Studies on Boric Acid and Borates. (I)

The Effect of Boric acid and of Borates on the Polarographic Wave of Fructose*

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   It is konwn that fructose gives a well-defined wave in 0.02M– lithium chloride or hydroxide solution and boric acid or borate reacts with polyalcohols such as mannitol or glycerol to form the complex.

   In this report, an effect of boric acid and of borate on the polarographic wave of fructose was studied.
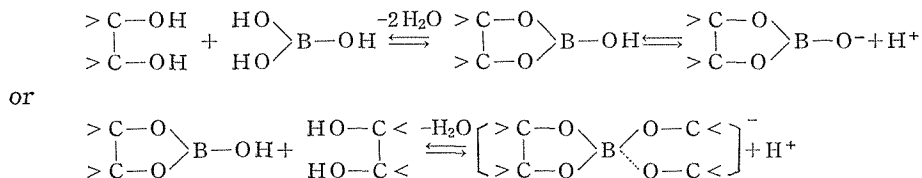
   The fructose wave is depressed markedly by the addition of boric acid or borate.

   The mole ratio of boron to fructose in this complex are determined to be approximately 1 to 1 by amperometric titration.

INTRODUCTION

   Heyrovský and Smoler[1] found that fructose gave well-defined waves in 0.02 M- lithium chloride or hydroxide, starting at -1.8 V (*vs.*N.C.E).

   The well-known facts of the condensation reaction between boric acid and polyalcohols such as fructose[2] has induced the present authors to study the effect of boric acid and borates on the polarographic wave of fructose. Potentiometric and conductometric studies have already been reported on the condensation reactions between boric acid and polyalcohols such as mannitol or glycerol. Besides boric acid, a similar complex formation of telluric, germanic and arsenic acids with polyalcohols has been reported. Boeseken[2] presented the following scheme with regard to the condensation reaction between boric acid and polyalcohols.

$$
\begin{array}{l}
>\!C\!-\!OH \\
\quad| \\
>\!C\!-\!OH
\end{array}
+
\begin{array}{l}
HO \\
\quad\diagdown B\!-\!OH \\
HO\diagup
\end{array}
\xrightarrow{-2H_2O}
\begin{array}{l}
>\!C\!-\!O \\
\quad|\quad\diagdown B\!-\!OH \\
>\!C\!-\!O\diagup
\end{array}
\rightleftharpoons
\begin{array}{l}
>\!C\!-\!O \\
\quad|\quad\diagdown B\!-\!O^- + H^+ \\
>\!C\!-\!O\diagup
\end{array}
$$

or

$$
\begin{array}{l}
>\!C\!-\!O \\
\quad|\quad\diagdown B\!-\!OH \\
>\!C\!-\!O\diagup
\end{array}
+
\begin{array}{l}
HO\!-\!C< \\
\quad| \\
HO\!-\!C<
\end{array}
\xrightarrow{-H_2O}
\left[
\begin{array}{l}
>\!C\!-\!O \\
\quad|\quad\diagup B\diagdown \\
>\!C\!-\!O
\end{array}
\begin{array}{l}
O\!-\!C< \\
\diagdown \\
O\!-\!C<
\end{array}
\right]^-
+ H^+
$$

EXPERIMENTAL AND RESULTS

1. Apparatus and Materials

Polarographic measurements were made with a Yanagimoto recording polaro-

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graph. The experiments were made at 15°. To make the solution of fructose, a sample of pure fructose was presented by Professor R. Gotō of this Institute. Stock solutions prepared and used in this experiments are as follows : 1.0 % fructose solution, 0.04 M-lithium chloride (Merk Co.) solution, 0.1 M-lithium hydroxide solution, prepared from lithium chloride and wet silver oxide, 0.1 M-boric acid, phosphoric acid, hydrochloric acid and acetic acid, 0.025 M-sodium borate solution, 0.1 M-dipotassium hydrogen phosphate solution and sodium acetate solution, and 0.2 % gelatin solution.

2. Polarograms of Fructose

Into a 50 ml-volumetric flask, 25 ml of 0.04 M-lithium chloride solution and 2.5 ml of 0.2% gelatin solution were taken and diluted with distilled water to a mark.

Aliquot amount of the above solution was poured into a conventional polarographic cell, in which mercury pool was used as an anode. In order to remove the dissolved oxygen, a stream of hydrogen, which was purified from oxygen by means of an alkaline solution of pyrogallol, was bubbled through the cell solution for about fifteen minutes.

The polarograms were taken from –1.6 V $vs.$ mercury pool anode. The anode potential in 0.02M-lithium chloride solution was $+0.13V$ $vs.$ S.C.E. Similar polarograms were taken with the solutions containing 0.05, 0.1 and 0.15% fructose respectively besides 0.02 M-lithium chloride and 0.01 % gelatin. Fig. 1. shows the polarograms of fructose waves.
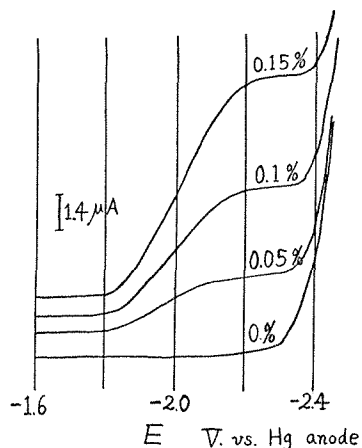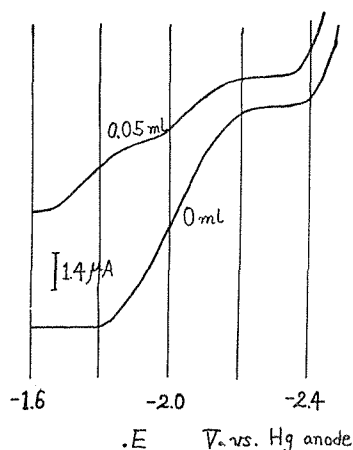

Fig. 1. Polarograms of fructose.　　Fig. 2. Effect of acetic acid.

3. Effect of Acids and Alkali on the Fructose Wave

An effect of acetic acid on the fructose wave was examined ; to a 5 ml of electrolytic solution consisted of 0.02 M-lithium chloride, 0.15 % fructose and 0.01 % gelatin, was added a 0.05 ml of 0.1 M-acetic acid.

The polarogram showed hydrogen wave starting from $-1.6V$ and the following fructose wave was depressed markedly, as is shown in Fig. 2.

Similar depression of fructose wave was also observed with the cases of

the addition of phosphoric acid or hydrochloric acid. Heyrovský has already observed on the similar phenomena, however little explanation was given there. In view of the appearance of hydrogen wave, the decrease of the fructose wave might be due to the chemical reduction of fructose at the electrode surface by the active hydrogen electrolytically produced on the electrode.

These mutually interfering phenomena are rarely observed in polarography; the decrease in wave height of hydrogen ion by the presence of dissolved oxygen which produces hydroxyl ion by electrolytic reduction, is one of the well-known examples.

On the contrary to the effect of acid, the fructose wave was not influenced by the addition of alkaline solution. Fig. 3. shows the waves of 5 ml of 0.15 % fructose in 0.02 M-lithium chloride after addition of 0, 0.05 and 0.1 ml of 0.1 M-lithium hydroxide. Little difference is seen on each waves. (The positive shift of the wave according to the addition of hydroxide is attributed to the negative shift of the potential of mercury pool anode.)
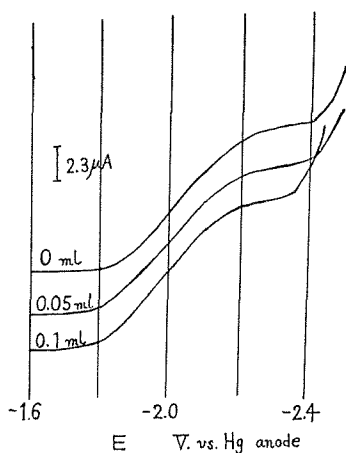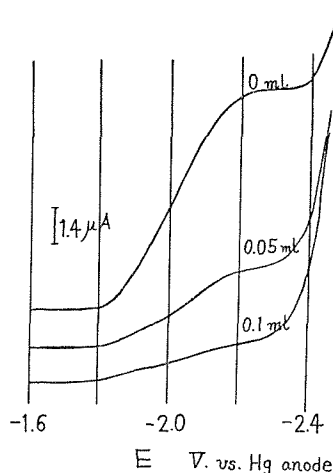

Fig. 3. Effect of lithium hydroxide.   Fig. 4. Effect of boric acid.

4. Effect of Boric Acid and Borate on the Fructose Wave

The fructose wave is depressed markedly by the addition of boric acid or borate, the behavior of which is fundamentally different from that observed with acids. Fig. 4. demonstrates the effect of addition of 0.05 and 0.1 ml of 0.1 M-boric acid respectively to a 5 ml of 0.15 % fructose solution in 0.02 M-lithium chloride. Although no hydrogen wave is observed by the addition of boric acid, the fructose wave decreases its height with increasing boric acid concentration.

The reason of decrease in the height of fructose waves may be attributed to non-reducible character of the boric acid-fructose complex. Similar behavior was observed not only by boric acid, but also by borax which forms complex with polyalcohols. Fig. 5. demonstrates the effect of addition of 0.05, 0.1 and 0.15 ml of 0.025 M-sodium borate respectively to a 5 ml of 0.15 % fructose solution in 0.02 M-lithium chloride.

In either case, it is clearly demonstrated that the reduction of fructose is suppressed markedly.

Almost identical effect was obtained with dipotassium hydrogen phosphate (figures saved).

However, sodium acetate did not show such a depression effect on the fructose wave, because it does not form complex with fructose. Fig. 6 demonstrates the effect of addition of 0.05, 0.1 and 0.15 ml of 0.1 M-sodium acetate
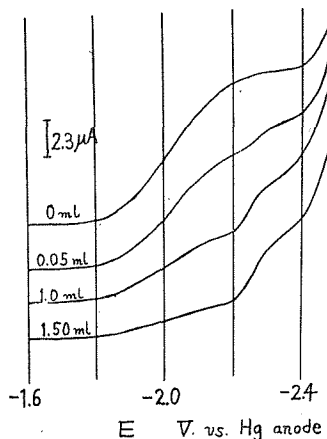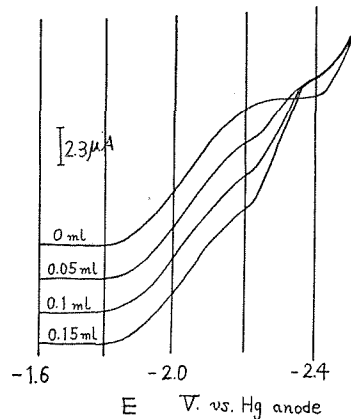

Fig. 5. Effect of borax.

Fig. 6. Effect of sodium acetate.

solution respectively to a 5 ml of 0.15 % fructose solution in 0.02 M-lithium chloride. The wave height of each curve are almost equal, but the fructose wave becomes ill-defined owing to the interference of the wave of sodium ions with increasing amount of sodium acetate.

5. Mole Ratio of Components in the Complex

In order to determine the mole ratio of boron to fructose in the complex, the following experiments were performed.

A simple polarizing unit consisting of a battery and potential divider, 50-microammeter and H-type cell, which is conventionally used in amperometric titrations and provided with 3 % agar bridge containing 20 % lithium chloride in its side tube, were used.

A dropping mercury electrode as indicator electrode and silver-silver chloride electrode in saturated lithium chloride as anode were used. Anodic potential was $-0.106V$ $vs.$ S. C. E. Polarograms of fructose were again obtained with this anode and they showed the same figures as those obtained in the above experiments, but the waves shifted to a positive applied voltage about $0.2V$.

In amperometric titrations the limiting currents were measured at $-2.2V$ $vs.$ Ag–AgCl anode. Into the main tube of H-type cell, a 30 ml of 0.02 M-lithium chloride solution containing 0.01 % gelatin, and 0, 5 and 10 ml of 0.03 M-boric acid respectively, was taken and dissolved oxygen were removed as usual and the residual current at $-2.2V$ were measured. Then aliquot amount of the solution of 1.1 % fructose was added from a burette to the above electrolytic

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solution.

The solution was mixed by bubbling with hydrogen stream and the current was measured at the same potential. The current values corrected for residual current and dilution, were plotted against an amount of 1.1% fructose solution added. Although the amperometric titration curves, as shown in Fig. 7, were not typical, the amount of fructose solution used until the equivalence point in
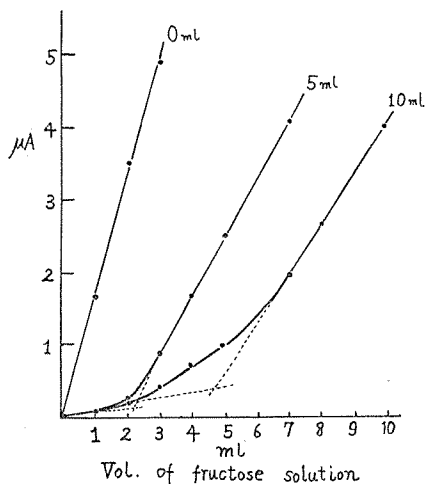

Fig. 7. Titration curve.

curve 5 ml and curve 10 ml was 2.2 ml and 4.6 ml respectively.

Calculated from these amounts, the mole ratio of boron to fructose at the equivalence point was determined as approximately 1 to 1. This result coincides with the value which has been obtained in the complex of boric acid with mannitol.[2]

SUMMARY

The effects of acids, alkali and salts on the polarographic wave of fructose were studied. Boric acid, borate and phosphate depressed the wave height of fructose markedly. The reason of decrease in the height of fructose waves may be attributed to non-reducible character of the boric acid-fructose complex.

The mole ratio of boron to fructose in the complex was determined as approximately 1 to 1 by amperometric titration.

REFERENCES

(1) J. Heyrovský and I. Smoleř, *Collection Czechoslov. Chem. Communs.*, 4, 521 (1932).
(2) F. Feigl, "Chemistry of specific, selective and sensitive reactions,"p. 354 (1949).