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A pH Effect of Hydroxyl Group
Containing Compounds

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Brief::

Hydroxyl containing compounds have the ability to affect pH by generally increasing the acidity, the degree of increase depends on the number of hydroxyl groups on the compound.

This result is not consistent with any known theory.

Abstract:

Compounds containing hydroxyl groups are shown to have the effect of lowering the pH of acid type solution when the compound contains more than three hydroxyl groups, and it is observed that the greater the number of hydroxyl groups on the compound, the greater the increase in the hydrogen ion activity as measured by a glass electrode. It was further discovered that the effect of raising the hydrogen ion activity is greatest in the more acid solutions. Increasing the ionic strength of the buffers also enhanced this hydrogen ion activity increase. No explanation has been discovered to account totally for the observations.

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Franks and Ives (1) recently have published a review on alcohol-water mixtures which indicated that the alcohols interact with water in at least two different ways as is reflected in data from entropies and heats of mixing, water activities, Cp studies, etc.. And failure of the Hammett H_0 and H_- functions at high concentrations of alcohol in water observed by Gutbezahl and Grunwald (2) would also indicate peculiar behavior of the alcohol-water association. Consequently the behavior of alcohols

and, in general, hydroxyl containing compounds in aqueous solutions must receive some special attention.

The approach of this paper will be to attempt to demonstrate peculiarities of polyhydroxyl compounds on the pH of dilute aqueous solutions. An anomalous effect of sucrose in 0.1 M HCl of raising the hydrogen ion activity (a_H) was first observed by Jones and Lewis (3) and in NaOH by Smolenski and Kozlowski (4). Also Colvin (5) observed a slight increase in a_H for glycerol in NaOH. These effects are anomalous because a higher a_H is not what one would anticipate from the Hammett considerations as expanded by Bates (6) and is not compatible with the mono-alcohols--specifically ethanol and methanol as observed by Haynes (7).

One way of correlating these two "anomalous" phenomena, i.e. the odd behavior of alcohol solutions at high concentrations and the increased acidity of aqueous polyhydroxyl solutions is merely to note that the hydroxyl concentration is very large in each case. Whereas the concentration of hydroxyls for ethanol at one molal is only one molal, the concentration for one molal sucrose is 8 molal in hydroxyls. And if the observations of Franks and Ives are correct, and the hydroxyl is indeed the culprit, the influence of the hydroxyl should be amplified by the polyhydroxyl compounds such as sucrose or glycol as compared to the monohydroxyl compounds such as ethanol or methanol.

Hence, approaching the problem using the pH meter would be a very simple and fairly direct method of observing some of the complications of hydroxyl groups in solution. A typical result of this approach is presented in figure 1. Here the results of earlier workers is confirmed and at the same time a uniformity is seen to be attached to the behavior of aqueous polyhydroxyl solutions--the greater the number of hydroxyls the greater the slope of their acidity increase.

Materials and Methods:

Most of the experiments consisted of adding specified amounts of solute to a buffered solution of 0.10 molar ionic strength and calculating the resulting concentration of the solute on a molal basis. The pH of the buffered solution was in general made near or at the pK of the weak acid or weak base except in the obvious cases of water and HCl. The buffers and acids were prepared with double distilled water in the conventional manner using only potassium salts. All the substances used were at least as pure as Fisher certified grade reagents. Sucrose was dried at approximately 65°C in an oven over night before the experiment. To check the effect of purity of sucrose an experiment was carried out in phosphate buffer in which sucrose which was only dried was compared to sucrose which had been twice recrystallized as well as dried; the comparison indicated that further purification was of little use.

All the experiments were done in the temperature range of 20-22°C, using a model 1019 Beckman research pH-meter with a calomel-glass electrode pair (Beckman glass electrode No. 41263). The experiments were all of a differential nature, i.e., the pH-meter was standardized against a standard buffer of known pH and all readings for a particular system were made in relation to this one individual standardization at the same temperature and within a very short time.

All readings were made in air within an hour of the addition of the solute to the buffer. To check the effect of changing carbon dioxide solubility in the solution upon addition of substrate, a duplicate experiment was carried out. In this experiment pH measurements were first made on sucrose-HCl solutions in air; then pH measurements were made in an air-tight chamber through which clean nitrogen gas was passed over the HCl solution for fifteen minutes with occasional stirring before sealing the cell with silicone grease at the gas inlet. The results when plotted together showed no appreciable difference between the two indicating that there is no appreciable change due to CO₂ solubility upon solution of sucrose in HCl.

An experiment to determine the effect of sucrose on pure water was also carried out using essentially the same nitrogen flow technique given above, except the water sample was distilled, boiled, sealed and then cooled to remove as much as CO₂ as possible before being anaerobically transferred to the cell. Even in this case an increase in the a_H occurred upon the addition of

sucrose. The slope of the obtained line is included in figure 7 in order to show the relative size of this effect compared to the results in various 0.10 ionic strength solutions.

The data were plotted a_H versus molality of substrate and found to be very close to a straight line up to a concentration of one molal--however, these lines are definitely not rectilinear. Yet the rectilinearity is sufficient enough to provide a good parameter to quantify the effect.

Results:

The hydroxyl series: By far the most important fact arising from this research is that the hydrogen ion activity increase seems to be dependent on the number of hydroxyl groups on the solute molecule--the more hydroxyl groups on the solute molecule the greater the acidifying effect of the solute molecule. Hence a series is formed by the hydroxyl containing solutes which is readily observed in a plot of the slopes due to the various solutes in the same buffer versus the number of hydroxyl groups on the different solute molecules (see figures 4, 5, and 6). This phenomenon seems to be independent of the system used--whether it be buffer or any otherwise nonreactive aqueous solution. One observes that for the substrates containing three or less hydroxyl groups there is no increase in the hydrogen ion activity but instead either no change or a decrease in the hydrogen ion activity. This decrease is especially prominent in hydroxylamine buffer.

Of special interest is the alcohol series. Here dilution and dielectric effects are most evident, i.e., a lowering of a_H occurs with the decrease in dielectric constant and the increase of dilution. In general the mono-alcohol with the larger alkane group has the lower dielectric constant at the same molal concentration (8) and the effect of the dielectric variation is observed in figure 4. This effect indicates that molecular size is probably not the criterion to base the increase in the a_H due to the sucrose, dextrose, etc.--since the increase of the size of the highly soluble alcohols apparently depresses rather than raises the a_H .

Variation of effect with acidity: Another unusual fact found in these experiments is that the magnitude of the effect depends on the degree of acidity of the system used. The best illustration of this fact is a graph of the common logarithm of the slopes of the sucrose curves in systems of various pH values made using the results of sucrose in HCl, acetate buffer, cacodylate buffer, phosphate buffer, hydroxylamine buffer and the result of Smolenski and Kozlowski in NaOH (4) (figure 7). All of these readings were carried out in systems of 0.10 ionic strength for the buffer or strong electrolyte. The fact that a plot of \log_{10} (slope) versus pH_0 (pH_0 being the pH of the solution with molality of sucrose at zero) yields a fairly smooth line is startling--especially since the increase in a_H due to added solute is greatest in the region of greatest a_H indicating that the effect is "autocatalytic."

Not appropriate

Ionic strength effects: The effect of ionic strength on the increase in the a_H due to sucrose additions was carried out in phosphate buffer at various ionic strengths obtained by dilution of a 1.00 molar ionic strength solution. The slopes of the various lines obtained for phosphate buffers of different ionic strength were plotted against the ionic strength. The resulting graph (figure 8) indicates that the effect tends to increase with the ionic strength. An experiment with acetate buffer confirmed this (figure 9). However, Smolenski and Kozlowski found for NaOH solutions of sucrose an opposite effect, i.e., the greater the NaOH concentration the smaller the increase in the a_H . This disparity can be explained at least partially by the fact that in the acetate buffer and phosphate buffer the pH is almost the same at any concentration since the ratio of acid to salt is always nearly the same, but in the case of NaOH the pH changes greatly with dilution and as may be seen from figure 7--if the pH of the solution becomes lower with the decreasing concentration of NaOH the change in the hydrogen ion activity increases.

Exceptions: Rimbach and Ley (10) have observed an a_H rise in boric acid and molybdic acid upon addition of glycerol not typical of the pattern observed in this paper. Figure 10 gives the result of an experiment for glycerol and sucrose in boric acid performed in the manner of this paper. These effects are much greater than those observed in the other buffers and

glycerol yields a greater increase in the hydrogen ion activity than sucrose which is the opposite of the effect observed in the other buffers. The abnormality of boric acid is fairly well known. R.J. Cann (11) observed anomalous results involving proteins with borate buffers. Frei & Solcova (12) has given evidence that boric acid has a coordination type binding with oxygen containing solutes. Hence one must be aware of the different chemical interactions of the buffers.

Discussion:

There seems at the moment to be no way to clarify the situation using conventional arguments. The following is a tabular presentation of possible conventional explanations and their refutations as seen by the author.

Hammett expressions:

The Hammett expressions as expanded by Bates (6) require the acidity to vary with the dielectric constant of the aqueous solution. Since the dielectric constants of all the solutions studied decrease with increasing hydroxyl solute concentration, the acidity should decrease only. However, acidity may either increase or decrease depending on the specific solute as may be seen in figures 1, 2, and 3.

Mole fraction dilution and hydration effects: Mere dilution should decrease the activities of all ions provided the solute used to dilute the buffer solutions is relatively

non-ionizing compared to the most ionized solute. Obviously this situation is not the case since the a_H increases in the instance of sucrose. Hydration would do the same in pure water, where the uptake of water would drive the reaction $H^+ + OH^- = H_2O$. Again this is not observed. Hydration in a buffer solution would drive this same reaction; however, with the presence of an extra source of hydrogen ions in the case of an acid buffer or an extra source of hydroxyl ions in the case of a basic buffer one would expect an increase in the a_H with the acid buffer and a decrease of the a_H with the basic buffer. However, the acidity increases in all cases for sucrose and the expected hydration effect is inconsistent.

Liquid-junction effects: Extensive studies are not available for the effect of sucrose or glycerol on glass electrodes or liquid-junctions. Gelsema et al (13) have observed that this effect is small for dilute aqueous solutions of alcohols. Jones and Lewis (3) and also Colvin (5) have observed the effect for sucrose and glycerol respectively using the hydrogen electrode indicating that the results of the glass electrode is not an artifact. Also it was possible to observe the effect in sucrose-phosphate solutions using the colored indicator 2-(2,4-dinitrophenylazo)-1-naphthol-3,6-disulfonic acid sodium salt.

Since none of these explanations seem adequate it seems necessary to specify an interaction between the hydroxyl bearing solute and water or water's ions.

The Franks and Ives review indicates the same conclusion; however, the interaction was left rather unspecified except for the entropic interaction. The properties observed in this paper are as follows:

1. The greater the number of hydroxyl groups on a compound, in general, the greater the acidifying effect of that compound.
2. The smaller the pH, the greater is the effect of the compound in raising the activity of the hydrogen ion.
3. Buffering the aqueous solution with acid type buffer does not check the increase in the hydrogen ion activity and even tends to abet the increase.

Having assigned such properties to the interaction of hydroxyls with water one must question the validity of sucrose as a mere polyhydroxyl compound since sucrose has two ring oxygens as well. Sucrose was used primarily to emphasize the observed effects since the disparities were greatest for it. Also the solubilities for simple polyhydroxyl compounds such as inositol are limited, again indicating an advantage of sucrose with its rather large solubility. And even if the data of sucrose are ignored the hydroxyl series still stands--sucrose appearing to be an extension of the data portrayed in graphs 4, 5, and 6 of the simple alcohols, glycol, glycerol, etc.

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Figure 1: Plots of hydrogen ion activities of various hydroxyl-containing substrates vs. the molality of the hydroxyl-containing substrate in 0.10 molar ionic strength phosphate buffer. Note: The value of the hydrogen ion activity when molality is zero is the hydrogen ion activity of the buffer alone and is a common point on all the lines. This also applies to figures 2 and 3.

Figure 2: Plots of hydrogen ion activity of various hydroxyl-containing substrates vs. the molality of the hydroxyl-containing substrate in 0.10 molar ionic strength hydroxylamine buffer.

Figure 3: Plots of hydrogen ion activities of various hydroxyl-containing substrates vs. the molality of the hydroxyl-containing substrate in 0.10 molar HCl.

Figure 4: Plot of the slopes of the various hydrogen ion activity curves of figure 1 vs. the number of hydroxyl groups of the substrate for 0.10 molar ionic strength phosphate buffer. Note that dextrose possesses an anomeric hydroxyl group which has been reported to have a pK of 12.5 which makes dextrose a special case when compared to the other hydroxyl containing solutes. (9).

Figure 5: Plot of the slopes of the various hydrogen ion activities of figure 2 vs. the number of hydroxyl groups of the substrate for 0.10 molar ionic strength hydroxylamine buffer.

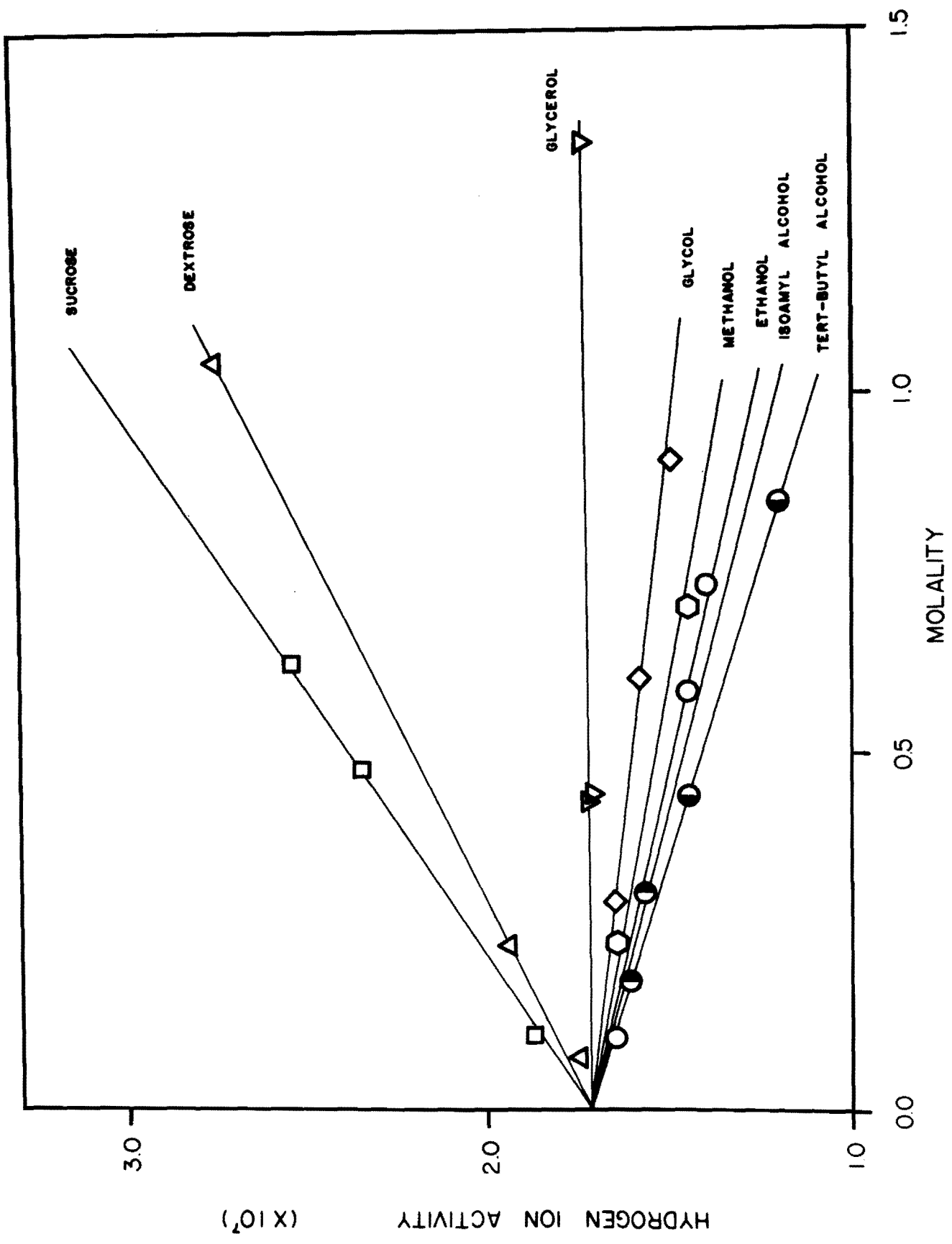
Figure 6: Plot of the slopes of the hydrogen ion activity curves of figure 3 vs. the number of hydroxyl groups of the substrate for 0.10 molar HCl.

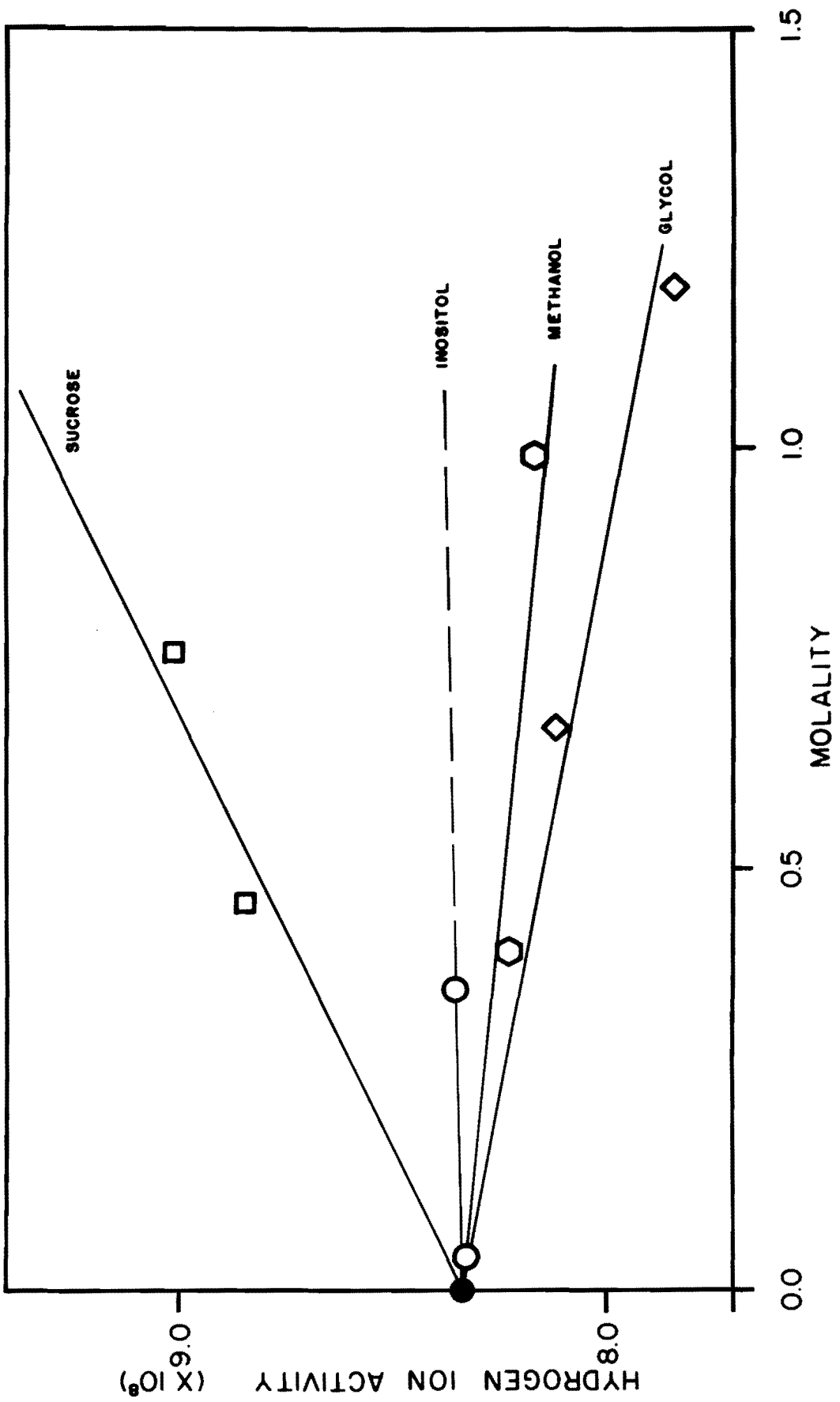
Figure 7: Plot of the slopes of the sucrose curves in the various 0.10 molar ionic strength systems (except water which was purified as described in the text) vs. the pH of the sucrose free system. (The data for NaOH are those of Smolenski and Kozlowski, who measured sucrose concentration in normality rather than molality.)

Figure 8: Plot of the slopes of the hydrogen ion activity curves of figure 11 vs. the ionic strength of the phosphate buffer.

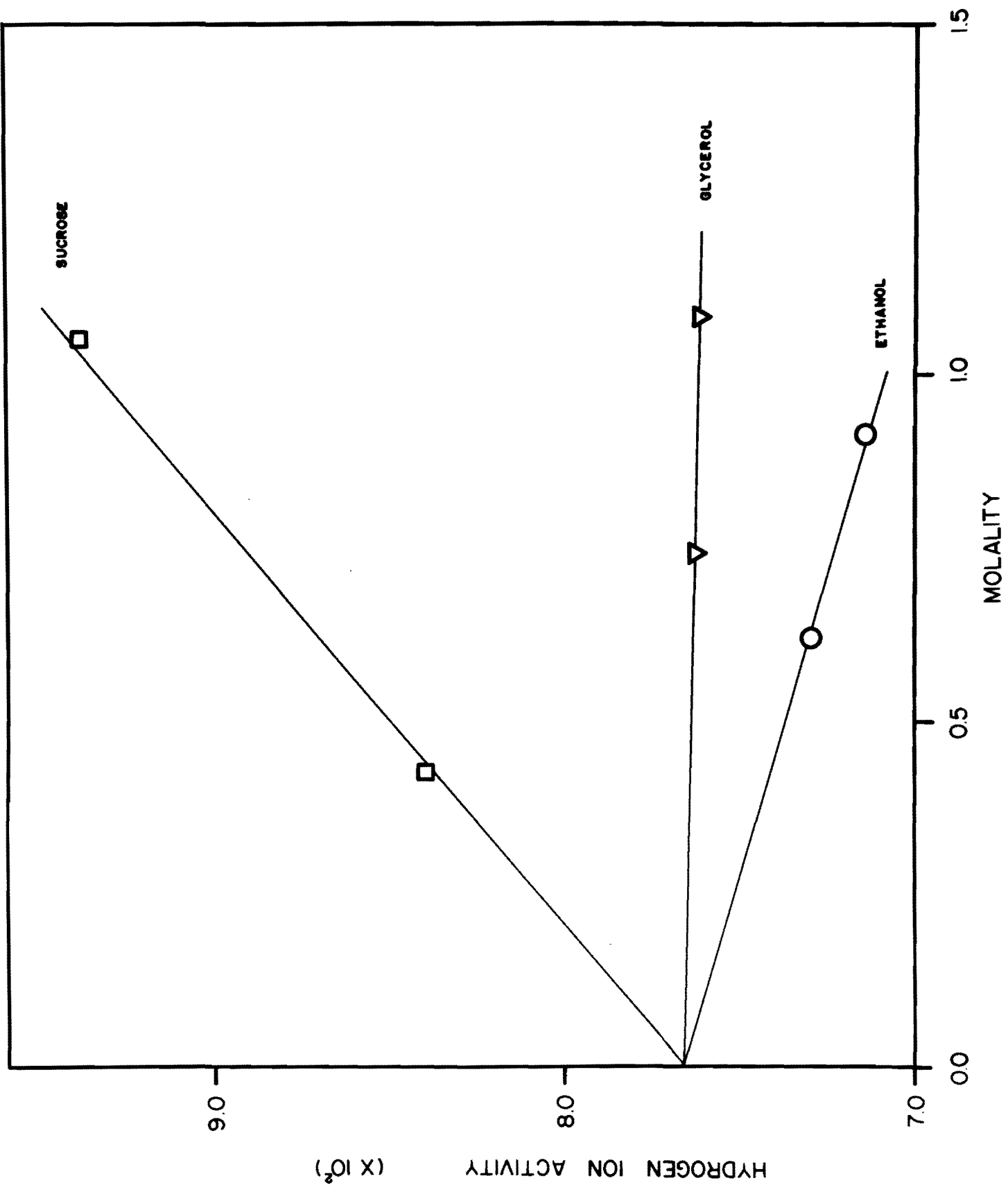
Figure 9: Plot of the slopes of the hydrogen ion activity curves for various ionic strength acetate buffers ($\text{pH}_0 = \text{pK}$) vs. the ionic strength of the acetate buffer.

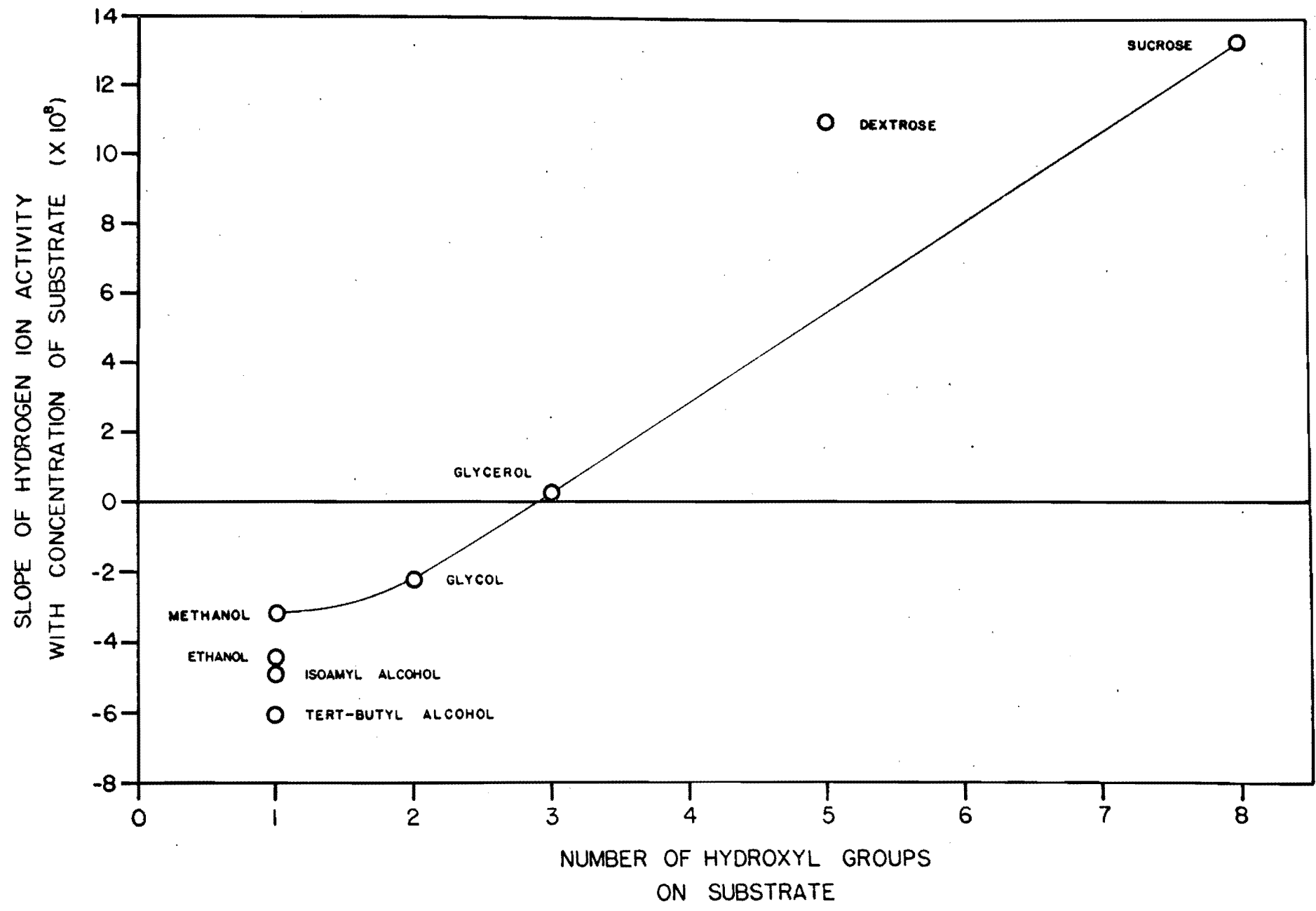
Figure 10: Plots of hydrogen ion activities of glycerol and sucrose vs. their molalities in 0.10 molar ionic strength borate buffer.



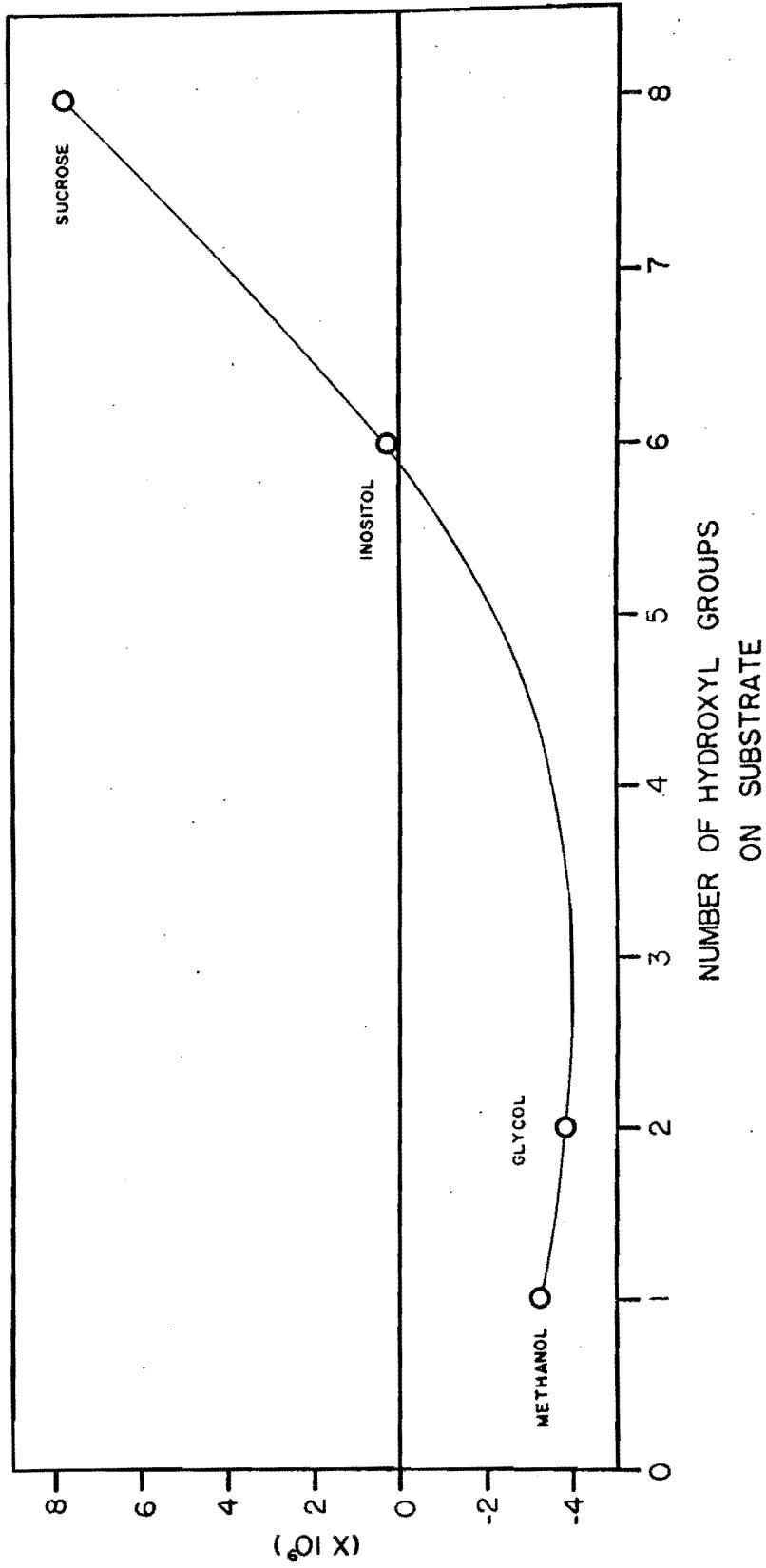


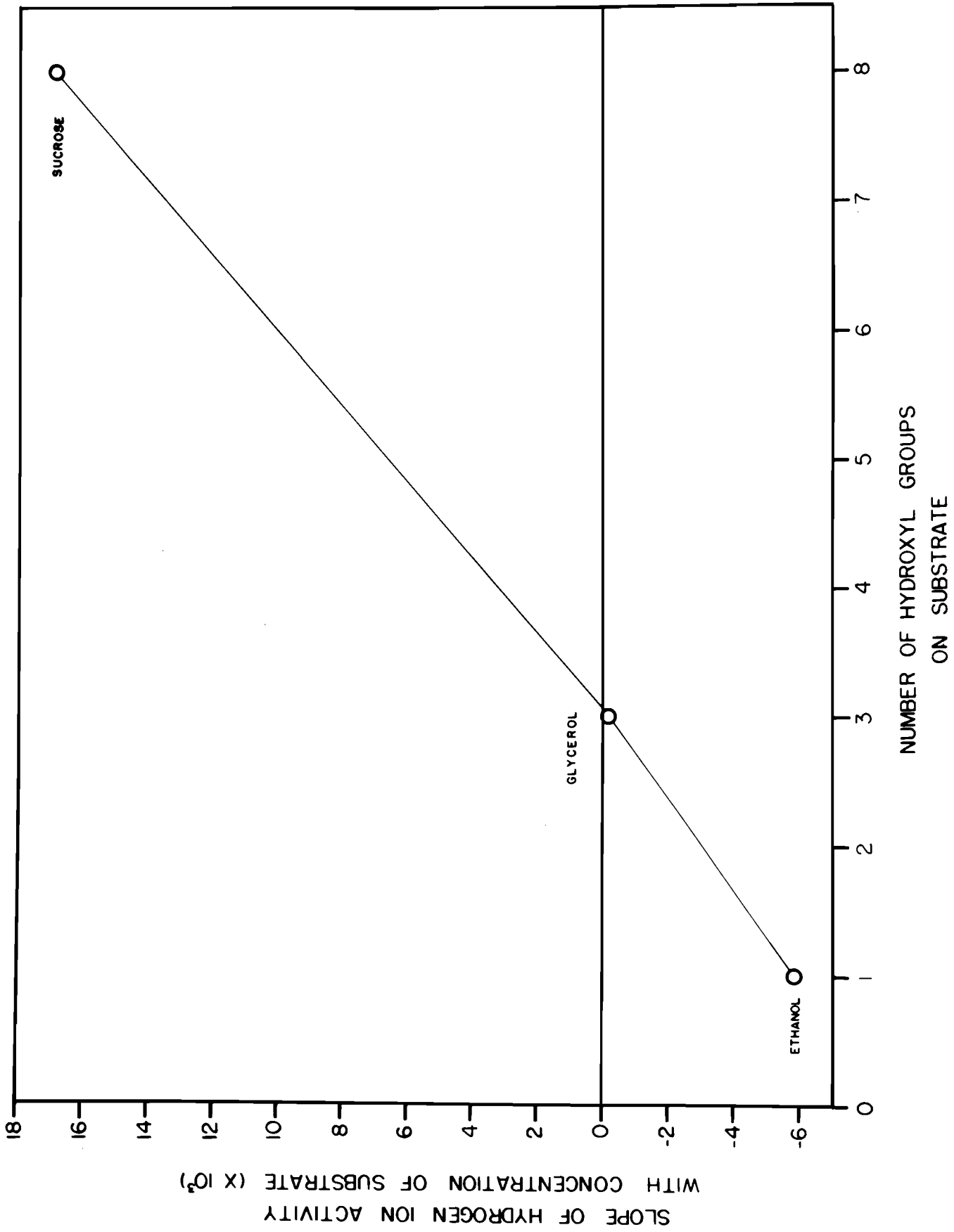
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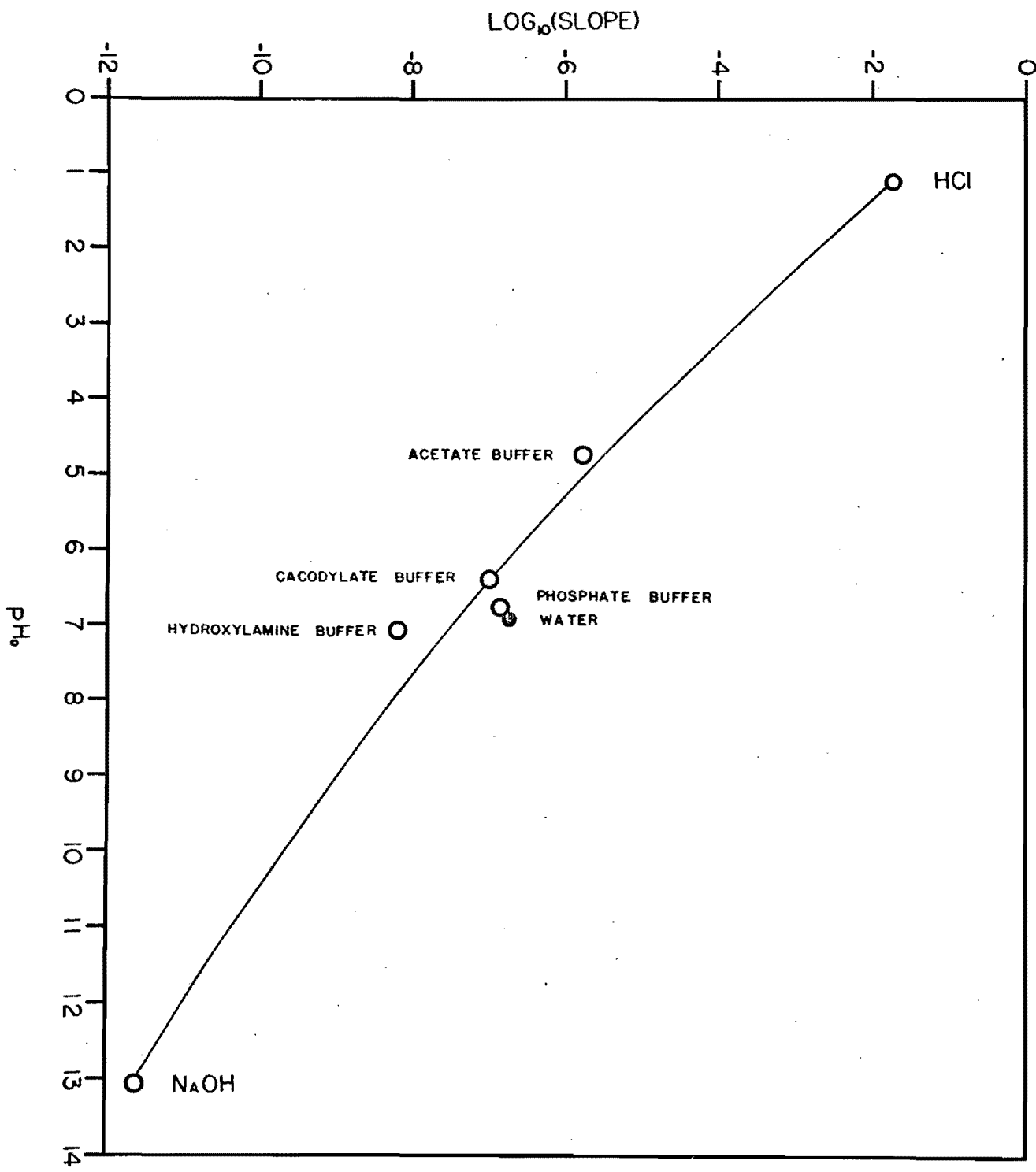




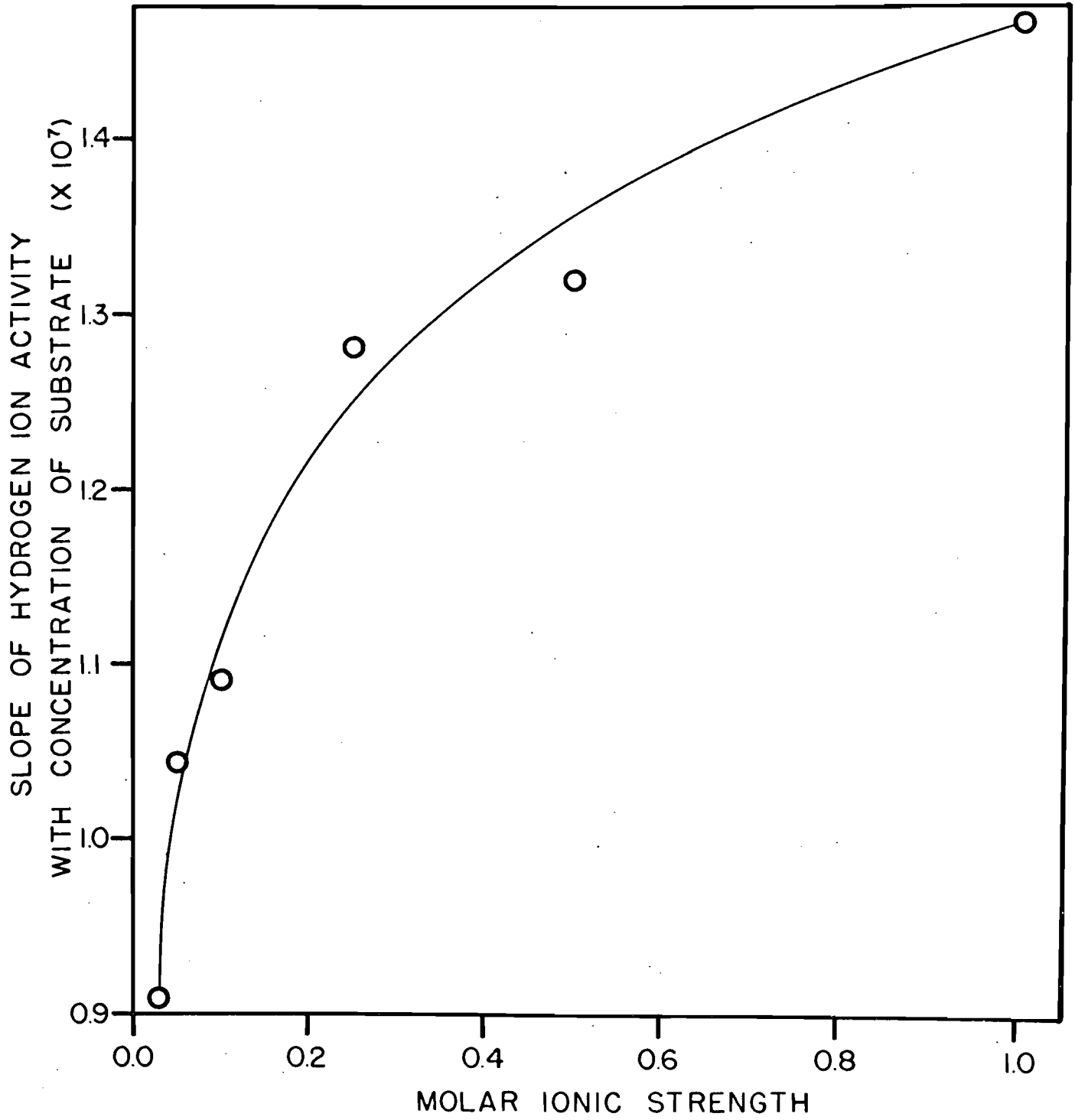
SLOPE OF HYDROGEN ION ACTIVITY
WITH CONCENTRATION OF SUBSTRATE







JH



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