Cations of Tellurium in Disulphuric Acid

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Summary Tellurium dissolves readily in disulphuric acid to form red and yellow solutions: from u.v., magnetic susceptibility, conductance, and cryoscopic studies the red solutions are indicated as due to Te_4^{2+} ions while the yellow solutions are due to Te_2^{2+} ions.

SULPHUR,[1] selenium,[2] and tellurium[3] form blue, green and yellow, and yellow and red coloured solutions when dissolved in disulphuric acid. These fascinating colours have been attributed to the existence of the compounds S_2O_3, $SeSO_3$, and $TeSO_3$ respectively. However, it has been shown recently that in the case of selenium, the green and yellow solutions are due to the presence of unusual cations of the type Se_8^{2+} and Se_4^{2+} respectively.[4] Interest has also been shown in the homoatomic cations of some other elements in unusual oxidation states.[5–7] These cations have been stabilised either in highly acidic media[6,8] or in fused salts.[9,10] Though the unusual cations in the case of selenium are established, yet no attempt seems to have been made to characterise the coloured solutions in the case of tellurium. In this communication, unusual cations of tellurium which may be responsible for the colours in disulphuric acid are postulated.

Tellurium readily dissolves in disulphuric acid to form red solutions. Similar coloured solutions are also obtained in sulphuric acid but only at 60°. The dissolution of the element is accompanied by the evolution of SO_2, suggesting a redox reaction. When these solutions are left over for a few days (depending upon the concentration of the metal), they become yellow and finally colourless in about two weeks. The colourless solutions change back to red through yellow on the addition of hydrazine sulphate. When these coloured solutions are poured on to crushed ice, elemental tellurium separates out quantitatively. This implies that the coloured tellurium species are positive oxidation states, that the yellow species is in a higher oxidation state than the red, and that the colourless solutions may be of tellurium(IV).

The absorption spectra of tellurium in disulphuric acid under different conditions show clearly the existence of two distinct species. These species appear to be quite stable as they obey the Beer–Lambert Law. The red solution (Spectrum A) has an intense absorption band at 520 nm and a weak shoulder at 440 nm (*cf.* ref. 11), while the yellow solutions (Spectrum B) have three absorption bands at 280, 380, and 480 nm. A similar spectrum for tellurium Te_4^{2+} ions has been reported in Te–$TeCl_4$ melts.[10] The intensity of the 520 nm peak decreases with time and after two weeks completely disappears; new peaks appear at 480, 380, and 280 nm. On adding a small amount of hydrazine sulphate the peaks at 480, 380, and 280 nm disappear and the peaks at 520 and 440 nm again appear. Spectrum A may be attributed to Te_4^{2+} ions but spectrum B could be attributed to any of the ions and, therefore, further information has been obtained from cryoscopic, conductance, and magnetic susceptibility measurements.

Possible effects of further oxidation of the red solution were eliminated by extrapolation of results recorded over several hours to zero time. For the yellow solutions, sufficient time was given so that the solutions were completely free of the 520 nm peak. As pointed out earlier,[12] it is not possible to calculate the value of γ, (the number of $HS_3O_{10}^-$) or that of ν, (the number of the particles or ions produced per mole of the solute) in the same straightforward manner as for sulphuric and fluorosulphuric acids mainly because of the extensive self-dissociation of the solvent.[13] The mode of the ionisation of the solutes is best established by comparison of the observed freezing point and conductance curves with "theoretical curves" constructed from the results obtained with certain reference solutes. The general equation may be represented as:

$$\text{Solute} + Z\mathrm{H_2S_2O_7} \rightarrow a\mathrm{X^+} + a\mathrm{HS_3O_{10}^-} + b\mathrm{Y} + c\mathrm{H_2SO_4}$$

The value of c (moles of sulphuric acid produced) can be found by titrating against sulphur trioxide cryoscopically.[14] The good agreement between the observed and calculated curves clearly establishes that the overall reaction, to produce the red solution, may be represented as:

$$4\mathrm{Te} + 6\mathrm{H_2S_2O_7} \rightarrow \mathrm{Te_4^{2+}} + 2\mathrm{HS_3O_{10}^-} + 5\mathrm{H_2SO_4} + \mathrm{SO_2}$$

Sulphur dioxide is very soluble in disulphuric acid and behaves as a nonelectrolyte.

The amount of sulphuric acid formed in the reaction was determined by cryoscopic titration with SO_3. The freezing point rises, passes through a maximum, and then decreases on the addition of SO_3. The titration exhibits a maximum in the freezing point at the molar ratio $SO_3 : Te = 1{\cdot}30$ (expected value for above equation $5/4 = 1{\cdot}25$). The somewhat high experimental value may be explained by partial further oxidation which involves the formation of more H_2SO_4 per gram atom of Te.

Comparison of the freezing points and conductivities of the yellow solutions with the theoretical curves suggests that the overall reaction in this case may be represented by the equation:

$$2\mathrm{Te} + 6\mathrm{H_2S_2O_7} \rightarrow \mathrm{Te_2^{2+}} + 2\mathrm{HS_3O_{10}^-} + 5\mathrm{H_2SO_4} + \mathrm{SO_2}$$

The amount of sulphuric acid formed was determined by cryoscopic titration with SO_3; the end point occurs at 2·5 which is in agreement with the theoretical value. The yellow coloured species may, therefore, be Te_2^{2+}.

The existence of cations of the type Te_6^{5+}, Te_6^{3+}, Te_6^{+}, Te_3^{5+}, Te_4^{5+}, and Te^{+} *etc.* with odd electrons has been ruled out because both the red and yellow coloured solutions are diamagnetic. Similar types of cations are already known in the case of selenium,[4] antimony,[7] and bismuth.[9] Such cations having lower oxidation states of elements are strongly electrophilic and are stable only in weakly nucleophilic or in highly acidic solvents.

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