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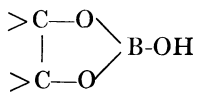
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ELECTRODIALYSIS OF SUGAR BORATES

GEORGE H. COLEMAN AND AARON MILLER

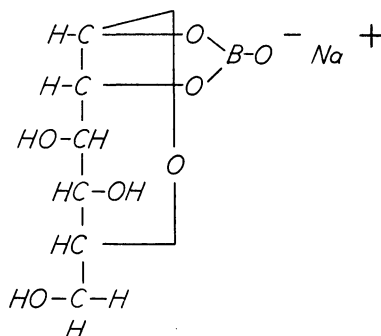
The reaction of glycols with boric acid in aqueous solutions to form an easily saponified ester has long been known. This acid ester is a stronger acid than boric acid and an increase in conductivity results.

Klein (1878) described the glycol-boric acid complex as an ester of metaboric acid. This may be represented by the following formula:



Magnanini (1890) showed that two hydroxyl groups on adjacent carbon atoms are necessary while Boeseken (1913) proved that the effect was greater if the two hydroxyl groups possessed a cis configuration as in λ -D-glucose.

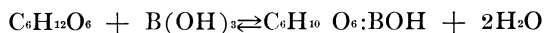
The ester which is formed dissociates as a stronger acid than boric acid so it is to be expected that the addition of alkali would favor the formation of the glucose-borate ester and ionization would occur as follows:



If these formulations are correct the ions would be expected to migrate in an electrical field.

In the present work in which glucose-borax solutions were subjected to electro-dialytic conditions the glucose was found to migrate preferentially toward the anode. As expected a small amount of glucose diffused toward the cathode.

The reaction between glucose and boric acid may be represented by the following equation:



The type of apparatus used was a three compartment electrolytic cell as described by Cox, King, and Berg (1929) using heavy sheet cellophane membranes. The electrodes were graphite plates for the cathode and platinum plates for the anode. Attempts to use graphite or nickel anodes were unsatisfactory due to decomposition. One hundred and ten volt direct current was used.

The results of electro dialysis experiments on glucose-borax solutions are given in Tables I and II.

TABLE I.
Electro dialysis of Glucose-Borax Solutions*

Time (hours)	<i>Barfoed Sugar Reduction Test</i>	
	Anode	Cathode
0	Compartment Negative	Compartment Negative
4	Positive	Very slight
7	Strong positive	Very slight

*The results are only qualitative in character due to the interference of the boric acid with reduction determinations.

TABLE II.
Electro dialysis of Glucose-Borax Solutions

Time (hours)	<i>Observed Rotations</i> *	
	Anode Compartment	Cathode Compartment
0	0.00°	0.00
2	+0.16°	+0.07°
16	+1.06°	+0.32°
28.5	+1.69°	+0.43°
41	+1.91°	+0.68°
44	+2.00°	+0.82°

*The samples were withdrawn, acidified with phosphoric acid and the precipitated boric acid filtered off. The angular rotation of the filtrate was observed in a 2 dm. tube using the sodium D line as the light source.

Maltose was also found to migrate preferentially in an electrical field in the presence of borax. The results are tabulated in Table III showing the comparison between maltose borax solutions in an electrical field and in the same apparatus by diffusion only.

TABLE III.
Electrodialysis and Dialysis of Maltose-Borax Solutions

Electrodialysis			Dialysis		
Time (hours)	Observed Anode	Rotation Cathode	Time (hours)	Observed Anode	Rotation Cathode
0	0.00	0.00	0	0.00	0.00
4	+0.33°	+0.69°	11	+0.78°	+0.65°
11.5	+1.10°	+1.12°	22	+1.48°	+1.22°
23.5	+1.97°	+1.55°	36.5	+2.09°	+1.89°
29.5	+2.39°	+1.75°	59.5	+2.94°	+2.49°
51.5	+3.51°	+2.42°	84.5	+3.49°	+3.18°
76.5	+4.62°	+3.14°	111.5	+3.96°	+3.75°
Wt. of maltose at end	18.75 g.	11.12 g.		11.3 g.	12.1 g.

The electrolysis experiments with glucose and maltose borax solutions indicate that the velocity of electrolysis of the glucose-borate ion was somewhat greater than that of the maltose-borate ion. In an attempt to separate glucose and maltose by electrolysis of a borax solution there was an indication of some concentration of the disaccharide. After 19 hours of electrolysis the glucose/maltose ratio had changed from 1.43 to 1.28.

TABLE IV.
The Effect of Borax on the Determination of Sugars
by Reduction

Ml. saturated borax solution added.	Other additions	Mg. glucose found.
<i>Glucose</i> — 800 mg. glucose in 100 ml. solution.		
0	-	795
0	-	795
10	-	628
10	-	630
10	4 ml. glycerol	720
10	8 ml. glycerol	758
10	10 ml. glycerol	786
10	10 ml. mannitol solution *	759
25	-	656
25	10 ml. mannitol solution	720
25	20 ml. mannitol solution	742
25	26 ml. mannitol solution	768
25	20 ml. glycerol	813
<i>Maltose</i> — reducing value, an amount equivalent in 100 mg. glucose.		
0	-	947
25	-	777
25	20 ml. glycerol	1123

*A saturated aqueous solution of mannitol was used.

Levy and Doisy (1928, 1929) have shown that sugar oxidation methods yielded erroneous results in the presence of borax. This was verified in the present work using the Lane and Eynon (1923) method for sugar determination. Addition of glycerol or mannitol raised the values for sugar found but they did not yield true values. The results are given in Table IV.

The specific rotation of D-glucose is greatly affected by borax. Murschhauser (1923) has shown that the specific rotation of D-glucose was reduced from $+52.5^\circ$ to $+42.5^\circ$ by the addition of borax. Rimbach and Weber (1905) had previously discovered that when D-glucose had stood at room temperature in a borax solution for 117 hours the specific rotation was -3.5° . They concluded that a Lobry De Bruyn interconversion had taken place.

In the present work it was found that the specific rotation of D-glucose in borax solution ranged from $+52^\circ$ to -8° depending upon the relative concentration of the sugar and the borax. When any of these solutions were acidified with phosphoric acid the specific rotation returned to normal. Maltose showed a slight increase of specific rotation (from $+131.4^\circ$ to $+142.6^\circ$) upon addition of borax.

The different rotations of various concentrations of glucose in a 10% borax solution is shown in Table V.

TABLE V.
The Effect of Borax on the Rotation of Glucose

% Glucose	Observed Rotation	Specific Rotation
0.25 (in water)	$+0.26^\circ$	$+52^\circ$
0.25	-0.04°	-8°
0.50	-0.05°	-5°
0.75	-0.06°	-4°
1.00	-0.07°	-3.5°
1.25	-0.01°	-0.4°
1.50	$+0.09^\circ$	$+3.0^\circ$
1.75	$+0.18^\circ$	$+5.1^\circ$
2.00	$+0.38^\circ$	$+9.5^\circ$

On acidification of the 1.25% glucose-borax solution with sirupy phosphoric acid the specific rotation was $+52^\circ$.

Addition of a small amount of solid potassium hydroxide to the 1.25% glucose-borax solution caused the specific rotation to drop to -7.6° indicating a further shift of the equilibrium with increasing pH.

The different rotations of various concentrations of maltose in a 10% borax solution are shown in Table VI.

TABLE VI.

The Effect of Borax on the Rotation of Maltose

% Maltose (hydrate)	Specific Rotation
10.0	+133.5°
7.5	+140.0°
5.0	+139.7°
2.0	+142.6°

The depression of the specific rotation of a glucose-borax solution to approximately zero while the maltose was raised slightly made it possible to calculate the concentration of glucose and maltose in an aqueous-borax solution of a mixture of these two sugars.

SUMMARY

1. Glucose and maltose have been found to migrate preferentially toward the anode in an electrical field in the presence of borax.
2. The reduction values of glucose and maltose are lowered considerably in the presence of borax. Addition of glycerol or mannitol will raise these values, but true results are not obtained.
3. The specific rotation of D-glucose is greatly affected by borax, and values from $+52^\circ$ to -8° are obtainable by varying the concentrations of the glucose and the borax. The specific rotation of maltose is raised slightly by the presence of borax, and will change with varying concentrations.

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