On the Acidity of Boric Acid. I. Neutral-Salt Effect Observed by Alkali-titration

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(Received January 21, 1952)

Introduction

It is a well known fact that the solution of boric acid is too weak to be determined by alkali-titration. But the solution is so strongly acidified by the addition of polyalcohol, glycerine, mannit, etc., that it can be titrated by adopting phenolphthalein as indicator. This is one of the methods of quantitative analysis of boric acid.⑴ A. Deutsch and S. Osoling⑵ studied the complex formation between boric acid and mannit by the conductometric and potentiometric methods and concluded that the equilibrium is as follows:

$$H_3BO_3 = H^+ + H_2BO_3^-$$
$$H_2BO_3^- + \text{Mannit} = [H_2BO_3\ \text{Mannit}]^-$$
$$H_2BO_3^- + 2\,\text{Mannit} = [H_2BO_3\ 2\,\text{Mannit}]^-.$$

Recently, D. Setten⑶ has shown that the boric acid solution becomes more acidic than expected from the law of mass action in the case of concentrated solution (above 0.1 M), and that the polymerization of H_3BO_3 molecule occurs.

It is clear that the increase of acidity could be caused by the stabilization of the dissociated ion $H_2BO_3^-$ or H^+ owing to the complex formation or polymerization, but the reason why the stabilization and the ionization could be correlated directly with each other has not been explained sufficiently.

The new fact of neutral-salts effect has been discovered in this laboratory, which gives the hint for the explanation of this phenomena as shown in the following section.

Experimental Procedure and Result

(A) Titration by the addition of mannit, glycerine, ethylene glycol and methyl alcohol.—20 cc. of the solution of boric acid (0.1 M/1) added with 10 cc. of distilled water the mixture is titrated with 0.2 N. sodium hydroxide solution in the presence of phenolphthalein. The alkali solution is added until the colour of the solution turns to light pink (pH-8.5) and the added volume of alkali solution is read. This is the initial titration volume (itv). Then, the moderate volume of alcohol (volume added) is added. When the solution discolours, it is again titrated with the alkali solution in order to read the second titration volume. The titration is repeated and the titration curves can be obtained. When the quantity of alcohol is enough, the colouring points (each end point) become clearer, because the dissociation constant is increased. Some results are shown in Fig. 1. We can easily understand from these curves that the strength of acidifying effect is demonstrated by the initial inclination of the titration curve. These values are listed in Table 1. Similar effects are observed in the system of two components of CH_3OH-$C_2H_4(OH)_2$ and CH_3OH-$C_3H_5(OH)_3$, and the results are shown in Table 2 and Fig. 2.

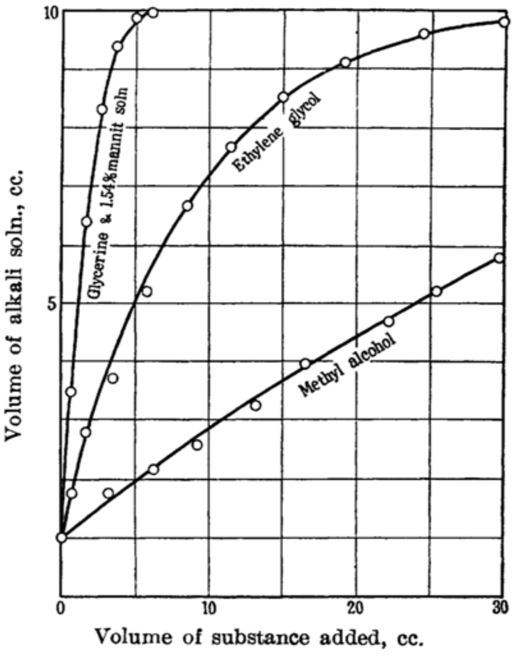

Fig 1.

Supplementally, the effect of aceton and dioxan has been investigated without virtue, and the results are rather negative.

(B) Titration by the addition of neutral-salts.—20 cc. of the solution of boric acid (0.1 M) is added

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⑴ F. P. Treadwell, "Analytische Chemie".

⑵ A. Deutsch and S. Osoling, *J. Am. Chem. Soc.*, **71**, 1637 (1949).

⑶ D. Setten, *Anal. Chem.*, **23**, 1777 (1951).

Table 1

Subst.	Initial inclination		
	cc./cc.	cc./mol	Relative value
Methyl alcohol	1/6	6.7	1
Ethylene glycol	4/6	36	5.4
Glycerin	4/1	280	42
1.54% Mannit Soln.	4/1	4000	100

Table 2

Methyl alcohol~Ethylene glycol		Methyl alcohol~Glycerin	
Mol ratio (M:E)	Init. incli., cc./cc.	Mol ratio (M:G)	Init. incli., cc./cc.
4 : 0	0.17	4 : 0	0.17
3 : 1	0.35	3 : 1	2.2
2 : 2	0.60	2 : 2	3.2
1 : 3	0.65	1 : 3	4.0
0 : 4	0.67	0 : 4	4.0

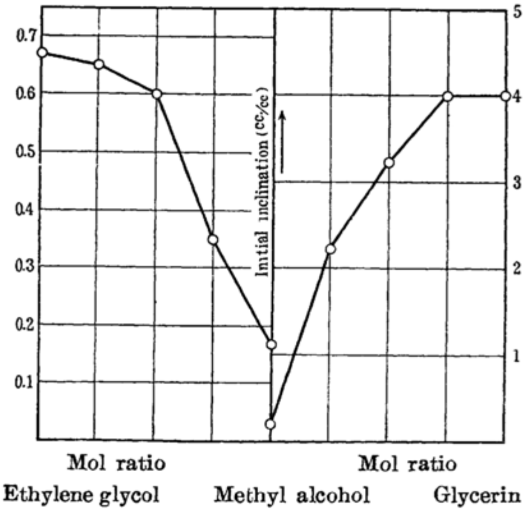

Fig. 2.

by the neutral-salt at first and 10 cc. of distilled water, and then the mixture is titrated by the similar way described in (A). The titration curves are obtained mainly with ethylene glycol. The results in the presence of NaI and K_2SO_4 are shown in Fig. 3. The curves are displaced from the original (ethylene glycol only) mainly in the next two points:

(1) initial titration volume (itv).

(2) sufficient quantity of ethylene glycol which needs to reach the final end point decreases when the initial titration volume increases as compared with the case of ethylene glycol only.

From these observations, the effects examined are divided into three classes, which are,

(a) strongly effecting salts: LiCl, $CaCl_2$, $BaCl_2$, NaBr, NaI, $Ca(NO_3)_2$, $Ba(NO_3)_2$,

(b) moderately effecting salts: NaCl, $NaNO_3$, KBr, KI,

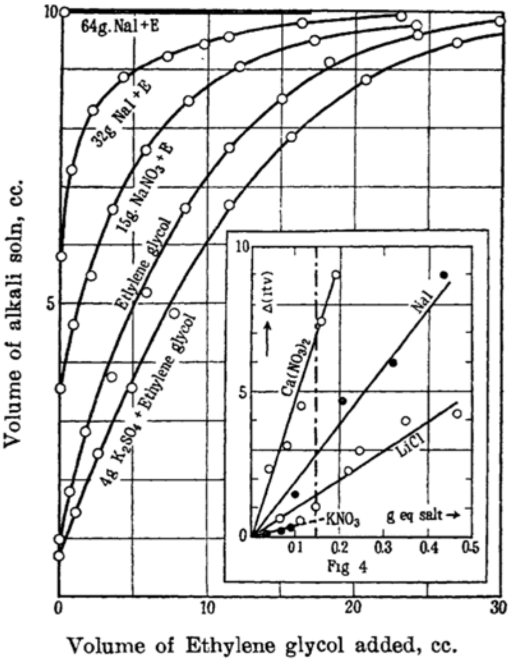

Fig. 3.

(c) little or negatively effecting salts: KNO_3, Na_2SO_4, K_2SO_4.

In order to discuss the effect quantitatively, the author examined the relation between initial titration volume and salt concentration. Generally, the change of initial titration volume △(itv) is linear with the salt concentration. Some results are shown in Fig. 4. From this linearity, we can determine the strength of acidifying effect as the change of initial titration volume △(itv)* at the salt concentration of one gram equivalent to the solution of 20 cc. of 0.1 M boric acid and 10 cc. of distilled water. These values are listed in the last column in Table 3.

Result and Discussion

The effects of polyalcohols and their mixtures, as well as acetone and dioxan, showed the results expected from the previous works. But the neutral-salt effect was remarkable. Therefore, it is important to discover the correlation between the acidifying effect and the other properties of salts.

After various speculation, the author has concluded that there is a distinct relation between the strength of the acidifying effect (△(itv)*) and the energy of hydration of ions. When we compare the △(itv)* with the difference of the hydration energy between positive and negative ions ($\triangle U$(Cal./g. eq. ion) $= U_+ - U_-$) in Table 3,(4) we can easily perceive the simple relation as

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(4) J. D. Bernal and R. H. Fowlers, *J. Chem. Phys.*, **1**, 538 (1933). The values for NO_3^- and 1/2 SO_4^{--} are assigned as 58 kcal./g.eq. ion and 85 kcal. respectively from the expectation that the effect of KNO_3 and Li_2SO_4 lies on the curve on Fig. 5.

Table 3

Salts	Hydration energy, kcal./g. eq. ion				$\triangle$(itv)*, cc.
	U_+	U_-	$\sum U$	$\triangle U$	
LiCl	136	65	200	75	+1.7
$LiNO_3$	136	(56)	(192)	(80)	+1.8
NaCl	114	65	179	49	+1.6
NaI	114	47	161	67	+3.0
$NaNO_3$	114	(56)	(170)	(58)	+1.2
$\frac{1}{2}Na_2SO_4$	114	(85)	(199)	(29)	±0
KCl	94	65	159	29	±0
KBr	94	57	151	37	+0.5
KI	94	47	141	47	+1.4
KNO_3	94	(56)	(150)	(38)	+0.6
$\frac{1}{2}K_2SO_4$	94	(85)	(179)	(9)	−1.0
$\frac{1}{2}CaCl_2$	207	65	272	142	+4.5
$\frac{1}{2}Ca(NO_3)_2$	207	(56)	263	(151)	+6.7
$\frac{1}{2}BaCl_2$	174	65	239	109	+4.7
$\frac{1}{2}Ba(NO_3)_2$	174	(56)	230	(118)	+3.0

shown in Fig. 5, that is, $\triangle$(itv)* is larger as $\triangle U$ increases.

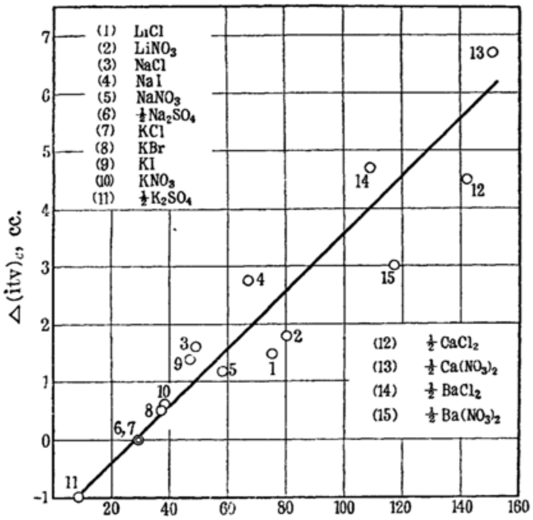


Fig. 5.

Concerning the acidity of boric acid solution, the following three principal features have been discovered;

(1) complex formation with polyalcohol⁽¹⁾⁽²⁾

(2) polymerization of itself in concentrated solution⁽³⁾

(3) present neutral-salt effect.

In virtue of the effort to obtain the consistent explanation of these three features, the author has reached the following conclusion:

(A) Since the electron configuration in boron atom is $(1s)^2(2s)^2(2p)^1$, it could be bound in either of two ways; that is, tricovalent bond as trimethyl boron $B(CH_3)_3$ molecule (pyramidal) or of tetracovalent bond as fluoroboronate ion $(BF_4)^-$ (tetrahedral). Actually, the various structures, which are derived from the above principal bond, are reasonating.⁽⁵⁾

(B) The structure of crystalline boric acid is considered, from the various facts,⁽⁵⁾ to be a resonance form mainly among the tetravalent plane structures (Fig. 6) accompanied with the separation of formal charge, rather than tricovalent.

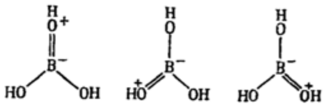
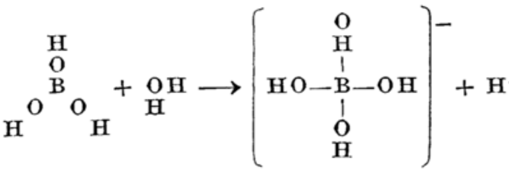


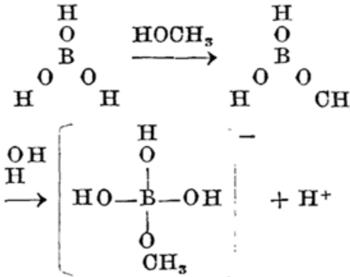
Fig. 6.

Therefore, when there are favourable circumstances for the separation of the formal charge of bond as in H_3BO_3 and $(BF_4)^-$, boron prefers to be bound in tetracovalent. In the case of aqueous solution of boric acid, the separation of charge becomes more easy in the process of electrolytic dissociation (complete separation of charge):



This is the mechanism of electrolytic dissociation of H_3BO_3, although it is very weak. The unstabilization accompanied slightly with the complete separation of charge can be cancelled by the increase of bond energy of regular tetrahedral bond which may be larger than that of the deformed tetravalent plane structure of H_3BO_3 molecule.

(C) When methyl alcohol coexists in an aqueous solution of boric acid the combination can form the methyl ester of boric acid more or less by the dehydrating action owing to the strong affinity of methyl alcohol to water. The separation of formal charge in the molecule of this ester becomes more difficult. Consequently, the bond nature should be inclined to tricovalent and becomes more unstable (for an example $B\cdot(OCH_3)_3$ molecule). But, if the ionization of methyl ester is easy, it can be stabilized by the possibility of complete separation of charge (*i.e.*, ionization) and of formation of regular tetracovalent bond.



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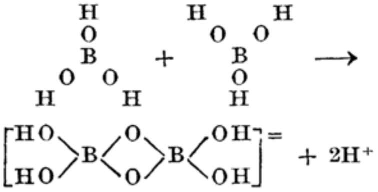
(5) L. Pauling, "The Nature of the Chemical Bond".

The ester formation and the ionization are parallel in this example, because any system should be existing in the most stable state. This is the acidifying mechanism of these compounds and their mixtures, and it depends mainly on the possibility of ester formation. Aceton and dioxan may have the sufficient affinity of water, but not the possibility of ester formation, therefore, they can not show the acidifying effect, but are rather negative.

(D) The fact that the acidity of the more concentrated aqueous solution of boric acid is larger than the value predicted from the law of mass action in the dilute solution is considered to be caused from polymerization.(3) According to the author's theory, this is the expectable result of the cooperative separation of charge to form a regular tetracovalent bond, for an example:



(E) Since the water molecule in the salt solution is hydrated strongly by the ion as in Fig. 7, the water molecule behaves like the OH radical in polyalcohol or the O atom in the aceton and dioxan molecule in the neighborhood of the cation or anion, respectively. In a more concentrated neutral-salt solution, these two tendencies are counter-balancing, according, to the relative strength of hydration of cation and anion.

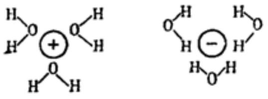


Fig. 7.

When the hydration of cation is greater than that of anion, the water molecule of the solution may behave like polyalcohol, and for the above reasons (A, B, C and D) the acidity of boric acid is increased. On the contrary, when the anion hydrates the water molecule more strongly than cation, the water molecule behaves like aceton or dioxan and rather decreases the acidity of boric acid solution.

This is the mechanism of the acidifying effect of neutral-salt solution. The author will give the quantitative explanation in detail later on.

Summary

The acidifying effect of various solutions (CH_3OH, $C_2H_4(OH)_2$, $C_3H_5(OH)_3$, $C_6H_8(OH)_6$, their mixture, CH_3COCH_3, $O(CH_2CH_2)_2O$, and neutral-salts) is measured by the alkali-titration method, and the simple relation between the hydration energy of neutral-salts and their acidifying effect is found. The consistent explanation for these phenomena is proposed on the view of the nature of the tricovalent and tetracovalent bond of boron atom.

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