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TITRATION OF BORIC ACID
IN AQUEOUS SOLUTION
A STUDY OF SOME TITRATION VARIABLES

Livermore, California

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SUMMARY

The effects of varying the mannitol concentration, type of ions, ionic concentration, and temperature on the titration of aqueous solutions of boric acid with NaOH were studied. The volume of titrant and the pH at the equivalent point were determined from potentiometric curves and by calculating the second derivative of the curve. Data are presented to show that the pH of the solution at the equivalent point may vary from 6.3 to 9.2. The use of potassium hydrogen phthalate rather than boric oxide to standardize the titrant is discussed.

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Boric acid, which seems to have an abnormal ionization constant ($K_a 10^{-10}$ to 10^{-8} , depending upon concentration), is rarely titrated with a strong base.¹ In general some compound is added to an aqueous solution to increase the acidity, so that the titration may be performed with greater ease and accuracy. The effect(s) of the addition of such compounds, ionic strength, and temperature upon the potentiometric titration have been examined as well as the determination of the end or equivalence point.

Various workers²⁻⁴ have shown that variations in the ionic strength effect the pH at the equivalence point. The K_a of a boric acid solution can be shifted to 10^{-4} by the addition of calcium chloride.⁴

Generally some polyalcohol is added to a boric acid solution to obtain a complex acid, which tends to titrate as a strong acid. Many investigators^{3,5} have examined different polyols and the effect of their concentration as related to the equivalence point. In this report the effect of the polyalcohol, mannitol, has been studied.

*This work was performed under the auspices of the U. S. Atomic Energy Commission.

The temperature effect was studied because the apparent ionization constant of the boromannitol complex seemed to change with temperature variation. Mention has been made¹ that the stability of this complex varies with temperature.

Accuracy of "fixed" pH is dependent upon the reproducibility of the equivalence potential as well as a full knowledge of the titration curve. Advantages of using the method of the second derivative potentiometric titration² were investigated.

To obtain the greatest accuracy the effect(s) of the above mentioned variables must be considered. If boric oxide is used to standardize the base, then the method of preparing the oxide assumes a critical role.⁶

APPARATUS AND REAGENTS

A Beckman Zeromatic pH meter with a glass electrode and a calomel, glass sleeve, electrode, standardized with Beckman pH 7 and pH 10 buffers, was used. Burettes were small bore, 25 ml capacity, and graduated to 0.05 ml. Reagents used were:

Sodium hydroxide, 0.2 molar, carbonate free, prepared from Hellige certified sodium hydroxide concentrate (Hellige, Inc., Garden City, N. Y.), stored in a 2-liter reservoir protected from carbon dioxide by an "Ascarite" absorption tube.

Baker and Adamson reagent grade boric acid, lots No. T-159 and T-052.

Baker and Adamson reagent grade mannitol having no NaOH blank.

Baker and Adamson reagent grade $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$, LiCl, and NaCl.

NBS Primary Standard potassium hydrogen phthalate (KHP).

Merck Primary Standard KHP.

Approximately 0.2 molar boric acid solution prepared with Baker and Adamson reagent grade boric acid lot T-052.

PROCEDURES

The pH meter was standardized with Beckman pH 7 and pH 10 buffer solutions. The temperature compensation of the pH meter was set manually at each temperature. The pH was recorded to the nearest 0.05 pH unit, and is accurate to the nearest 0.10 or better. All solutions were prepared with freshly boiled deionized water. Salts to give the desired ionic concentration were weighed and dissolved in 100-125 ml of water. The pH was adjusted to pH 7.0 with dilute HCl or NaOH. Boric acid was added by pipette, and the volume adjusted to 150 ml. The calculated amount of mannitol to give the desired mole ratio in the mannitol variation studies was weighed and dissolved before starting the titration. All titrations were done at ambient temperature ($22^{\circ}\text{C} \pm 2^{\circ}\text{C}$) except the temperature variation studies. The temperature was controlled to $\pm 2^{\circ}\text{C}$ in the temperature studies by placing the sample beaker in a large water bath controlled by a hot plate or ice bath. A 16:1 mannitol to boric acid mole ratio (approximately saturated at 0°C) was used in the temperature variation studies. An excess of mannitol (so that a small amount remained undissolved at the end of the titration) was used in all other titrations. Approximately four millimoles of boric acid were titrated with 0.2 molar NaOH unless otherwise noted. The pH of the solution vs volume of NaOH was recorded to obtain a potentiometric curve. Small increments (0.05 ml) of base were added near the end point. The volume of NaOH and the pH at the equivalence point were determined by calculating the second derivative and/or graphically⁷ from a plot of pH vs volume of base.

RESULTS AND DISCUSSION

Effect of ionic strength

Martin and Hayes³ reported that the apparent ionization of boric acid in aqueous solution increases with increasing concentration of Ba, Li, and Ca ions. They studied the effect of Na ions from 0.0 to 0.25 molar NaCl on the titration of boric acid and reported a negligible effect in that range.

Frank² found that the pH of stock boric acid solutions titrated in saturated mannitol solution varied from pH 8.0 to pH 8.2 at the equivalence point. When relatively large concentrations of Na, Ca, and Cl ions were added, the pH at the equivalence point shifted from pH 6.8 to pH 7.2.

The ionic strength of Ca ion is so noticeable that Schäfer and Sievert⁴ were able to develop a method for titrating boric acid in a solution saturated with CaCl_2 . It is of interest to note that no polyol was used.

Figure 1 shows the effect of the three salts, sodium, lithium, and calcium chloride, upon the equivalence point as the concentration is varied from zero to four moles. Table I indicates the effect of varying salt concentration on the slope of the potentiometric titration curve.

Mannitol concentration

Martin and Hayes³ state that the pH at the equivalence point is dependent on the polyalcohol concentration. Hollander and Rieman⁸ have shown that varying the mannitol to boric acid mole ratio will effect the pH at the equivalence point. They have also shown its effect on the precision of the mannitol-borate titration using a visual indicator. They found that the pH varied from pH 9.70 to pH 7.65 as the mannitol concentration was increased from a 2:1 mole ratio to 64:1 in a 100-ml volume at the end of the titration.

In general we have confirmed their findings. Figure 2 shows that the pH at the equivalence point varied from pH 9.90 to pH 7.85 as the mannitol concentration was increased from a 2:1 mole ratio to 37:1 in a 150-ml volume at the start of the titration. Figure 3 shows the marked variation of volume of NaOH required to titrate equal amounts of boric acid to fixed pH values as a function of mannitol concentration.

The effect of temperature

The effect of temperature on any pH measurement is inherent in the basic equation for potentiometric measurements:

$$E = E^{\circ} + 2.303 \frac{RT}{nF} \text{ pH.}$$

Kolthoff and Stenger¹ further point out that the stability of the boro-polyalcohol complex varies with changing temperature. Therefore, the effect of temperature variation on the boro-mannitol titration from 0 to 60°C was studied. Figure 4 shows that both the magnitude and the slope of the potentiometric break decreases with increasing temperature from 0 to 60°C. The pH of the solution after the addition of a given volume of titrant also increases with increasing temperature except in the immediate vicinity of the equivalence point, where the pH is essentially the same.

The effect of temperature upon the volume of base needed to titrate the same concentration of boric acid to a given pH is shown in Fig. 5.

Determination of the equivalence point

Lingane⁷ indicates the advantages of second-derivative potentiometric titrations and shows that the accuracy of fixed pH titrations depends upon the reproducibility of the equivalence point potential. Frank² has recently reviewed the mannitol-borate titration and recommends second-derivative

potentiometry as a means of avoiding end point error. Data presented in this report shows that the pH at the equivalence point may vary as much as 3.5 pH units. Therefore, only full curve and second-derivative potentiometry was used in this study.

Table II tabulates data obtained from nine titrations in which both methods of determining the end point were used in each titration. The standard deviation is 0.076 mg of boron for the second-derivative method and 0.078 mg for the full curve method. There is no statistically significant difference between the two methods. However, for manual titrations, the second-derivative method is more convenient.

Standardization of sodium hydroxide

Judson⁶ has reported difficulty in preparing 100% boric oxide for use in standardizing sodium hydroxide. He found that boric oxides prepared from several sources of boric acid were about one part per thousand low compared to KHP. His efforts to purify the boric acid by recrystallization resulted in increasing the impurities. He also reported that leaching the boric oxide in hot water caused a loss of two to three parts per thousand. Frank² reported that he prepared boric oxide, which averaged 0.3 parts per thousand low, as standardized vs KHP.*

In this study, three attempts were made to prepare pure boric oxide. Five samples of approximately 0.250 g of boric acid were used each time. In the first two trials Baker and Adamson reagent grade boric acid, lot number T-052 and T-152, was heated in platinum crucibles for 3 hours in a furnace

* However, in a private communication, Frank states that the above statement is a misprint and should have read 0.3% low.

set at 800°C. The crucibles were cooled in a desiccator, weighed in air, and the boric oxide leached in hot deionized water. The crucibles were re-ignited to 800°C, cooled in a desiccator and then weighed. The weight difference was taken as boric oxide. Using the normality for NaOH obtained from standardization with NBS and Merck KHP, the boric oxide from lot T-052 averaged $99.65\% \pm 0.2\%$ SD and that from lot T-152 averaged $99.70\% \pm 0.2\%$ SD. In the third trial, boric acid from lot T-052 was treated as above except that it was heated to 900°C for 4 hours and leached in freshly boiled deionized water at 20°C. The boric oxide averaged $99.74\% \pm 0.15\%$ SD.

Several titrations of individual weighings of approximately 4 mM of Merck KHP, lot number 52263A, 99.9% pure, were titrated in 150-ml aqueous solution, 150-ml saturated mannitol solution, and 150-ml 1.0 M LiCl and saturated with mannitol. The NaOH solution averaged 0.2017N, 0.2018N, and 0.2016 N, respectively, for the three sets of titrations (see Table III).

The accuracy of the standardization of basic solutions with boric oxide is compared with a primary standard acid by most investigators. Data presented here show that errors of a few tenths of a percent may be encountered when NaOH is standardized with boric oxide. We recommend the use of KHP for standardization since it can be obtained with the necessary certification of purity and requires no further preparation for use.

One or more of the new organoboron compounds may, after sufficient investigation, prove to be a much better material for a standard than boric acid, boric oxide, or tetraborate. At present this Laboratory is investigating some of these compounds.

CONCLUSIONS

Loss of precision and errors are inevitable when titrating to any fixed pH unless the variables, mannitol concentration, type of ions, ionic concentration, and temperature are carefully controlled. It is possible to adjust these variables to obtain an equivalence point pH in the range of 6.3 to 9.2.

Potentiometric titrations with the equivalence point determined from the potentiometric curve or determined by calculation of the second derivative of the potentiometric curve give good precision over the range of variables studied. However, at least a 16:1 mole ratio of mannitol to boron and a temperature below 25°C is recommended to obtain a steep slope on the curve.

A good boron standard is not available at present. This Laboratory has been unsuccessful in preparing boric oxide for the standardization of the base with the desired accuracy and precision, and, therefore, has used KHP to determine the normality of the sodium hydroxide. It is advisable to carry boric acid of known purity through the sample treatment as a check on the procedure.

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TABLE I

The effects of NaCl, LiCl, and CaCl₂ upon the slope of the potentiometric curve at the equivalence point. Numbers given are the pH change per 0.05 ml of 0.2 N NaOH.

	<u>Salt concentration (moles/liter)</u>					
	0	0.25	0.50	1.0	2.0	4.0
NaCl	1.15	1.20	1.10	1.10	1.10	1.20
LiCl	1.15	1.00	0.95	0.90	0.90	0.80
CaCl ₂	1.15	0.75	0.58	0.35	0.33	0.30

TABLE II

Comparison of boron recovery by (1) equivalence point determination from the potentiometric curve and (2) calculation of the second derivative.

Data from calculating the second derivative					Data from full potentiometric curve		
B taken (mg)	B found (mg)	Diff. (mg)	pH _{ep}	$\Delta\text{pH}_{\text{ep}} / 0.05 \text{ ml}$	B found (mg)	Diff. (mg)	pH _{ep}
10.805	10.843	+0.037	7.63	1.30	10.858	+0.053	7.65
21.610	21.692	+0.082	7.52	1.25	21.716	+0.106	7.82
32.416	32.516	+0.100	8.02	1.20	32.531	+0.115	7.98
43.221	43.215	-0.006	7.80	1.15	43.193	-0.028	7.78
43.221	43.182	-0.039	7.81	1.00	43.171	-0.050	7.85
43.221	43.178	-0.043	7.82	1.20	43.171	-0.050	7.75
43.221	43.174	-0.047	7.89	1.25	43.150	-0.071	7.78
43.221	43.257	+0.036	8.19	1.30	43.233	+0.012	7.85
64.832	64.970	+0.138	8.06	1.00	64.953	+0.121	8.08

TABLE III

The effect of mannitol and ionic concentration on the titer of standard NaOH solution.

Solution	Number of determinations	$\Delta \text{pH}_{\text{ep}}$ / 0.05 ml, average	Average pH_{ep}	pH_{ep} range	Normality	Standard deviation
Aqueous	5	1.23	8.75	8.67-8.91	0.2017	0.0003
Saturated mannitol	6	0.81	8.23	8.03-8.34	0.2018	0.0008
Saturated mannitol 1 M in LiCl	6	0.74	7.70	7.50-7.96	0.2016	0.0001

Fig. 1. Effect of ionic strength. Solutions saturated with mannitol after addition of salt. Final volume of solution approximately 170 ml.

Fig. 2. Effect of mannitol concentration. All titrations done at $22 \pm 2^\circ\text{C}$ using 4 mM boric acid in an initial volume of 150 ml. Titration performed with 0.2023 N NaOH. Volume at end of titration was approximately 170 ml.

Fig. 3. Effects of mannitol concentration vs volume of titrant (base) in fixed pH titrations.

Fig. 4. Effect of temperature on the titration of boric acid with sodium hydroxide.

Fig. 5. Effect of temperature vs volume of titrant (base) at the end of the titration.

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