

Stannate (IV) and Antimonate (V) Hexahydroxy-anion complexes with Di- and Polyhydric Phenols

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Abstract

An identification has been achieved of only 1:1 and 1:2 chelates of hexahydroxystannate (IV) anions with ortho (i.e., 1,2)-diphenols, using potentiometric and conductimetric techniques. Lack of evidence for organo-richer complexes in aqueous media is in contrast to antimonite (V) hexahydroxy anions and tellurate (VI), which are each able to form a tris (catecholate).

Key words: Stannate (IV), Antimonate (V), Tellurate (VI), Diphenols, Complex-formation

Introduction

The reactions in aqueous solution of hexahydroxystannate (IV) $[\text{Sn}(\text{OH})_6]^{2-}$, hexahydroxy antimonate (V) $[\text{Sb}(\text{OH})_6]^-$ and telluric (VI) acid $[\text{Te}(\text{OH})_6]$, three isostructural and isoelectronic inorganic species, with a wide selection of organic polyhydroxy ligands (hereinafter referred to as polyols), have been reported^{1,2}. Quantitative data arising from extensive equilibrium and kinetic studies on the Sn (IV) system³ have enabled the postulation of a mechanism involving the species $\text{Sn}(\text{OH})_5^-$ for the formation of the stannate (IV)-polyol chelates. As recently as in 2007, a report emerged⁴ regarding a fresh patent in the United States in connection with the invention of a new biologically active complex. The successful invention, which quotes as having hinged among others on earlier published work on sugar complexes of Te (VI) hydroxyanions² carried out in these laboratories, relates to a chelate of tellurium (IV) oxide with saturated organic polyhydroxy compounds (polyols). This has been successfully used to stimulate living cells to produce cytokines and for treating mammalian diseases and conditions responsive to increased production of cytokines. The complex may also be used for treating mammalian cancer which is not responsive to increased production of cytokines⁴. The present study reports an extension of this work

to fill in the gaps left by the hitherto unreported similar reactions of Sb (V) and Sn (IV) hydroxyanions with polyhydric phenolic ligands. This is done in the hope that, as in the present case, it is often the basic research of today that may be the badly needed applied science of tomorrow.

A host of organic polyhydroxy compounds do exist, and in order to systematically study their reactions with the oxyanions in point it is logical to categorise them into groups, preferably in order of increasing molecular complexity. A convenient starting point in this direction was to investigate the reactions of the oxyanions with the relatively simple diphenolic compounds. These compounds, unlike the equally structurally simple 1,2-ethanediol, have a fixed conformation of the OH groups about the parent C-C carbons in the benzene ring, and as such their behaviour may be used as a basis for the study of the reactions of structurally more complex polyols such as sugars and sugar alcohols. Such was the case when these investigations were some time ago initiated on telluric (VI) acid, the results of which are the subject⁵, and also part⁶, of an earlier study. It is therefore now known that tellurate (VI) anions and the parent telluric acid in the presence of sufficient amounts of the diphenols may complex with up to three molecules of catechol (1,2-dihydroxybenzene)⁵. We now report on the reactions

of Sn (IV) and Sb (V) oxyanions with similar compounds.

In the light, therefore, that chelate formation between weak inorganic oxyacids and their anions with organic polyhydroxy ligands continues to be a subject of research interest⁷⁻¹¹, the investigation on the three isostructural and isoelectronic inorganic species is extended to cover the interaction of stannate (IV) and antimonite (V) hexahydroxyanions with di- and polyhydric phenols. The results are herein presented and discussed. The behaviour in the presence of phenolic compounds of oxyacid anions such as germanate, molybdate¹², tungstate¹³, borate¹⁴, to mention but a few, has over the years aroused considerable interest. The reactions of antimonic acid, HSb (OH)₆, with catechol (1,2-dihydroxybenzene) is referred to in the literature¹⁵, and previous workers have mentioned¹⁶ the probable formation of up to a 1:3 Sb-catecholate.

Notwithstanding, the behaviour of hexahydroxystannate (IV) with similar compounds has up to now not receive the same degree of attention: the information available on the subject is rather sketchy¹⁷. The object of the present investigation is to clarify its position in the light of parallel systematic studies on tellurate⁵ and antimonate (this work).

Materials and Methods

Potassium antimonate (KSb(OH)₆, supplied by BDH, UK) and sodium stannate (Na₂Sn(OH)₆, supplied by Hopkin and Williams, UK), both of reagent-grade purity, were used as received. Stock solutions of potassium antimonate were prepared by a published method¹⁸. The pH of the solutions of both salts was raised using solid KOH¹⁹. To lower the pH, potassium antimonate solutions were acidified with dilute HCl. Test solutions were prepared by adding various quantities of the solid phenol to a suitable constant volume of the stock inorganic solution (0.010 M), so as to obtain a series of oxyanion-phenol mixtures with mole ratios in the range 0.10 - 3.00. The tightly stoppered solutions were then left at 25°C to equilibrate, the pH and conductance being measured at various intervals of

time. These data, obtained at constant oxyanion concentrations, were subsequently plotted against the oxyanion/diphenol mole ratio according to the method of Yoe and Jones²⁰, otherwise referred to as the mole ratio method. In this technique, a series of solutions is prepared in which the concentration of one reactant is held constant while that of the other is varied. One parameter, e.g., electrolytic conductance, pH, absorbance etc. of each solution is measured and plotted against the mole ratio of the reactants. Assuming the complex conducts or absorbs more than the reactants, this plot will produce an increasing absorbance up to the combining or stoichiometric ratio. At this point, further addition of reactant will produce less increase in conductance, pH or absorbance. Thus a break in the slope of the curve occurs at the mole ratio corresponding to the stoichiometry of the complex.

In this study, all masses were measured to within ± 0.0001 g using an Oertling analytical balance. A Wayne-Kerr Universal Bridge B224 (UK), and a Mullard conductivity dip cell of type E7591/B (UK) with a cell constant = 1.37 cm^{-1} , were used for electrolytic conductance measurements. Potentiometric measurements were made on a Corning Model 12 Research pH meter (UK), connected to a combined glass electrode. Most of the organic compounds used were each of reagent-grade purity or better; those that were not, such as technical grade catechol, were recrystallised several times from a suitable solvent, e.g., benzene, until their melting points were within one degree of the literature values. All the runs were performed in a carbondioxide-free atmosphere using a glove-box previously flushed with nitrogen.

Results and Discussion

Hexahydroxyantimonate (V) anions: The addition of sufficient amounts of catechol (1,2-dihydroxybenzene) lowered the conductance and pH of aqueous potassium antimonite (V) solutions. A plot of the measurements, obtained after various lengths of time up to seven days in some cases, against the antimonate/catechol mole ratio revealed clear evidence for the stepwise formation of 1:1, 1:2 and 1:3 antimony (V)-diphenol chelates (figure 1).

The corresponding pH data varied in the same fashion, with discontinuities at similar mole ratios (Figure 2). It should be noted, however, that the solutions did not have the same final pH, in much the same way as they did not have the same final electrolytic conductance (*cf.* Figure 1). The decrease in pH of each solution depended on the amount of diphenol initially added (*cf.* Figure 2). In order for them to have the same final pH would require that they be buffered, which would not only obscure the vital or useful pH changes, but also create the undesirable possibility of the antimonate or stannate anions being masked by some of the buffer ions. Also, aqueous stannate (IV) solutions are particularly sensitive to electrolyte. The curve in Figure 2c is in contrast to that in Figure 1c. This however does not imply that no complex was present, or that it was of indefinite composition, but rather that its composition was not indicated by this indirect method of determining it.

Of notable significance was the sluggish time-dependence of the formation of the Sb (V)-tris (catecholate) in the neutral pH range, which was substantially reduced at higher pH values. This is presumably attributable to increased complex stability^{1, 2}, rather than a kinetic factor, especially as there are indications from this and other studies²¹ that this reaction may be acid-catalysed. Thus at initial pH 12 only 1:1 and 1:3 chelates were indicated in the solutions within only 18 hours of mixing (Figure 3). The ability of the potentiometric method to indicate a 1:1 chelate in the presence of a 1:3 complex in the solutions after 40 hours of standing (Figure 4) whereas conductance measurements indicate only a 1:3 complex (Figure 3b) shows the importance of using complementary analytical techniques in such investigations. The absence of the 1:2 chelate at high pH and its presence as a transient species at lower pH (*cf.* Figure 1b) was indicative of its intermediary role.

The acidity of antimonate solutions initially at pH 4 increased markedly in the presence of the diphenols (Figure 5), with evidence for only 1:2 chelates at equilibrium. Beyond the 1:2 Sb-diphenol stoichiometric points, further addition of catechol

had little effect on the conductivity of the solutions. This suggested that no more antimonate was being complexed, and any excess diphenols only slightly raised the pH but little altered the conductivity, presumably as in this pH range its weak ionisation was expected to be highly suppressed. It is thought that the absence of the tris (catecholate) at this pH is due to its low stability in acidic media.

It is noteworthy that at initial antimonate pH 7.45 only a 1:1 chelate was indicated within 12 hours, while the 1:2 analogue appeared in detectable amounts after 24 hours. At initial pH 4, however, the 1:2 chelate could be detected after only 12 hours. It appears therefore that in this range of pH complexation proceeded more rapidly, probably indicating the significance of possible acid-catalysis²¹. In each case complex stability was sufficient to prevent opalescence in acidified potassium antimonate solutions (0.010 M) which otherwise appeared in a day or two at pH 4.

Similar results were obtained with other 1,2-diphenolic group-containing compounds, namely: 3,4-dihydroxytoluene; 3,4,5-trihydroxybenzoic acid (gallic acid); 1,2,3-trihydroxybenzene (pyrogallol); 1,2-dihydroxybenzene-3,5-disulphonic acid (tiron), and 1,2,3-trihydroxybenzene (hydroxylhydroquinone). At acidic pH, complexation was observed to proceed more rapidly, probably indicative of acid-catalysis. The behaviour of 1,3- and 1,4-diphenols showed a sharp contrast to that of their 1,2-counterparts. The presence of 3,5-dihydroxytoluene, 1,3-di-, 1,4-di-, and 1,3,5-trihydroxybenzene (orcinol, resorcinol, hydroquinone, and phloroglucinol, respectively) raised, rather than lowered, the pH of acidified aqueous potassium antimonite (V) solutions – an unambiguous indication of weak or no complexation. In such solutions turbidity due to polyantimonates and precipitation of insoluble antimonates of heavy metal cations (e.g., Hg²⁺ and Pb²⁺) soon occurred, in contrast to the (ortho-diphenol)-antimonate systems in which such reactions were absent, indicating that most of the oxyanions were firmly bound to the organic ligands and so were not available for aggregation or precipitation to occur. It seems therefore that there is

no apparent reaction between these compounds and the antimonate anion, in agreement with an earlier observation with phloroglucinol²².

Job's method²³ using conductance and pH did not yield reliable confirmatory evidence for complex-formation at any pH with any of the diphenols. Plots of the conductance data so obtained against the mole fraction of the diphenols were in most cases linear with gentle negative slope. In this method, also known as the method of continuous variations, metal cation M and ligand L solutions with identical concentrations are mixed in different amounts such that the total volume of the mixture solutions and the total moles of reactants in each mixture are constant. This procedure causes the mole ratio of reactants to be varied across the set of mixture solutions. The electrolytic conductance, pH or absorbance of each solution is then measured and plotted against the mole fraction of one of the reactants (M or L). Assuming the complex conducts or absorbs more than the reactants, a maximum occurs at a volume ratio V_M/V_L corresponding to the combining ratio of cation and ligand in the complex. At other volume ratios, one of the reactants is a limiting reagent.

Hexahydroxystannate (IV) anions: The pH (figure 6) and conductance (figure 7) of aqueous sodium stannate (IV) solutions decreased in a fashion which indicated the formation of 1:1 and 1:2 tin (IV)-catecholates, the higher chelate being the only detectable species at pH 13. In each case the 1:1 chelate was detectable in the solutions within 12 hours at initial pH 11.7 (the natural pH of 0.010 M aqueous solutions of sodium stannate), whereas the higher chelate appeared after a further 12 hours had elapsed. These results are consistent with the view that the 1:1 complex is initially formed, but the 1:2 chelate is obtained as more diphenol is added and the mixture allowed to stand. It therefore seems reasonable to suggest that oxyanion-diphenol complexation occurs in a stepwise manner, the 1:1 and 1:2 chelates being in equilibrium with each other, and consequently detection of the higher chelate depending on both the extent and rate of attainment of this equilibrium. Similar results were obtained with each of the ortho-diphenols mentioned

earlier (this section). That in no instance was evidence for a 1:3 Sn (IV) chelate obtained should not be overemphasized. There was simply no evidence for a 1:3 tin (IV)-chelate.

Sodium stannate solutions by themselves (pH 11.7, 0.010 M) are unstable, going opalescent within 10-15 minutes of standing, due to the formation of a colloidal modification of stannic acid, but *freshly* prepared solutions are usable. Stability is however significantly increased by higher pH and the presence of sufficient amounts of ortho-diphenols, but decreased even more by para- and meta-analogues. Immediate turbidity is also observed on the slightest addition of dilute acid. With 1:3-and 1:4-diphenols complexation of a lesser significance was therefore apparent.

General: Telluric (VI) acid⁵ forms a 1:3 Te(VI)-catecholate even at its mildly acidic natural pH (4.8, 0.010 M), but as we have seen a similar 1:3 Sb (V) chelate may not be detectable in the solutions at the same initial oxyanion concentration unless neutral or higher pH are used. With stannate anions only 1:2 such chelates are indicated even at extreme alkaline conditions. In view of the observed pH dependence of the complex stabilities and the increasing pH required for organo-richer complexes to be formed in detectable amounts, the relative stability of the chelates appear to be in the order: Te > Sb > Sn. As a result, it is presumed that the lower stability of the stannate complexes is insufficient for the $\text{Sn}(\text{OH})_6^{2-}$ anion to accommodate three catechols in aqueous solution, a feature otherwise clearly exhibited in these studies by tellurate⁵ and antimonate (this work).

The foregoing results are consistent with structural considerations. Tin, antimony and tellurium are three consecutive members of the same period in the periodic table. Calculations based on the Te-OH bond distance in $\text{Te}(\text{OH})_6$ octahedra give an average value of 0.271 nm for the O-O distance between neighboring oxygen atoms in telluric acid in the solid state²⁴ and 0.274 nm in aqueous solution²⁵. The corresponding distance in $\text{Sb}(\text{OH})_6^-$ is quoted as 0.280 nm²⁶ in the solid state and like that in

$\text{Te}(\text{OH})_6$, is expected to be slightly longer in aqueous solution due to H-bonding²⁵. In view of these bond distances, it therefore still remains that in aqueous solution the O-O separation in the hexahydroxyantimonate anion is undoubtedly larger than that in telluric acid. The O-O distance in $\text{Sn}(\text{OH})_6^{2-}$ is, on the basis of periodicity, expected to be longer than that in $\text{Sb}(\text{OH})_6^-$ by about 0.01 nm. This is consistent with the predicted value of 0.288 nm using the Shannon and Prewitt ionic radii of 0.069 and 0.135 nm for the Sn^{4+} and O^{2-} ions, respectively, which gives a value of 0.204 nm for the Sn (IV)-O ionic bond. The value of 0.290 nm calculated using the average length of the Sn-O bond²⁷ of 0.206 nm in crystalline $\text{CaSn}(\text{OH},\text{OD})_6$ is also in unison. Thus the O-O distances in $\text{Te}(\text{OH})_6$, $\text{Sb}(\text{OH})_6^-$ and $\text{Sn}(\text{OH})_6^{2-}$, three isostructural and isoelectronic species are respectively 0.271, 0.280 and 0.29(0) nm in the solid state, but become slightly longer in aqueous solution due to hydrogen bonding¹. The O-O distance between neighboring oxygen atoms is quoted as 0.260 nm in catechol¹³. These values show that the O-O separations are sufficiently close for the oxygen atoms of an *ortho*-diphenol to fit into the MO_6 (M = Te, Sb, Sn) octahedra to form a five-membered (presumably planar) ring chelate via two M-O-C links (figure 8). None the less, owing to the increasing difference in the O-O distances of the ligand and the oxyanion it is reasonable to expect that the instability-creating strain in the ring chelates will be in the increasing order: $\text{Te} < \text{Sb} < \text{Sn}$, which is consistent with the observed reverse order (mentioned earlier) for the relative stabilities of the catecholates. Lack of evidence in favour of chelates with other phenolic compounds is in agreement with the O-O separations in 1,3- and 1,4-diphenols being too large (0.490 nm in 1,3-dihydroxybenzene, resorcinol) for complexation to occur by the usual bidentate mechanism.

Attempted extraction of the complexes: Numerous attempts to extract some of these chelates into the solid state were made. It was anticipated that a large complex aggregate such as the $[\text{antimonate}(\text{catechol})_3]^-$ anion could be induced to precipitate out of solution as its sodium (or indeed some other

cation) salt. A 1:3 antimonate-catechol mixture (0.010 M in antimonate) was kept at pH 11 for periods of up to three months at room temperature, and at 0°C, but in both cases there was little precipitation. At higher Sb(V) concentrations there was slow deposition of polyantimonates. Attempts to induce precipitation by dropwise addition of ammonia or a solution containing a heavy metal cation such as Pb^{2+} or Ba^{2+} , yielded no positive result. Since both catechol and potassium antimonate are only slightly soluble in ethanol, it was expected that the 1:1 complex would probably be even more insoluble. Addition of small quantities of ethanol to the aqueous mixtures and keeping them at 0°C overnight precipitated only antimonate. Perhaps, therefore, these may be presenting themselves as yet other known cases of complex stability only in aqueous solution, e.g., the long established polyolborates so useful in the determination of the extremely weak boric acid by direct alkalimetric titration²⁸ have never been isolated; neither have the intensely coloured catechol-molybdate complex¹² nor the equally intense Fe(III)-1,2-dihydroxybenzene-3,5-disulphonate²⁰.

Conclusion

Complex-formation between dihydroxybenzenes and the hexahydroxy anions of tin (IV), $\text{Sn}(\text{OH})_6^{2-}$, and antimonite (V), $\text{Sb}(\text{OH})_6^-$, occurs only in aqueous solution. The stability of the chelates is enhanced by high pH. There is evidence that these oxy-species may bind more than one diphenol per anion.

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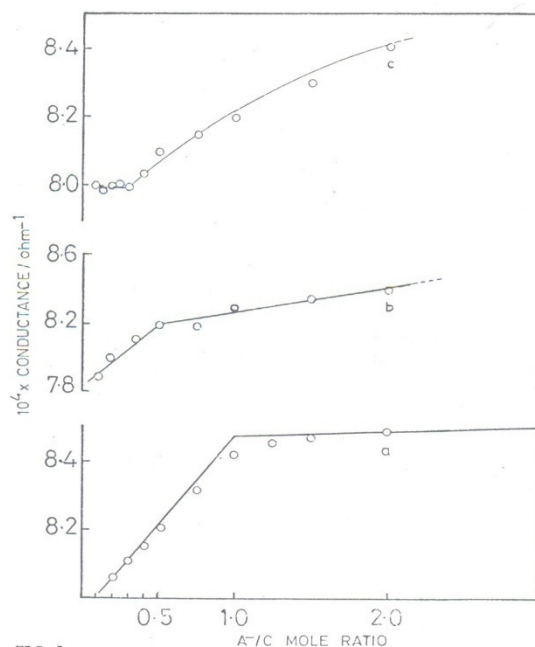


Figure-1: Effect of catechol (C) and time on the conductance of 0.010M potassium antimonate (A), initially at its natural pH (7.45), after (a) 12 hours, (b) 36 hours, (c) 5 days or longer of standing, at 298K.

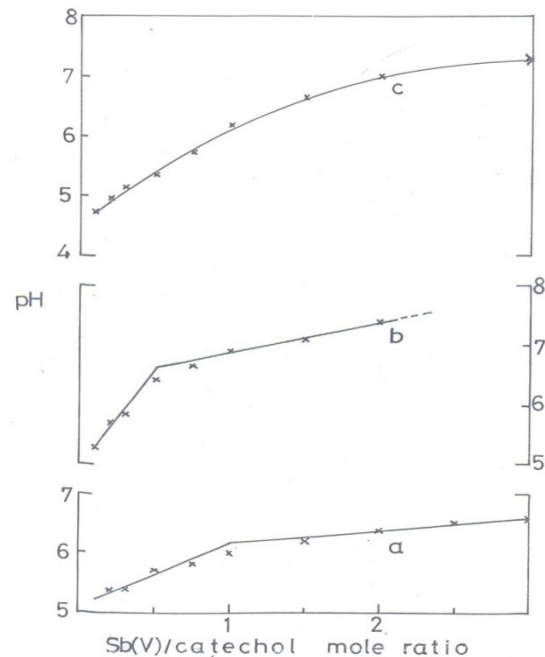


Figure-2: Effect of catechol and time on the pH of potassium antimonate (0.010M) initially at its natural pH (7.45), after (a) 12 hours, (b) 36 hours, (c) 5 days or longer, at 298K.

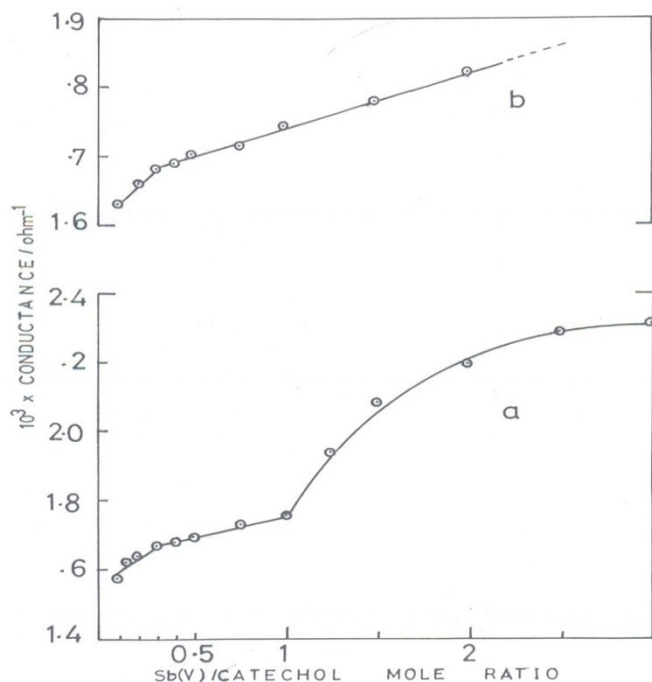


Figure-3: Conductances of potassium antimonate (0.010M) initially at pH 12.0 in the presence of catechol after (a) 18 hours, (b) 40 hours or longer, at 298K.

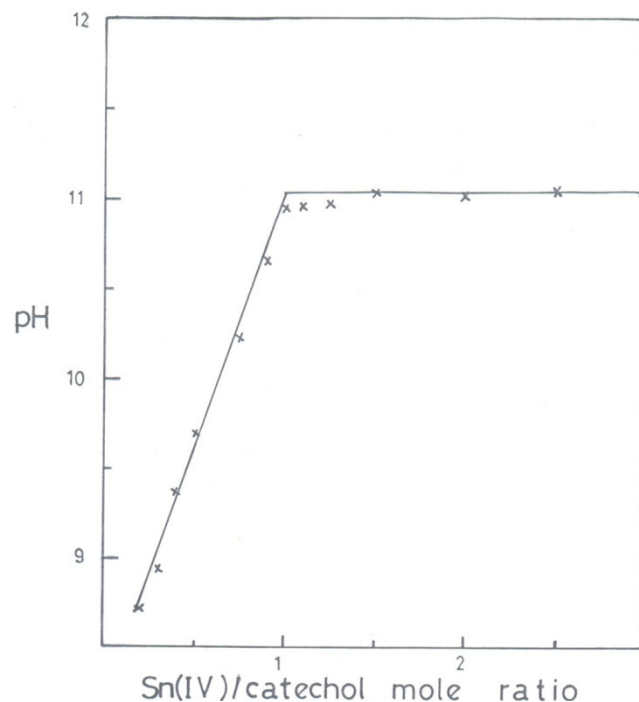


Figure-5: Final conductance and pH values, after 12 hours or longer, of 0.010M potassium antimonate initially at pH 4.0, to which various quantities of catechol have been added, at 298K.

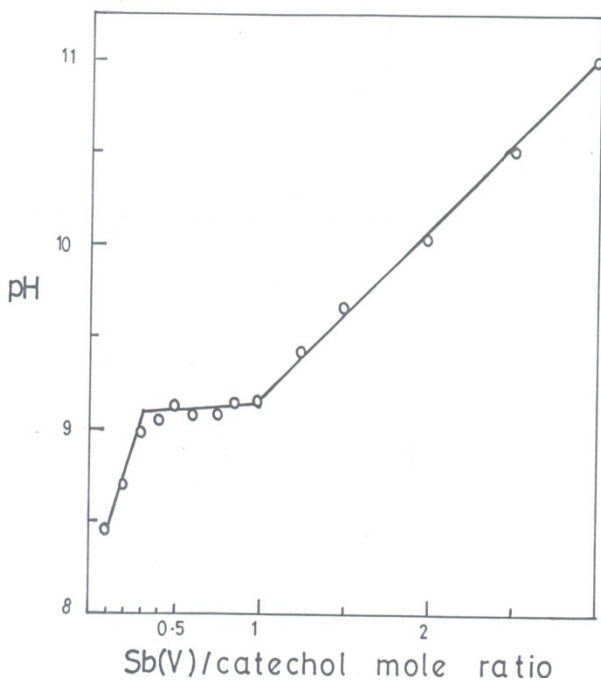


Figure-4: Values of pH of potassium antimonate (0.010M) initially at pH 12.0 in the presence of catechol, after standing for 40 hours or longer, at 298K.

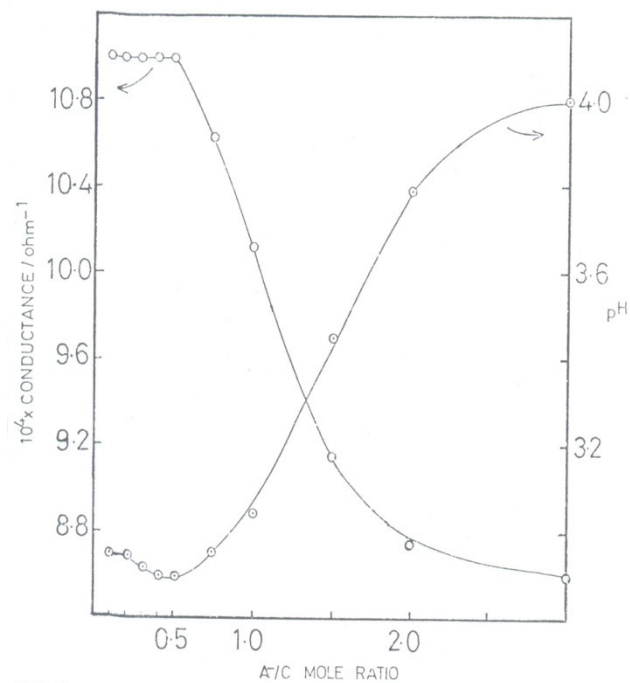


Figure-6: Final pH values of sodium stannate-catechol aqueous solutions initially at pH 11.7, after 24 hours or longer, at 298K. ([stannate]₀ = 0.010M)

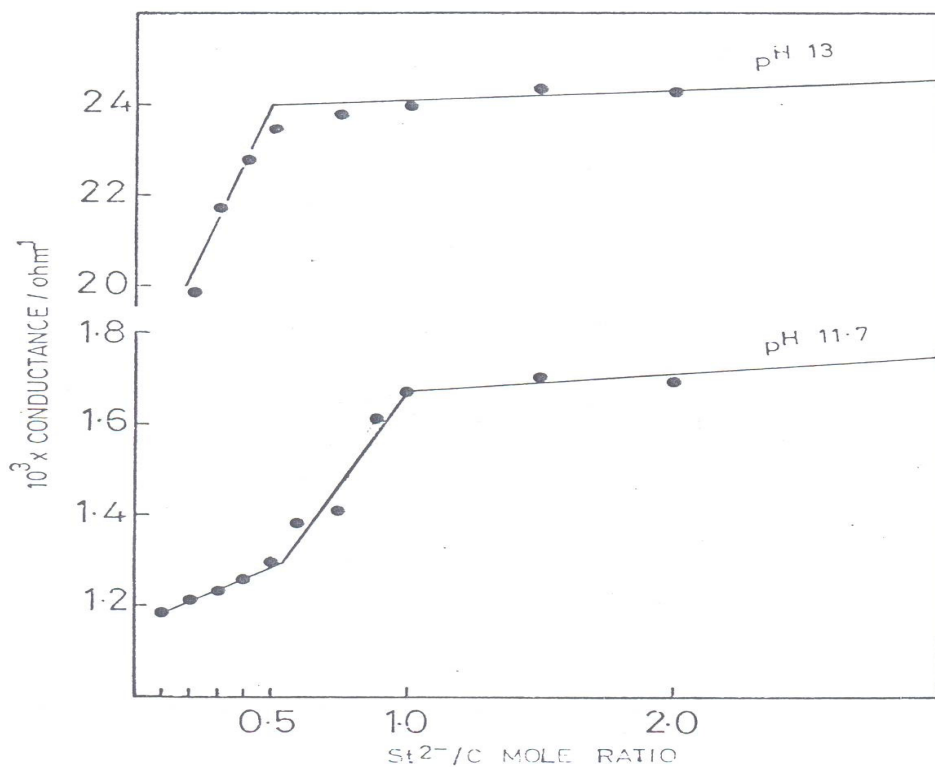


Figure-7: Effect of catechol (C) the conductance of 0.010M sodium stannate (St²⁻) at various *initial* pH, after 24 hours or longer, at 298K.

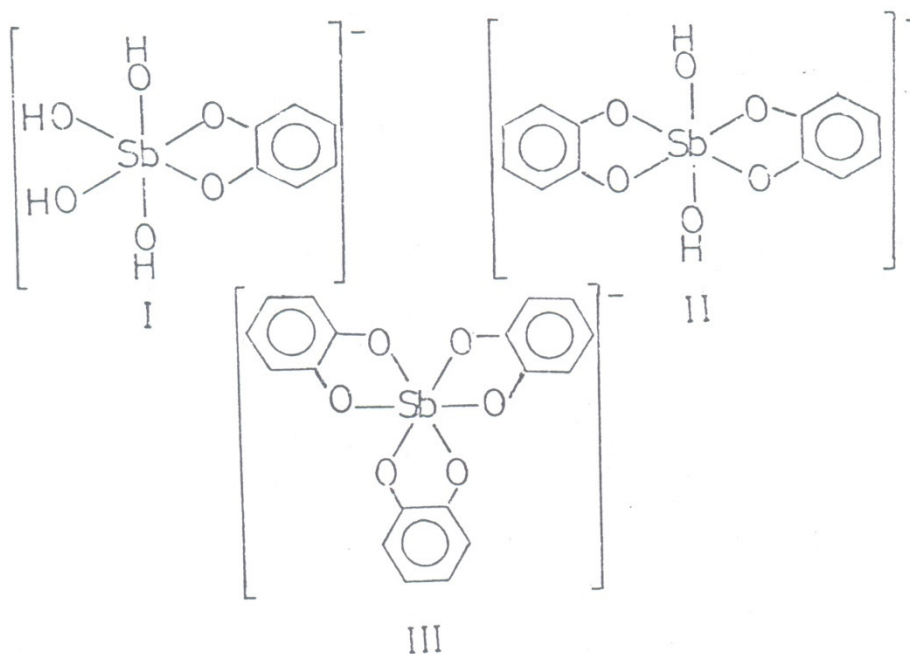


Figure-8: Presumed structures of 1:1 (I), 1:2 (II) and 1:3 (III) anionic Sb(V)-catecholates.