

Behaviour of Boron Trichloride & Tribromide, Boric Anhydride & Boric Acid in Disulphuric Acid

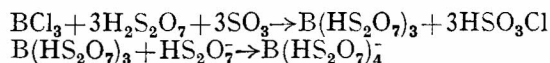
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Boron trichloride, boron tribromide, boric anhydride and boric acid form condensed structures having bridging sulphate groups with the overall composition, $H[B(HSO_4)_4]$ when dissolved in disulphuric acid. Acid-base titrations have been carried out to show that $H[B(HSO_4)_4]$ is a strong acid of the system. Cryoscopic studies show that at higher concentrations $H[B(HSO_4)_4]$ polymerises to form condensed borate rings through B-O-B linkage.

CRYOSCOPIC and conductometric measurements on dilute solutions of boric acid and boric anhydride in 100% sulphuric acid and dilute oleum have been interpreted in terms of the formation of tetrahydrogensulphato boric acid^{1,2} which has been found to be fairly strong acid of the solvo system sulphuric acid³. Arotsky and Symons⁴ studied the behaviour of boron salts in 65% oleum and suggested the reactions:



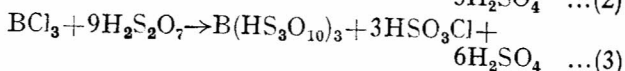
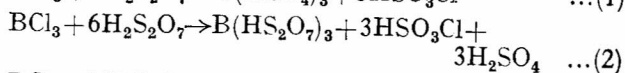
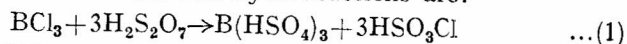
As it has been established by Gillespie and co-workers^{5,6} and also by Paul and coworkers⁷⁻¹⁰ that most labile anion in disulphuric acid is HS_3O_{10} rather than $HS_2O_7^-$, it was, therefore, of interest to investigate the behaviour of boron compounds, viz. boron trichloride and tribromide, boric anhydride and boric acid in disulphuric acid. Presently we have carried out conductometric and cryoscopic studies of some boron compounds in disulphuric acid to explore the possibility of formation of the solvo acid of this solvent.

Materials and Methods

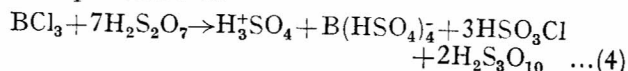
The design of the conductance cell and the cryoscopic set up, the method to obtain parameters γ , ν and c have been discussed earlier^{5,7,11}. The solvent of stoichiometric composition was prepared using indicators, its freezing point in cryoscopic experiments and its specific conductance in conductometric experiments. Boric acid and boric anhydride were BDH (AR) reagents and were used as such. A slow stream of boron trichloride was passed through a weighed amount of disulphuric acid for 2 hr and then weighed. The difference in the weight gave the amount of boron trichloride dissolved in known weight of disulphuric acid. A known weight of this solution was then added to the solvent for conductance and cryoscopic studies.

Results and Discussion

Boron trichloride is highly soluble, to the extent of 15%, in disulphuric acid and solutions up to this concentration range could be easily prepared without any precipitation. At low concentration of the solute, the values of γ and ν are low but increase rapidly at higher concentrations. From the values, it is evident that boron trichloride undergoes solvolytic reaction in it. Various possible modes of the solvolytic reactions are:

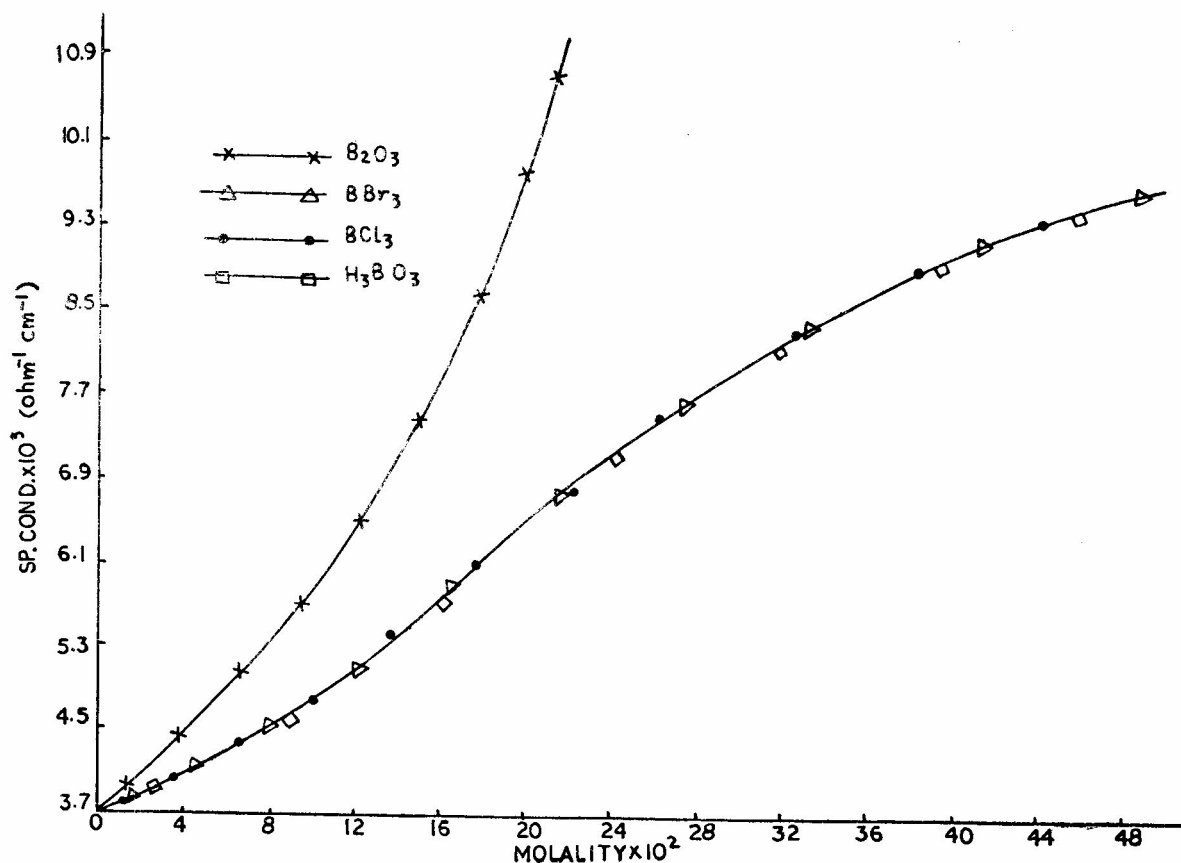


As the solutions are fairly conducting, the solvolytic reaction cannot be represented by any of the above equations. When potassium hydrogensulphate (a strong base) is added to the above solution, there is a decrease in the conductance of the solution suggesting that the solvolysed product behaves as an acid of the system. Possible reaction involving the formation of $H_3^+SO_4$ ions in the solution may be represented as



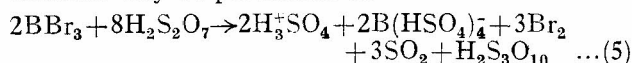
A lower value of ν in dilute solutions is due to the fact that trisulphuric acid formed is one of the products of molecular self-dissociation of the solvent and does not contribute to ν value of one. At higher concentrations, a lower value of ν than expected from Eq. (4) is due to polymerization of $B(HSO_4)_4^-$ to form long chain molecules. The tendency of $B(HSO_4)_4^-$ to polymerize has already been reported by Gillespie and coworkers¹². Cryoscopic titrations against sulphur trioxide rule out the formation of any sulphuric acid in this solvolytic reaction; rather titrations against sulphuric acid show the presence of two moles of sulphur trioxide ($H_2S_3O_{10}$) per mole of boron trichloride providing support to the reaction represented by Eq. (4). The present cryoscopic studies do not support the presence of

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Fig. 1 — Specific conductance of some boron compounds in H₂S₂O₇ at 25°

the ions of the type H₃⁺S₂O₇ or H₃⁺S₃O₁₀ or B(HS₂O₇)₄⁻ or B(HS₃O₁₀)₄⁻, etc., as these species would have produced different number of particles. The conductometric and cryoscopic data are graphically presented in Figs. 1 and 2.

In the case of boron tribromide, bromine is evolved in the conductance cell and the conductivity set up. Unlike hydrochloric acid, hydrobromic acid produced as a result of solvolysis is oxidized to bromine. From the values of ν , ν and c , the possible solvolytic reaction may be postulated as:

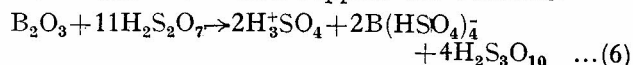


Both sulphur dioxide and bromine are known to behave as non-electrolytes in disulphuric acid and, therefore, contribute a value of one to the ν factor. UV spectrum of the solution shows an absorption band at 290 nm confirming the presence of sulphur dioxide¹⁴ in the solution, thereby supporting the above reaction.

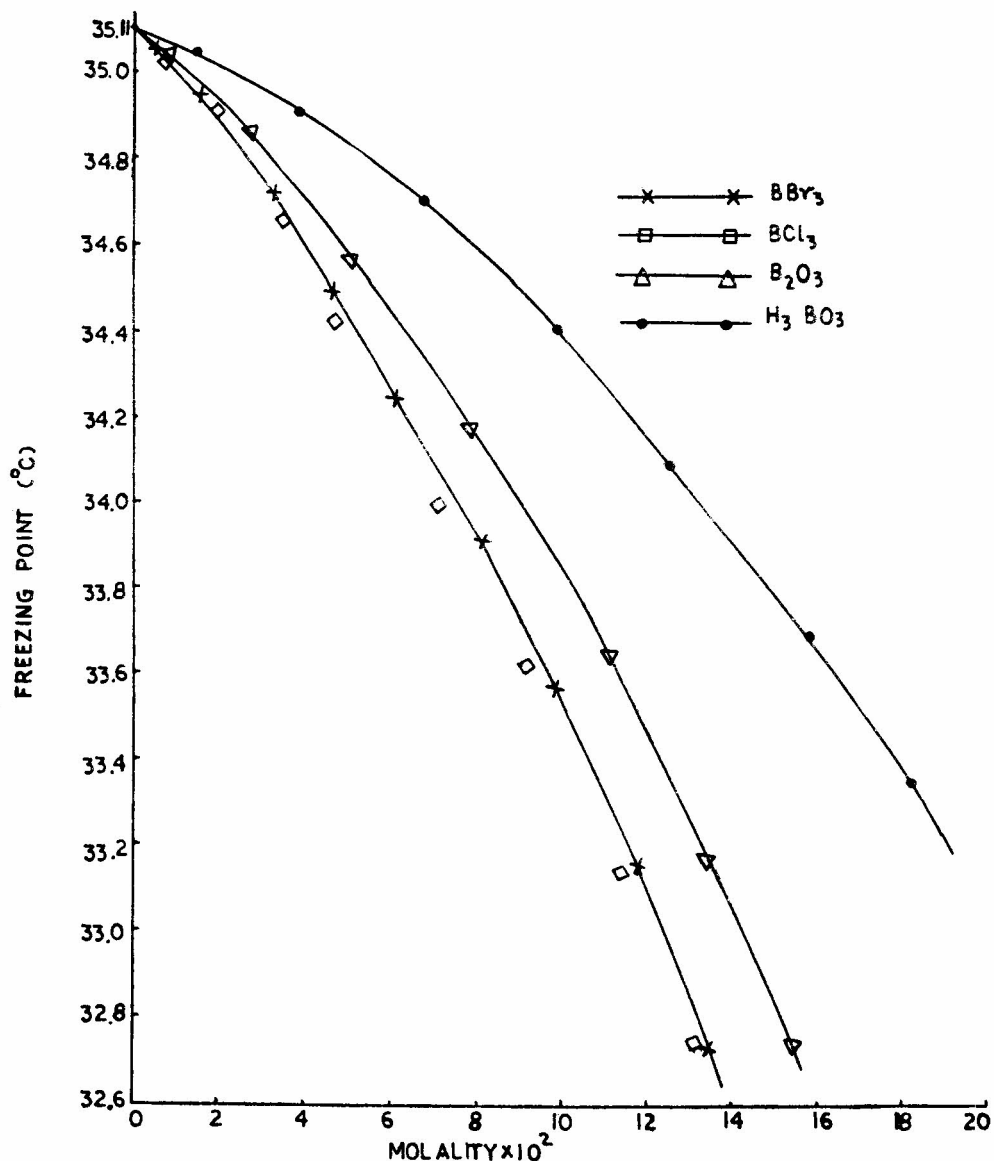
Conductometric titrations between boron trichloride solutions and some bases have been carried out to ascertain whether these solutions are acidic in nature or not. A decrease in the conductance of the solution on the addition of a base is due to the removal of H₃⁺SO₄ ions from the solution as H₃⁺SO₄ + HS₃O₁₀⁻ → 2H₂S₂O₇. The conductance-molar ratio curves pass through a minima (sharp) which occurs at base/acid molar ratio of 1:1 suggesting that tetrahydrogensulphatoboron behaves as a strong acid of the system. The conductance

of the solution at the maximum has the same value as that of the pure solvent. It suggests that the ions non-specific to the autoionization of the solvent contribute very little to the conductance of the solution. This seems reasonable as the process of diffusion is quite negligible in a solvent of high viscosity.

Boric anhydride dissolves very slowly in disulphuric acid. Its solubility increases at higher temperature and the solutions up to 0.5 molal concentration can be prepared but the conductance of the solution does not change much. At low concentration, the value of ν is only 3.1 but increases considerably at higher concentration. Cryoscopic and conductance data support the reaction:



The existence of the species B(HS₂O₇)₄⁻ or B(HS₃O₁₀)₄⁻ does not seem to be possible as the acid H[B(HSO₄)₄]⁻ formed is far stronger than H₂S₃O₁₀ or H₂S₂O₇ and, therefore, would not be solvolyzed. The slope of the conductance curve for B₂O₃ is concave in the low concentration range which shows that because of the extensive self-dissociation and ionization of the solvent the formation of H₃⁺SO₄ is sufficiently suppressed. Here again the tendency of B(HSO₄)₄⁻ to polymerize at higher concentration is quite evident as at low concentration the value of ν is 3.2, and at 0.2 molal concentration the value of ν is 5.8. After that the value of ν starts decreasing. Cryoscopic and conductometric data are graphically

Fig. 2 — Freezing points of some boron compounds in H₂S₂O₇

presented in Figs. 1 and 2 respectively. Similarly, boric acid undergoes solvolytic reaction in disulphuric acid. From the value of γ , ν and c , the possible solvolytic reaction may be represented as $B(OH)_3 + 3H_2O_2S_7 \rightarrow H_3^+SO_4 + B(HSO_4)_4 + H_2SO_4 \dots$ (7) Conductometric acid-base titrations against nitromethane, potassium hydrogen sulphate, etc., have been carried out to ascertain its acidic character. The trends of these titrations are the same as has been discussed in the case of boron trichloride solutions.

It is observed that for all these solutes, the value of ν decreases at higher concentrations of the solute. Possibly the tetrahydrogensulphate boron anion polymerizes to give condensed structures having bridging sulphate groups. These structures may be similar to the structures of hydrated polyborates wherein the basic structure is a six-membered ring wherein one or at the most two of the boron atoms have a tetrahedral four coordinated configuration

while the remainder have a trigonal three coordinated configuration^{15,16}. It is also possible that there may be more than one type of the condensed polymers present in the solution with the overall composition $H[B(HSO_4)_4]$.

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