

THE ELECTROMETRIC TITRATION OF BORIC ACID IN THE PRESENCE OF POLYPHENOLS AND ORGANIC ACIDS.

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It has been recognized for some time that boric acid is too weak to be titrated alone. The addition of certain polyhydroxy-organic compounds, such as mannitol, permits of an accurate titration of this acid. In a previous article by the authors,¹ there was published the results of titrations of boric acid in the presence of a number of polyalcohols and sugars. The present work, an extension of the previous investigation, presents the results of titrations in the presence of two other types of polyhydroxy-organic compounds; namely, polyphenols and hydroxyacids.

Although it has never been definitely established, the usual assumption is that the organic substance unites with the boric acid to form a complex acid, which is ionized to a much greater extent than is the boric acid alone. Consequently, the complex can be titrated with a standard solution of a base, using phenolphthalein as the indicator.

As in the previous investigation, the titrations were made with an electrometric apparatus. By this means it is possible to obtain the hydrogen ion concentration, or, what is more generally desired, the pH value after each addition of basic solution. Plotting the pH curve, with milliliters of base as abscissas and pH values as ordinates, provides an easy means of following the course of the neutralization.

Previous Work.—The bearing of previous work on the present investigation was discussed, in general, in the authors' earlier paper. Specifically, it should be mentioned that it was Magnanini² who made the first observations that various hydroxyacids increase the electrical conductivity of boric acid to a marked degree. In recent years Boeseken³ and his students have studied the effect of a large number of polyhydroxy compounds, including polyphenols and hydroxyacids. He concluded that a complex acid, much stronger than the components, is formed, and that, for the formation of such a complex, two OH groups must be situated on the same side of the adjacent carbon atoms to which they are attached. When such a configuration does not exist, as with the beta and gamma polyhydroxy arrangements, a negligible or slightly negative effect on the conductivity was observed.

Present Work.—It has been the general practice to add either mannitol or glycerol to boric acid before making a titration of the latter. The authors have pointed out in their previous article that invert sugar and manna are more economical than either mannitol or glycerol for this purpose. The work of Manganini and Boeseken indicated that there were still other substances, among the polyphenols and

¹ Ind. Eng. Chem., 16, 123 (1924).

² Gazzetta, 21, 9 (1891); Z. Phys. Chem., 11, 281 (1893).

³ Rec. trav. chim., 40, 553, 578 (1921); 37, 120, 165, 178 (1918); 35, 211 (1916); 36, 167 (1917); Ber., 46, 2612 (1913).

"Proc. Ind. Acad. Sci., vol. 33, 1923 (1924)."

hydroxyacids, which increased the conductivity of boric acid. The present work was undertaken, therefore, having as its object the determination of the possibility of using any of the substances just mentioned in the titration of boric acid.

Apparatus and Materials.—As in the previous work, the Wendt Electro-titration apparatus was used, with the same electrodes and hydrogen purification train. Moreover, the boric acid and sodium hydroxide solutions were the same as previously described. The organic reagents were used as purchased, inasmuch as conditions simulating those of an industrial laboratory were desired.

Procedure.—Except in the case of lactic acid, the procedure consisted in the titration of a definite volume of the boric acid solution to which a weighed quantity of the organic substance had been added. In order to have the various titrations on a comparable basis, a definite ratio of four molecular weights of the polyphenol to one of boric acid was maintained. This was modified, in the case of the acids, to one equivalent weight of the organic acid to one of boric acid, the reason for the change being given under the discussion of the results obtained. Phenolphthalein was present in each titration, this indicator being the one generally used in volumetric determinations of boric acid. Errors due to temperature changes and to the absorption of carbon dioxide are neglected in view of the purpose of the work.

Experimental Data.—Although the original data are not included, the curves, plotted from these data, are shown. The usual methods are employed in the plotting of these curves, the pH values being the ordinates and milliliters of standard base the abscissas. The curve for boric acid alone has been repeated on each figure in order that the effect of the organic substance on the neutralization curve can be visualized. The curve for the titration in the presence of mannitol is also shown on figure 1, an effect similar to that of mannitol being the desirable effect.

Polyphenols.—The polyphenols selected were pyrocatechol, $\text{o-C}_6\text{H}_4(\text{OH})_2$, and pyrogallol, 1, 2, 3- $\text{C}_6\text{H}_3(\text{OH})_3$. The work of Boeseken⁴ indicated that the difference between the conductivity of the mixture and the sum of those of the components ($\text{K} \times 10^{-6}$) was in the case of glycerol, 9; mannitol, 685; pyrocatechol, 516, and pyrogallol, 573. Judging from these data alone, it would appear that the polyphenols promised an efficiency approaching that of mannitol and far in excess of that of glycerol. In the acid range, as indicated in figure 1, the results of the titrations were as expected, but upon approaching and passing the neutralization point, the expected upward break in the curve did not take place. With pyrocatechol, a yellowish-brown coloration developed during the titration, masking the color change of the indicator. A decided downward drift was noted in the readings of the millivoltmeter if the solution was allowed to stand after completing the titration. Similar developments were noted with pyrogallol.

Hydroxyacids.—Of the various acids which Boeseken found to increase the electrical conductivity of boric acid, some are recognized

⁴ Ber., 46, 2612 (1913).

at once as belonging to the group known as hydroxyacids, such as lactic, tartaric, etc. Others showing a positive effect, such as oxalic and malonic, one would not so classify. Boeseken has explained the action of the latter by assuming that we have to do with a polyhydroxy-compound formed by the hydration of the carboxyl group at the carbonyl oxygen so that the OH groups are favorably situated. Several members of each of these types of acids were selected.

In titrating boric acid in the presence of another acid stronger than itself, one would expect a pH curve quite different from those

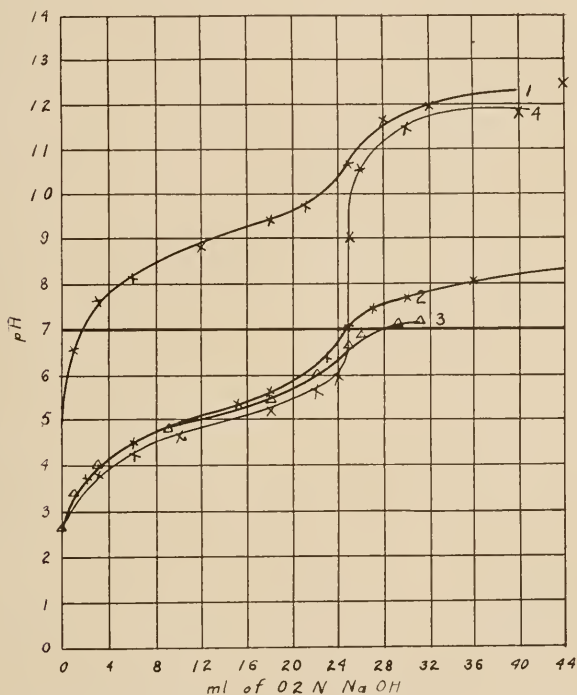


Fig. 1. Titration of boric acid (50 ml. of a solution 0.0994 N) in the presence of polyphenols: (1) acid alone, (2) pyrocatechol, (3) pyrogallol, (4) mannitol.

obtained in titrating boric acid in the presence of a polyalcohol. In the latter case boric acid is the only constituent being neutralized, and the general effect of the polyalcohol is to produce a complex acid more highly ionized than boric acid. This effect becomes apparent in a considerable drop, along the pH scale, of the initial portion of the neutralization curve and in the appearance in it of a comparatively long vertical portion. The titration of a mixture of boric and lactic acids, for example, is a different matter. In studying the electrical conductivity of such a system Boeseken had merely to prepare a given mixture and then to determine whether its conductivity differed from the value calculated as the sum of the contributions of each constituent to the total.

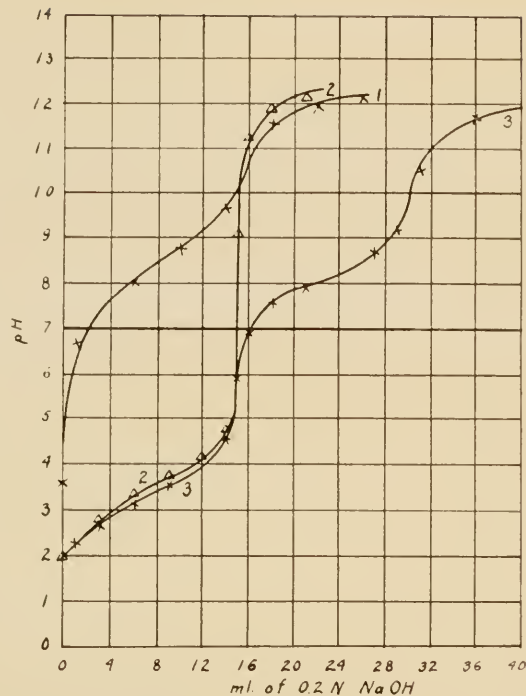


Fig. 2. Titration of boric acid (30 ml. of a solution 0.0994 N) in the presence of glycolic acid: (1) boric acid alone, (2) glycolic acid alone, (3) boric and glycolic acids together.

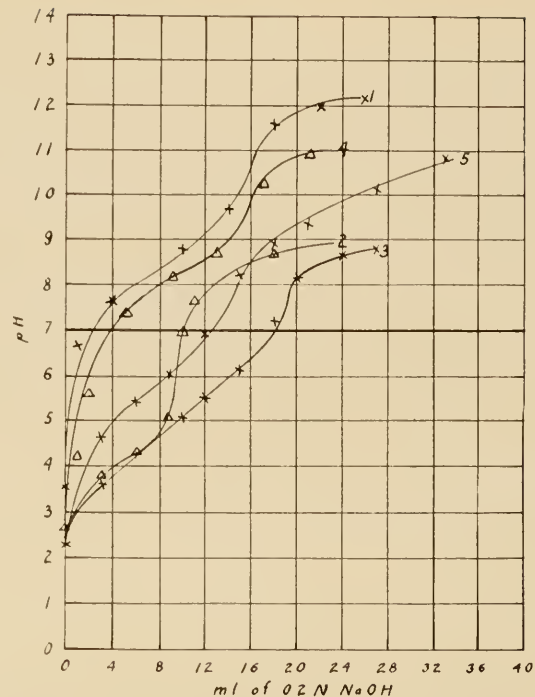


Fig. 3. Titration of boric acid (0.0994 N) in the presence of aromatic acids: (1) 30 ml. of the solution of boric acid, (2) gallic acid alone, (3) 20 ml. of the solution of boric acid together with the same amount of gallic acid used in 2, (4) tannic acid alone, (5) 30 ml. of the solution of boric acid together with the same amount of tannic acid used in 4.

The first titrations attempted indicated that the two constituent acids in the mixture were apparently neutralized separately. With the four to one molecular ratio used with the polyphenols, the two breaks in the curve occurred very close together so that it was considered desirable to select a different ratio. Therefore an amount of the organic acid was dissolved in the solution to be titrated equivalent to the boric acid contained therein. In determining the course of the neutralization for the two acids a titration was run for each acid alone and for the two together.

Titration were made using the following acids: oxalic, malonic, lactic, glycolic, malic and tartaric of the aliphatic series, and gallic and tannic of the aromatic series, assuming that the properties of tannic acid warrant its inclusion in this class. Salicylic acid was tried but its rate of solution was so slow that the results seemed to be of no value.

The results obtained for glycolic acid are shown in figure 2. These curves are representative of those for the other aliphatic acids, except in those cases involving a dibasic acid, where a small upward break occurs when the first hydrogen of this acid is neutralized. There is evident only a small downward displacement of the first portion of the curve for the organic acid when boric acid is present.

Figure 3 shows the curves for both gallic and tannic acids. It should be noted that the two acids were used on a different basis—20 ml. of boric acid with the gallic acid and 30 with the tannic—and that the curve for boric acid alone is for 30 ml. of the solution. In only one curve—that of boric and gallic—is there a break indicating the possibility of making a satisfactory volumetric determination. In these cases it is evident that the combination of two acids gives a curve distinctly different from that for either one alone. This change in the curve for tannic acid is much greater than the change for any other acid used.

DISCUSSION.

A study of the preceding curves brings out several conclusions regarding the complexes formed by boric acid and some polyhydroxy-organic compounds. These conclusions are concerned primarily with the possibility of utilizing these complexes in the volumetric determination of boric acid and may be stated as follows:

1. In every case the addition of the polyhydroxy-compound produced a downward displacement of the pH curve for boric acid, the degree of displacement varying with the substance used. In general, this may be attributed to the formation of a complex acid which ionizes to a greater extent than does boric acid alone, although in some cases the mere presence of the organic substance might account for the displacement produced, even if no complex were formed. While Boeseken's⁵ conductivity experiments may indicate the existence of a complex, the results of the present investigation show clearly that a complex, capable of being titrated accurately, is not necessarily formed.

⁵ *Loc. cit.*

2. In no case did the polyphenols or hydroxyacids give indication of the formation of a complex suitable for an accurate volumetric determination of boric acid with sodium hydroxide.

The polyphenols lowered the pH curve of boric acid to a considerable extent in the acid range but did not make the expected rise as neutralization was approached and passed. A search of the literature⁶ reveals the fact that among the oxidation products resulting from the exposure of alkaline pyrogallate to the air are carbon dioxide and acetic acid. This fact would explain both the failure of the curve to make the expected rise and the gradual decrease of the millivoltmeter readings upon allowing the solution to stand in the air. A similar reaction may be assumed in the case of pyrocatechol.

The aliphatic hydroxyacids all gave similar curves. Apparently the two acids were neutralized separately just as if no complex had been formed. If the assumption is made that no complex acid is formed, it is merely a matter of the effect of the addition of a stronger acid to the solution of a weaker one. Such a case is discussed by Lewis,⁷ who draws the conclusion that the degree of dissociation of the weaker acid—boric—is directly proportional to its dissociation constant and inversely proportional to the concentration of the stronger, glycolic for instance. Application of this conclusion to the present problem makes it obvious that as the amount of the glycolic acid is increased, the borate ions become fewer and fewer, so that practically speaking, the presence of the boric acid can be ignored during the titration of the glycolic. Not until the latter is nearly all neutralized does the ionization of the boric acid again need to be considered. During the latter part of the neutralization the system differs from a solution of boric acid alone only in that it contains in addition the salt of the organic acid neutralized in the first part of the process. The pH curve of the mixture then shows a sharp upward break at the point of neutralization of the glycolic acid, which break is much shorter than that for glycolic alone, however, since the boric acid is now ionizing and hydrogen ions are present. Then follows a gradual rise with a small upward break representing the neutralization of the boric acid.

Both of the aromatic acids, upon approaching the end point of the titrations, developed deep colorations, which would prevent any use of them in ordinary volumetric analysis. Reference to the curves of figure 3 shows that tannic acid is so inactive a substance that no conclusions regarding the nature of the complex formed can be drawn. Gallic acid on the other hand did give evidence of the formation of a complex capable of being titrated, but no application, other than electro-metric, could be made of this fact, for the reason stated above.

SUMMARY.

1. The fact that conductivity experiments indicate the formation of a relatively highly ionized complex acid when certain polyhydroxy-organic compounds are added to boric acid does not necessarily indicate

⁶ Meyer & Jacobson, "Lehrbuch der Organischen Chemie", 2, 423 (1902).

⁷ "A System of Physical Chemistry", 1, 423 (1916).

that the use of such compounds will enable one to obtain accurate results in the volumetric determination of boric acid.

2. Accurate titrations of boric acid in the presence of pyrogallol or pyrocatechol seem to be impossible under the conditions described, apparently due to the formation of acidic oxidation products of the organic compounds.

3. Certain organic acids, although believed to form a complex with boric acid, behave during a titration of the mixture of the two as if the process of neutralization involves two rather distinct steps, first, the organic acid, and second, the boric acid.

