]

Experimental Section

Mass spectrometric studies were performed with a Fisons VG-Quattro-SQ equipped with an electrospray ionization source and a micro-flow pump or a syringe pump. The spectrometer was calibrated in the negative ion mode with a NH_4I solution. All injected sample sizes were 10 mL with a flow rate of 4 mL/min, the capillary potential was −2.7 kV, the focus voltage was 65 V, and the probe temperature was 65 °C. Data were collected at 2 s/scan for 30 s over a scan range of 50−600 amu/e. Intensity comparisons between spectra are based on the counts and not the percent intensity. The percent intensity was not used as the largest peak in each spectrum varied. Peaks in the cesium spectrum between 175 and 275 amu/e were complicated by a persistent background pattern, and a subtraction of that interfering species was attempted and yielded the peaks with intensity below the baseline. All solutions were completely saturated with dissolved N_2 gas, as attempts to use completely degassed water did not allow efficient sprays and no signals were detected.

The polyselenide salts were prepared by mixing stoichiometric quantities of the desired alkali metal (Alfa, 99.9%) and elemental selenium (Johnson-Matthey, 99.999%) in an inert-atmosphere glovebox (generally, reactions were performed on a 5−10 g scale). The solids were combined in a 300 mL flask fitted with a cold finger for condensing liquid ammonia. In the case of the sodium and potassium salts, A_2Se_4 was prepared.[45] For the cesium salt, only Cs_2Se_3 and Cs_2Se_5 are known, and we chose to use the pentaselenide for our studies.[46−48] The method of Böttcher was used to prepare the cesium salt (*great care should be taken to control the addition of the Cs−NH₃ solution to the Se−NH₃ solution*). All solids used in this study were dried under vacuum and stored in an inert-atmosphere glovebox until used and no further purification was neccessary.

The solutions of the polychalcogenides were prepared with deoxygenated Millipore deionized water. Solutions of NaOH at various concentrations were used to prepare 30 mM solutions of Na_2Se_4 for the pH investigations. Solutions of 0.1 M NaOH, KOH, CsOH, and NH_4OH were used to prepare 30 mM Se_4^{2-} solutions for the cation studies. Attempts to use CsCl solutions as a source of cesium ions, in a comparison of ACl salts (A = Na, K, Cs) in a study of the effects of halide ion on the polyselenides, were unsuccessful due to the formation of $A_xCl_{x+1}^-$ clusters, which dominate the spectra. Determinations of the relative percent of observable Se_n ($n = 2-5$) were based on all Se_n species identified, including Se_n^{2-}, HSe_n^-, and $NaSe_n^-$ and all hydrated species.

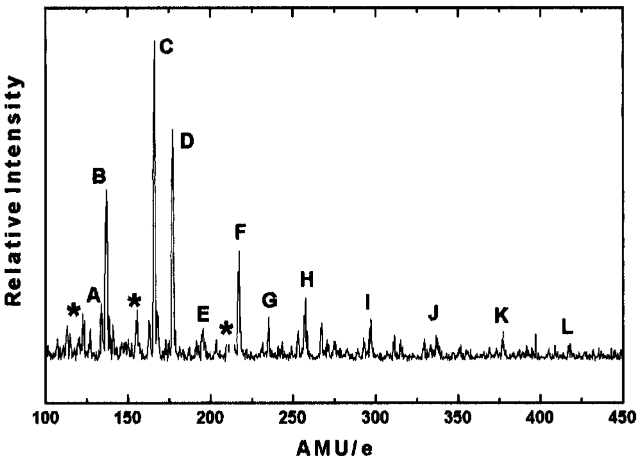

Figure 1. Representative electrospray mass spectrum of 30 mM Na_2Se_4 in 1.0 M NaOH. The peaks marked with an asterisk are interference peaks from the background. Peak assignments are as follows: **A**, $Se_2^{2-}\cdot 6H_2O$; **B**, $Se_3^{2-}\cdot 2H_2O$; **C**, $Se_4^{2-}\cdot H_2O$; **D**, $Se_4^{2-}\cdot 2H_2O$; **E**, $Se_4^{2-}\cdot 4H_2O$; **F**, $Se_5^{2-}\cdot 2H_2O$; **G**, $Se_5^{2-}\cdot 4H_2O$; **H**, $HSe_3^-\cdot H_2O$; **I**, $NaSe_3^-\cdot H_2O$; **J**, $HSe_4^-\cdot H_2O$; **K**, $NaSe_4^-\cdot 2H_2O$; **L**, $HSe_5^-\cdot H_2O$.

Results and Discussion

All peaks were identified by the largest peak in the mass/charge (amu/e) region of the isotopically broadened peaks. Simulated spectra based on the distribution of selenium isotopes were compared to the observed data, and the assigned peaks fit the models well.

Na_2Se_4. A representative spectrum of 30 mM Na_2Se_4 in 1.0 M NaOH is shown in Figure 1. The peaks marked with an asterisk are peaks present within the background and blank scans. The peak at 127 amu/e is due to I^-, and the peak at 276 amu/e is due to NaI_2^-. The source of the background peak at 212 amu/e is unknown but fluctuates greatly between samples, probably due to the presence of $Se_4^{2-}\cdot 6H_2O$ ($m/e = 213$ amu/e). Because of this background, this particular tetraselenide species was not included in the analysis.

Many polyselenide species could be identified within this apparently simple solution of a well-characterized salt: hydrated Se_n^{2-}, the protonated HSe_n^-, and $NaSe_n^-$ ($n = 2-5$). In all, we were able to identify the diselenide, triselenide, tetraselenide, and pentaselenide ions. The monoselenide species were not observed in these experiments due to the mass range selected; that is, these species would be observed at mass:charge ratios of <50 amu/e, where there are many other background interferences. Scans to mass:charge ratios of >450 Da/e did not reveal any other species. Finally, all ions observed were coordinated to at least one water of hydration and ions with fewer waters of hydration often existed as the protonated or sodated monoion, an observation consistent with those observations in the divalent sulfate/sulfite systems reported separately by Kebarle and Horlick.[38,42]

No complex ions, such as $Na(Se_n)_x^{2x-1}$, or higher polyselenides, such as Se_6^{2-} ions, were observed under the conditions investigated. The lack of higher order selenides ($n > 5$) in aqueous solution complicates the explanations provided earlier

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for the equilibria established between Se_3^- and Se_6^{2-} seen in acetone and DMF solutions.[28,35] It was reported that the hexaselenide ion was in a temperature-dependent equilibrium with the radical anion, Se_3^-, and that it was seen, in comparisons between solid-state and solution Raman spectra, the hexaselenide was preferred.[28] However, in aqueous solutions of polyselenides investigated by Licht, no polyselenides of $n > 4$ were reported under basic conditions.[30]

Another interesting observation in our ESMS spectra was the presence of the diselenide, Se_2^{2-}. Dance reported that it was unstable in DMF with respect to probable disproportionation to HSe^- and higher order polyselenides.[35] The diselenide species was, however, observed by Licht in aqueous solutions.[30] The major difference between our studies (together with those of Licht) and those reported by Haushalter and Dance is the solvent of study. As a consequence, we have begun investigating the speciation of polyselenides in nonaqueous polar solvents, both protic and aprotic, since the protic nature of the solvent appears to play a major role in the type of species observed.[49]

Effect of Cations on Polyselenide Speciation. Cation effects have been important in preparing many new polychalcogenide compounds; many compounds that have been prepared with one cation, such as K^+, have not been prepared as other salts, such as Na^+.[50] It is believed that this is possibly due to the size of the cation or lattice stabilization energy, that is, templating effects.[5,6] On the basis of our ESMS results, it appears that the cation affects the distribution of polyselenides (Figure 2) in aqueous solutions.

For the sake of comparison, all solutions were prepared as 30 mM using 0.1 M AOH (A = Na, K, Cs, and NH_4^+). The dominant species present in the K^+ and Cs^+ solutions was $Se_4^{2-}\cdot H_2O$, while in both the NH_4^+ and Na^+ solutions other polyselenide species were observed. Initially, we believed that the differences noted between the Na^+ and NH_4^+ solutions could have been related to observations by Arakawa et al. in tetraethylammonium chloride solutions of Ru(II) diimine complexes.[51] The loss of signal intensity within their system was linked to ionic strength changes brought on by the addition of the ammonium salt. The differences noted in our Na^+ and K^+ mass spectra were probably not attributable to these effects (as the ionic strengths were kept constant) and were possibly due to the differences in cation–anion complexation/interactions. Finally, for the Cs^+ solutions, we regularly observed small signals that were attributable to two hydrated complex-ion species, $Cs(Se_4)_2^{3-}$ and $Cs(Se_5)_2^{3-}$, peaks **K** and **L** in Figure 2, for which we have no other spectroscopic evidence and none has been suggested in the literature; however, it has been postulated that complex ion species may be responsible for the unique chemistry observed in the solvatothermal reactions of the cesium polychalcogenides.[5,6]

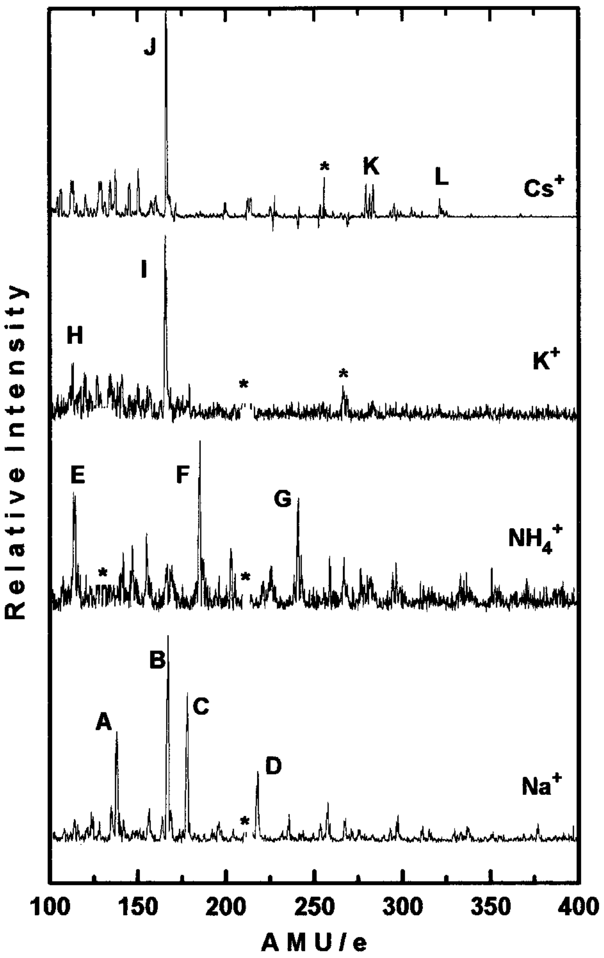

Figure 2. Electrospray mass spectra of 30 mM Na_2Se_4 in 0.1 M NaOH, K_2Se_4 in 0.1 M NH_4OH and in 0.1 M KOH, and Cs_2Se_5 in 0.1 M CsOH. The peaks marked with an asterisk are interference peaks from the background. The Na^+ spectrum is the same as in Figure 1. Peak assignments are as follows: **A**, $Se_3^{2-}\cdot 2H_2O$; **B**, $Se_4^{2-}\cdot H_2O$; **C**, $Se_4^{2-}\cdot 2H_2O$; **D**, $Se_5^{2-}\cdot 2H_2O$; **E**, $Se_2^{2-}\cdot 4H_2O$; **F**, $Se_4^{2-}\cdot 3H_2O$; **G**, HSe_3^-; **H**, $Se_2^{2-}\cdot 4H_2O$; **I**, $Se_4^{2-}\cdot H_2O$; **J**, $Se_4^{2-}\cdot H_2O$; **K**, $Cs(Se_4)_2^{3-}\cdot 4H_2O$; **L**, $Cs(Se_5)_2^{3-}\cdot 3H_2O$.

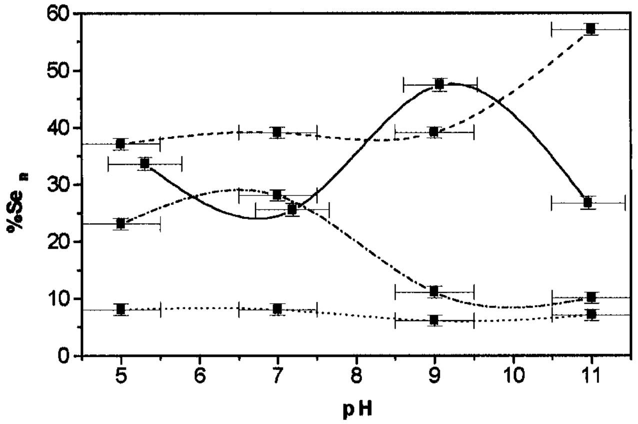

Figure 3. pH dependence of the percent Se_n. The lines represent trends in the species concentrations: Se_2 (-•-), Se_3 (—), Se_4 (- - -), and Se_5 (•••).

Effect of pH on Polyselenide Speciation. The pH dependence of the sodium polyselenide species in solution has also been investigated. Figure 3 shows the relationships of the different Se_n species to changing pH ($5 < pH < 11$) in NaOH solutions, where the relative polyselenide species include all possible species in solutions: Se_n^{2-}, HSe_n^-, and $NaSe_n^-$. First, the pentaselenide species is present over this pH range only in low abundance, while di-, tri-, and tetraselenide species vary considerably. These results indicate that from pH = 5 to 7, the diselenide and triselenide species are in nearly a 1 to 1 equilibrium. At pH > 7, the diselenide is depleted forming triselenide species. As the pH is increased further, the triselenides are converted to tetraselenide species. In order to explain these trends and satisfy charge balance constraints, monoselenide species must be involved but are not detectable under our experimental conditions. These results, however, parallel those observed by Licht using UV/visible spectoscopy to monitor the

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(49) Part 2 of this series: Raymond, C. C.; Dick, D. L.; Dorhout, P. K. *Inorg. Chem.*, to be submitted for publication.

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polyselenide species in equilibrium with selenium metal in aqueous solutions.[30] Licht provided equations describing the equilibra between the polyselenides. Our ESMS results indicate that $K_{eq}(1)$ must be near 1 for pH = 5−7 and less than 1 for pH > 7. The constant $K_{eq}(2)$ would also be less than 1 for pH > 9.

$$\mathrm{Se_3}^{2-} + \mathrm{Se}^{2-} \xrightleftharpoons{K_{eq}(1)} 2\mathrm{Se_2}^{2-}$$

$$2\mathrm{Se_4}^{2-} + \mathrm{Se}^{2-} \xrightleftharpoons{K_{eq}(2)} 3\mathrm{Se_3}^{2-}$$

Altering the pH should have also allowed us to investigate the pH dependence of the $\mathrm{HSe}_n^- \rightleftharpoons \mathrm{Se}_n^{2-}$ equilibrium. An investigation of this speciation would have provided some insight into the pK_{a2} for the polyselenide acids in solution. A comparison of the protonated versus unprotonated polyselenides for all species studied did not reveal a linear relationship between the pH and $\log[\mathrm{Se}_n^{2-}/\mathrm{HSe}_n^-]$ as would be expected. We attribute this behavior to the complex interactions between the waters of solvation associated with each species, and the formation of protonated species as the aerosol, and consequently the sprayed ions, becomes deficient in solvent, as was observed in the sulfate/sulfite/thiosulfite solutions of Kebarle and Horlick.[38,42] Thus, it seems that ESMS has several limitations in its ability to reveal all of the complex aqueous solution chemistry of the polyselenides.

Conclusions

In this study, the first in a series of reports on the use of ESMS to examine solutions of main-group metal ions, we have demonstrated that the ESMS technique can be effectively used to monitor the aqueous solution polyselenide species as a function of pH and cation. Results from our speciation studies indicate that it may now be possible to *direct* the major polyselenide species in aqueous solutions through a combination of cation control and pH adjustments and to monitor that speciation *in situ* through electrospray mass spectrometry. Until the advent of electrospray, these important doubly-charged smaller polyanions could not be produced in the gas phase and hence could not be studied in the mass spectrometer.[38]

The next in the series of reports will discuss the studies of polyselenide speciation in other polar solvents, such as CH_3OH, CH_3CN, and DMF; the latter solvent has allowed us for the first time to definitively identify the $\mathrm{Se_3}^-$ radical anion.[49] Future studies include using ESMS to study chemically and electrochemically produced Zintl ions in solution and to control the products of those reactions by careful selection of solvent, reduction potential, and cation.[52−54]

Acknowledgment. Financial support was provided by the Research Corp., as a Cottrell Scholar, and by NSF Grant CHE-9625378. We also thank Mr. Jeremy R. Brown for his assistance in preparing Cs_2Se_5 and Prof. Dr. W. S. Sheldrick, Bochum, Germany, for helpful suggestions.

IC9613366

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