

Do Doubly Charged Monatomic Anions Exist in Aqueous Solutions?



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Introduction

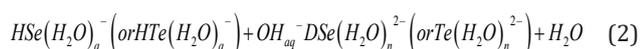
The chalcogenide atoms (X = oxygen, sulfur, selenium, tellurium, polonium) form doubly charged monatomic anions, X^{2-} , which exist in crystalline salts. The question arises whether, once such salts are dissolved in water, such species persist, or do they hydrolyze completely to form the hydrochalcogenide anion:



It is clear that in the case of oxygen this reaction proceeds to the right to completion: $O^{2-} + H_2O \rightarrow 2OH^-$. Recently it was shown that also in the case of sulfur the anion S^{2-} does not exist in aqueous solutions [1]. In attempts to push reaction (1) backwards by the addition of massive quantities (high concentrations) of hydroxyl ions, the necessarily added cations (say, Na^+) associate with the sulfide anion, yielding the ion pairs $(NaS(H_2O)_n)^-$, but not $S(H_2O)_n^{2-}$. On the other hand, spectroscopic evidence shows that the corresponding addition of $CsOH$ does not yield the hydrated sulfide dianions either. It was concluded that the doubly charged hydrated sulfide anions $S(H_2O)_n^{2-}$ do not exist.

It is therefore of interest to examine whether the reported evidence related to the existence of hydrated selenide $Se(H_2O)_n^{2-}$ and telluride $Te(H_2O)_n^{2-}$ anions in aqueous solutions can be re-interpreted in terms that negate their existence.

The evidence concerning the aqueous selenide and telluride dianions pertains to calculations of the second dissociation constant of hydrogen selenide and telluride or the dissociation constant of the aqueous hydroselenide and hydrotelluride anions, K_2 :

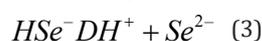


The existence of the dianions Se^{2-} and Te^{2-} in aqueous solutions was assumed a priori in earlier publications as a matter of course. In the polarographic study of the anodic oxidation of H_2X [2] it was stated that no experimental value of K_2 (for dissociation of HSe^- and HTe^-) was available, so a value was assumed (10^{-14} and 10^{-11} , respectively) in order to fit the half-wave potentials up to pH =

13.9 (1 M NaOH), but no fit was tried with the value $K_2 = 0$. For the telluride anion there was the added complication that the anodic oxidation resulted in the intermediate formation of elemental tellurium that yields the ditelluride anion Te_2^{2-} , which is then further oxidized. In fact, the polarography of the ditelluride dianion was studied in [3] in aqueous 0.01, 0.1 and 1.0 M NaOH (translated to pH = 12, 13, and 14) on the assumption that the disproportionation $Te_2^{2-} \rightleftharpoons DTe + Te^{2-}$ takes place, but, again, the nature of the reduced telluride species was not established. What was established was that the polarographic electrode reaction corresponded to a two electron change: $H_2Te \rightleftharpoons DTe + 2H^+ + 2e^-$.

In a subsequent examination of the $Se(-II)$ case [4], the change of pH of 0.2 M aqueous KOH on addition of H_2Se was interpreted as the formation of $HSe^- + Se^{2-}$, the latter constituting 8% of the total dissolved selenium. Conversion of pH values obtained with a glass electrode in mildly alkaline solutions to actual concentrations of the hydroxide anion is problematic, however, and avoidance of the assumption of Se^{2-} in solution could yield the same change in pH as that measured. The solubility of Na_2Se measured in [4] in aqueous NaOH solutions in the presence of high concentrations of Na^+ ions (4.31 M, but their source was not specified), was interpreted by inclusion of Se^{2-} species, but the formation of the $NaSe^-$ ion pairs was ignored. The complication of the formation of Se_2^{2-} by partial oxidation was mentioned in this study.

An ultraviolet spectroscopy (charge transfer to solvent spectra) study of the selenide species [5] again assumed the presence of the aqueous Se^{2-} anions in 0.12 to 11.6 M NaOH assigning to it and to HSe^- anions specific absorption maxima. The wavelengths of these depended, however, on the ionic strength of the solutions, and shifts had to be taken into account. The possibility that $NaSe^-$ ion pairs do occur but Se^{2-} species do not in the solutions was not taken into account. In a later paper [6] it was stated that the second dissociation step:



is completely shifted to the left at pH = 12.3, hence Se^{2-} does not play any role and fully reduced selenium appears only as the monoprotonated HSe^- . However, the polyselenidedianion Se_3^{2-} is a species that has to be taken into account.

The most recent study was that of the charge transfer to solvent ultraviolet spectra of telluride anions. The spectrum in 0.52M NaOH was assigned to the Te^{2-} species, whereas in a $\text{NH}_3/\text{NH}_4^+$ buffer at pH > 5 and ionic strength of 0.01 M the observed spectrum was assigned to HTe^- . However, the possibility that NaTe^- was formed in the 0.52 M NaOH solution and was responsible to the shift by the higher ionic strength of the NaOH solution in the direction of lower energies was not considered. Thus, there was no compelling reason to assign the spectrum in the NaOH solution to the dianion Te^{2-} species, and the assignment was due to the a priori assumption that such a species should exist in alkaline aqueous solutions [7]. Nothing appears to have been published regarding the polonium $\text{Po}(-\text{II})$ or polonide anion.

Conclusion

In conclusion, there is no compelling reason to interpret the experimental results concerning the chalcogenide $\text{X}(-\text{II})$ species as

ultimately forming the $\text{X}(\text{H}_2\text{O})_n^{2-}$ species by dissociation of the well-established $\text{HX}(\text{H}_2\text{O})_q^-$ in highly alkaline solutions.

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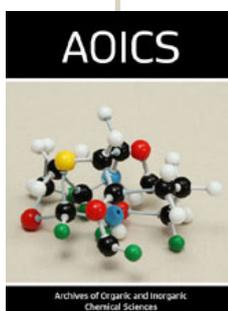
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