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The Interaction of Bentonite and Glass with
Aqueous Media

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Summary

It has been demonstrated that Si(OH)_4 is an important constituent of bentonite. In bentonite's natural state the Si(OH)_4 in the bentonite is permeable to the diffusible components of the aqueous medium in contact with it. As a consequence, the pH of the medium is a sensitive function of its ionic strength. Permeability of the Si(OH)_4 to salt is lost, however, by pretreatment of the bentonite with dilute acid to protonate fully the Si(OH)_4 . The pH-producing property of the Si(OH)_4 then is associated with its surface properties.

The glasses (ABS-39 and ABS-Y Marcoule) studied in this research program also contain hydroxylated oxide as an important constituent. These materials, however, are not observed to exhibit gel-like (three-dimensional) properties prior to or after acid pretreatment. Instead they function always as a surface (two-dimensional) and are impermeable to the diffusible components of the aqueous media that come in contact with them. As a result, the pH of the medium is dependent on ionic strength only so far as it affects the counter-ion screening efficiency of the charged surface.

In both systems, bentonite and glass, the pH of the medium is affected by the presence of CO_2 . The lowering of medium pH by CO_2 dissolution results in the neutralization of Si(OH)_4 in the untreated bentonite gel phase or in the surface of the acid pretreated bentonite or glass in contact with the medium. If glass and bentonite are in contact the action of CO_2 at their interface results in both systems striving to reach different equilibria. The result is enhanced chemical reactivity at the interface. To minimize such reactivity CO_2 must be excluded from the atmosphere in contact with the solid-liquid phases.

Introduction

i. The Differentiation Between a Two-Dimensional (surface) and Three-Dimensional Array (gel) of Polymeric Assemblies.

Potentiometric titrations of weakly acidic polyelectrolytes with identical functional groups yield results which depend strongly on the ionic strength of the aqueous medium and the physical state of the macromolecule (1). For linear polyelectrolytes, plots of $\text{pH} - \log \alpha/(1-\alpha)$ versus α based on data obtained at different ionic strengths result in a series of curves that converge at $\alpha = 0$ (where α is the degree of ionization of the polyacid). This characteristic property of linear polyelectrolytes is illustrated by Fig. 1 (2) and is explained as follows: The pH of a weakly acidic polymer is a function of the change in electrostatic free energy that accompanies the ionization process and can be expressed (2) as

$$\text{pH} = \text{pK}_{(\text{HA})_\nu}^{\text{int}} + \log \frac{\alpha}{1-\alpha} + \frac{0.434}{kT} \frac{\partial F}{\partial \alpha} \quad [1]$$

where $\text{pK}_{(\text{HA})_\nu}^{\text{int}}$ is the negative logarithm of the intrinsic dissociation constant of the weakly acidic group that is repeated ν times, α is the fraction of the total number of ionizable groups that are dissociated, and F is the electrostatic free energy of the system. The free energy change accompanying ionization is equal to the work of removing a proton from its ionized site to infinity against electrostatic forces of other charged groups. This makes the free energy change equal to the electrostatic potential energy at the surface of the polymer molecule and Eq. [1] can be rewritten as

$$\text{pH} = \text{pK}_{(\text{HA})_\nu}^{\text{int}} + \log \frac{\alpha}{1-\alpha} + 0.434 \frac{\epsilon \Psi(a)}{kT} \quad [2]$$

where $\psi_{(a)}$ is the potential at the polymer surface. Rearranging Eq. [2]

$$\text{pH} - \log \frac{\alpha}{1-\alpha} = \text{pK}_{(\text{HA})_{\nu}}^{\text{int}} + 0.434 \frac{e\psi_{(a)}}{kT} \quad [3]$$

since

$$\text{pH} - \log \frac{\alpha}{1-\alpha} = \text{pK}_{(\text{HA})_{\nu}}^{\text{app}} \quad [4]$$

and

$$\text{pK}_{(\text{HA})_{\nu}}^{\text{app}} = \text{pK}_{(\text{HA})_{\nu}}^{\text{int}} + 0.434 \frac{e\psi_{(a)}}{kT} \quad [5]$$

Thus, a plot of $\text{pH} - \log \alpha/(1-\alpha)$ versus α extrapolated to zero-charge conditions ($\alpha \rightarrow 0, \psi_a \rightarrow 0$) will, for any ionic strength, yield $\text{pK}_{(\text{HA})_{\nu}}^{\text{int}}$. The effect of ionic strength upon such a plot derives from its influence upon the value of ψ_a as α is varied. The extrapolated $\text{pK}_{(\text{HA})_{\nu}}^{\text{int}}$ value can be expected to be an insensitive function of ionic strength much as with simple mononuclear acids (e.g., acetic acid). Olander and Holtzer (3) have considered this aspect and the divergence of $\text{pK}_{(\text{HA})_{\nu}}^{\text{int}}$ with ionic strength that can be expected is within the uncertainty limits of the extrapolations to $\alpha = 0$.

For crosslinked polyelectrolytes (gels) the plots of $\text{pH} - \log \alpha/(1-\alpha)$ versus α for different ionic strengths result in a series of parallel curves and no convergence is observed at $\alpha = 0$ (Fig. 2a). At this point, it is important to realize that this system is most closely comparable in its equilibrium properties to a solution of the linear polyelectrolyte separated from simple salt solution at various concentrations by a membrane impermeable only to the macromolecule. By restricting partially the entry of water through osmosis by the tension of a flexible spring attached to the membrane the gel, simple salt system is approximated. To express properly

the potentiometric properties of the polyelectrolyte in this situation the activity of the H^+ ion in the polyelectrolyte phase must be used in Eqs. [3] and [4]. Similarly with the gel the activity of H^+ in the gel, (H_g^+) , must be employed in Eqs. [3] and [4]:

$$pH_{(g)} - \log \frac{\alpha}{1-\alpha} = pK_{(HA)_v}^{int} + F\psi_{(a)}/RT \ln(10) \quad [3a]$$

and

$$pH_{(g)} - \log \frac{\alpha}{1-\alpha} = pK_{(HA)_v}^{app} \quad [4a]$$

Since (H_g^+) is not directly accessible experimentally it must be calculated. Marinsky and Slota (4) have recently shown that in a system consisting of a solution of strong acid, HX, and its salt, MX, in equilibrium with a gel the distribution of M^+ and H^+ between the solution and gel phases is given by

$$\frac{(H^+)}{(M^+)} = \frac{(H_g^+)}{(M_g^+)} \quad [6]$$

Combining Eq. [6] with Eq. [3a] one obtains on rearrangement

$$pK_{(HA)_v}^{int} = pH - \log \frac{\alpha}{1-\alpha} + p(M_g^+) - p(M^+) - F\psi_{(a)}/RT \ln(10) \quad [3b]$$

The value of (M_g^+) , like the value of (H_g^+) , is not measurable and must be calculated. For this purpose $[M_g^+]$, the concentration of M^+ in the gel phase, is obtained first in the following way: The volume, $V_{(g)}$, of the gel phase is measured and a charge balance, based on (1) the stoichiometry of the neutralization reaction and (2) the requirement that the condition of electroneutrality be satisfied, is made to define the quantity of M^+ entering the gel during neutralization of $(HA)_v$. Imbibement by MX of the gel phase, presumed

accountable by a simple Donnan equilibrium, corrects for the introduction of additional M^+ . By introducing the value of $[M_g^+]$, so computed, into Eq. [3b]

$$\begin{aligned} pK_{(HA)_v}^{int} &= pH - \log \frac{\alpha}{1-\alpha} + p[M_g^+] - \log y_{M_g^+} \\ &- p(M^+) - F\Psi_a/RT \ln(10) \\ &= pK_{(HA)_v}^{app} - F\Psi_a/RT \ln(10) \end{aligned} \quad [3c]$$

and plots of $pK_{(HA)_v}^{app}$, so defined, versus α , obtained from experiments at low ionic strength (and thus negligible imbibement of the gel by MX), when extrapolated to intercept the ordinate axis at $\alpha = 0$ will yield the $pK_{(HA)_v}^{int}$ value of the repeating monomer unit, deviations from ideality being expected to vanish when the gel surface charge is zero.

The procedure, as outlined, has been applied to a crosslinked polymethacrylic acid gel (Amberlite/IRC-50, Rohm and Haas Company) and to a Sephadex gel (C-50-120, Sigma Chemical Company), using dilute sodium polystyrenesulfonate solution in place of simple dilute electrolyte (MX). The $pK_{(HA)_v}^{int}$ values of 4.83 and 3.25, respectively, that are resolved (4) are in excellent agreement with the $pK_{(HA)_v}^{int}$ values obtained for their linear analogues (2,5) demonstrating the validity, as well as the utility, of this approach. Indeed, this approach, when applied to the potentiometric data obtained with the sphagnum peat, NaCl system (1), leads as shown in Fig. 2b to convergence of the parallel lines (Fig. 2a) that resulted when these data were examined earlier.

To demonstrate how great the discrepancy between $pK_{(HA)_v}^{app}$ values computed directly from the measured solution pH (Eq. [3]) and the model-deduced $pH_{(g)}$ (Eq. [3c]) can be these two sets of values

obtained for the polymethacrylic acid gel system are plotted in Fig. 3 as a function of α .

With the above criteria available for classification of bentonite and glass as a two- or three-dimensional aggregate the potentiometric properties of bentonite and glass samples were studied as a function of the ionic strength of aqueous media in contact with them. The results of these studies are presented in the next section of this report.

Experimental and Results

For the pH measurements in this study an Orion Research Micro-processor Ion Analyzer (901) Instrument was used together with a Radiometer combination electrode (GK 2321 C). Prior to and after the potentiometric measurements the glass electrode was calibrated with standard buffer solutions over the pH range of the study. A precision Scientific Model 154 constant temperature bath maintained the temperature of the solution at $25.0 \pm 0.1^\circ\text{C}$. A CO_2 -free atmosphere over the sample was sought by covering the surface of the solution with N_2 gas. A 2.5 ml Roger-Gilmont ultra precision micrometer buret (accuracy $0.1 \mu\text{l}$) was used to dispense titrant in a majority of the experiments.

The Orion potentiometer was also used for the chloride ion concentration measurements. A Corning NAS11-18 sodium-ion selective electrode, Catalog No. 476210, was used in combination with a saturated calomel reference electrode to facilitate these analyses. A porous glass frit separated the M-nitrate solution containing the Na^+ -ion selective electrode from the calomel electrode compartment to which standard AgNO_3 solution was added just prior to titration with the chloride solution to be analyzed. Each end point was defined by the maximum rate of change in potential observed with addition of chloride solution.

i. Preparation of Bentonite for Study

Several 100 gram samples of the bentonite received from KBS for study were dispersed separately in 5.0 M NaCl or 4.5 M NaOAc solutions, respectively. Successive batch equilibrations with the

5.0 M NaCl in the one instance and with 4.5 M NaOAc in the other were carried out to assure complete conversion to the Na^+ ion form. After sufficient cycling of the respective bentonite samples in the NaCl and NaOAc solutions the bentonite product was washed free of supernatant solution by immersion first in distilled, deionized water. As the aqueous wash medium became more dilute in salt content with each change of wash water, decantation for separation of phases had to be facilitated by adding ethanol to the wash solutions. The addition of ethanol facilitated rapid settling of the bentonite which otherwise remained suspended in the solution.

The essentially complete removal of occluded NaCl from the bentonite sample was demonstrated by the absence of precipitate when AgNO_3 was added to the final wash solution. To demonstrate the complete removal of Ca^{+2} from the bentonite a small representative sample of the final product was equilibrated with sodium EDTA. Examination of the resultant solution using an atomic absorption measurement showed Ca^{+2} to be present in trace quantity (< 0.01%). The final bentonite products were oven-dried at 110°C to constant weight.

ii. Measurement of Bentonite Water Content at Several Sodium Chloride Concentration Levels.

Water uptake by bentonite in 1.00 M and 5.00 M NaCl solution was measured in the following way. A weighed quantity of the oven-dried bentonite was added to approximately 2 to 3 ml of 1.00 or 5.00 M NaCl in a volume-graduated cylinder. After at least a 48 hour equilibration period supernatant solution was removed for

potentiometric chloride analysis using standard AgNO_3 reagent. The volume of solution and gel as well as the apparent volume of the bentonite gel itself was then measured before dilution of the supernatant solution with a precisely measured quantity of water. The system was briskly agitated to assure complete mixing with solution contained in the spaces between bentonite particles before removal of this supernatant by filtration for a second chloride analysis. The change in solution concentration determined in this manner permitted estimate of the void volume and the gel volume could then be obtained by subtracting this number from the apparent gel volume measured initially. To compute the water content of the bentonite gel the skeletal volume, estimated by dividing the dry weight of the bentonite sample by its density (2.47 g/cm^3), was subtracted from the overall gel volume.

The measurement of water uptake by the bentonite in more dilute (0.010 M and 0.100 M) NaCl solutions had to be obtained by another approach because of their tendency to remain dispersed. Accurately weighed samples of the oven-dried bentonite were added to precisely measured quantities of the NaCl solutions. After equilibration for at least 92 hours the supernatant solution was removed by filtration through several thicknesses of fine filter paper and the concentration of the initial and final solutions was determined by potentiometric titration with standard AgNO_3 . To remove any bias in the measurements additional samples of the bentonite were equilibrated in distilled, deionized water to obtain a correction for elution of any residual sodium chloride remaining in the bentonite sources

after their preparation in 5.0 M NaCl. It was found that the appearance of Cl^- ion corresponded to less than 3% and 0.3% of the initial concentration of the 0.0100 and 0.100 M NaCl solutions used in these experiments. An additional correction for electrolyte imbibement of the gel had to be made as well in the eventual computation of water uptake by the bentonite in these NaCl solutions.

The following equation, employed to facilitate this portion of the research program, is a material balance statement that equates the redistributed salt and solvent with their initial distribution.

$$(M_i)(V_i) = (M_f - M_c)(V_f) + V_g \bar{M}_D \quad [7]$$

In this equation M represents molarity, V represents volume, subscripts i and f refer to the initial and final solutions, subscript c identifies the salt introduced to the solution by the sample and subscript D refers to the Donnan-imbibed salt of the gel identified by subscript g as well as by a bar placed above the molarity symbol. The value of V_g , the objective of this phase of the research is expressed by Eq. [8].

$$V_g = V_i - V_f \quad [8]$$

Only V_f , (V_g) and \bar{M}_D are inaccessible experimentally. To resolve these parameters a reiterative computation program had to be entered. For this purpose a trial estimate of \bar{M}_D is made to permit a first estimate of $V_f(V_g)$. With this value of V_g a better estimate of \bar{M}_D can be sought. At equilibrium

$$a_{\text{NaCl}} = \bar{a}_{\text{NaCl}} \quad [9]$$

$$\text{and } (\bar{y}_+)^2 (\bar{M}_D) (\bar{M}_B + \bar{M}_D) = (y_+)^2 (M_f)^2 \quad [9a]$$

where a and y_{\pm} represent respectively the mean molar activity and the mean molar activity coefficient of the salt in both phases and \bar{M}_B represents the molar capacity of the bentonite, i.e., its Na^+ ion capacity divided by V_g , which corresponds to its water uptake. By presuming y_{\pm} in both phases to be approximately equal and by using the experimentally measured capacity of the bentonite (see next section of this report) a second value of \bar{M}_D can be evaluated. These computations were repeated until an \bar{M}_D value consistent with the V_g value was resolved.

The data obtained, as described above, are presented below in Table I.

Table I. The Water Content of Na Bentonite at Several Different Sodium Chloride Concentrations.

NaCl Concentration	Grams Water/Dry Gram of Na Bentonite
0.010	7.3 ± 0.5
0.100	1.7 ± 0.2
1.00	1.4 ± 0.2
5.00	0.64 ± 0.1

iii. Isotope Dilution Measurement of the Na^+ -Ion Capacity of the Bentonite Samples

Weighed samples of oven-dried bentonite prepared in both 5.0 M NaCl and 4.5 M NaOAc were added to 50.0 gram portions of 0.010 M NaCl to which Na^{22} had been added. The activity per gram of solution before and after addition to the resin samples, equilibrated for at least a 48 hour interval, was measured to facilitate the capacity

determinations. Since small quantities of occluded salt remained with the bentonite from its preparation each equilibrated solution was passed through a column of Dowex-50 resin in the H^+ -ion form. The acid released was completely eluted from the column and the effluent was neutralized with standard base to permit precise assessment of the total quantity (meq) of Na^+ ion in the solution at the end of the isotope dilution experiment. A correction for solvent uptake at the experimental ionic strength was made to facilitate the precise apportionment of Na^{22} between gel and solution as well.

The results of these measurements are listed below in Table II.

Table II. Na^+ -Ion Capacity of Bentonite Samples

<u>NaCl Prepared</u>		<u>NaOAc Prepared</u>	
Sample No.	meq Na^+ /dry gram	Sample No.	meq Na^+ /dry gram
3,4	0.654	11,12	0.724
5,6	0.658	13,14	0.749
7,8	0.648		

The approximately 10% higher capacity of the bentonite prepared in 4.5 M NaOAc is undoubtedly due to the enhanced neutralization of the hydroxylated silica in the bentonite at the higher external pH of the sodium acetate solution.

iiii. The Extent of Bentonite Hydroxylation

It was determined that bentonite, equilibrated with NaCl at various concentrations affected pH values which were higher the

lower the concentration of the NaCl solution. Representative data to demonstrate this behavior are presented below in Table III where the equilibrium pH obtained for bentonite samples suspended in 0.010, 0.10, 1.0 and 5.0 M NaCl, respectively, are listed. These results

Table III. The pH of Aqueous Media in Contact with Sodium Bentonite

Sample	M NaCl	pH Measured
1	0.010	9.820
2	0.10	9.347
3	1.0	8.797
4	5.0	8.329

are believed to be due to the presence of hydroxylated silica as an important constituent of the bentonite. The estimate was that the equilibrium expressed below



controlled this pH behavior (see Introduction), the value of $\text{pH}_g - \text{pNa}_g$ in the gel, defined by the dissociation of $\text{Si}(\text{OH})_4$ and the ion-exchange capacity of the gel, determining the value of $\text{pH} - \text{pNa}$ in the equilibrating salt solution. If the external salt concentration is increased the external H^+ -ion concentration must also increase to equal their concentration ratio in the gel.

A quantitative test of this estimate has been made by examining the data compiled in Table III with the Donnan-based model. The results of this analysis are summarized in Table II. Column 3 of this Table lists the molarity of the Na^+ ion in the gel equilibrated with NaCl at the four different concentration levels. The measured capacity of 0.7 meq of Na^+ ion per gram of oven-dried bentonite, the measured

volume of the gel at each NaCl concentration and the Donnan equilibrium presumed to prevail were employed to yield these molarity assignments. The experimentally measured pH is listed in column 4. A Na-error correction of +0.36 and +0.13 pH units is made for the pH measurements in 5.0 M and 1.0 M NaCl, respectively, in column 5. The pH presumed to prevail in the gel phase is then obtained using these data in Eq.[6] for its computation. Apparently the model presumed to prevail is correct since the gel pH is uniquely defined as it should be.

Table IV. The Bentonite Gel pH in Equilibrium with NaCl Solutions at Different Concentration Levels

Sample	NaCl Conc.	$\overline{\text{Na}}_{(g)}^+$ Conc.	pH _(meas)	pH _(corr)	$\overline{\text{pH}}_g$
1	0.010	0.097	9.82	9.82	8.83
2	0.10	0.435	9.347	9.347	8.71
3	1.0	1.28	8.797	8.93	8.84
4	5.0	5.53	8.329	8.69	8.73

On the basis of this estimate of the situation the extent of silica hydroxylation in the bentonite was analyzed as described herein: Weighed samples of oven-dried bentonite were equilibrated in 50.0 ml of 0.010, 0.100, 1.00 and 5.00 M NaCl solution, respectively. After equilibration 0.010 M HCl was added to each supernatant solution until a pH value of 5.3 to 5.5 was reached. After 24 hours the pH had risen in each sample and a second addition of 0.010 M HCl was needed to readjust the pH to a value of 5.3 to 5.5. This procedure was repeated until the equilibrium pH of each supernatant solution after a 24 hour equilibration period did not exceed a value of

approximately 6. An excess of 0.10 M NaOH was then added and the various bentonite, salt, NaOH mixtures were equilibrated for another 24 hour interval. Aliquot portions of the supernatant solution were then potentiometrically examined during neutralization with standard 0.037 M HCl. Because of the dissolution of CO_2 by the samples during handling the endpoint was defined by the equilibrium pH of H_2CO_3 . The difference between the quantity of base added and the quantity of base remaining presumably yielded the total milliequivalents of $[\text{Si}(\text{OH})_4]_n$ that each particular bentonite sample contained.

The results obtained at the different sodium chloride concentrations examined are summarized in Table V. Some bias appears to

Table V. The Extent of Bentonite Hydroxylation

Salt Concentration	meq of hydrogen/dry gram bentonite
0.0100 M	0.17
0.100 M	0.21
1.00 M	0.21
5.00 M	0.28

enter into the measurement of the $\text{Si}(\text{OH})_4$ content, with hydroxylation content appearing to increase with ionic strength.

iiii. The Potentiometric Behavior of the $\text{Si}(\text{OH})_4$ Constituent of Bentonite

To examine the potentiometric properties of the fully hydroxylated constituent of the bentonite, samples of the oven-dried material were equilibrated, as before, in 0.010, 0.10, 1.0 and 5.0 M NaCl. After

complete conversion of the hydroxylated constituent of each bentonite sample to its acid form with standard HCl was assured by an equilibrium pH in the supernatant solution of ~ 5.7 to 6.0 , aliquot portions of 0.10 M NaOH were added to define different degrees of neutralization (α) in the gel samples for each salt concentration level studied. In order to maintain the salt concentration level constant sufficient solid NaCl was added to compensate for dilution of each sample during the periodic addition of 0.010 M HCl. After at least a 24 hour interval of equilibration the pH of each supernatant solution was measured. These pH data are plotted in Fig. 4 versus the quantity of standard base employed. A positive correction of 0.36 and 0.13 pH units has been incorporated in the pH values reported for the 5.0 and 1.0 M NaCl systems.

The similarity observed in Fig. 4 of the potentiometric properties of the hydroxylated constituent of these bentonite samples at the different salt concentration levels was completely unexpected. The independence of pH characteristics on ionic strength that is observed in the course of the neutralization with base was, for example, not observed with the untreated bentonite (refer to Tables III and IV). The conclusion from these results has to be that the hydroxylated silica constituent of bentonite, after acid treatment, has become impermeable to electrolyte and behaves as a two dimensional surface. Apparently the acid treatment, in which external pH is never lower than 5.1 , results in the elimination of the porosity obtained with the untreated natural sample. This result may be a consequence of dissolution of $\text{Si}(\text{OH})_4$ in the protonation step.

The pH value reported in Fig. 4 could not be maintained during an additional period of equilibration because of the inadvertent sorption of CO_2 during subsequent periodic pH measurements and the ultimate pH value employed to construct the apparent pK versus α plot in Fig. 5 was obtained just prior to separation of an aliquot portion of each supernatant solution for analysis of the residual base. Only the potentiometric data obtained with the 5.0 and 1.0 M NaCl systems could be used, however, to facilitate this presentation of the data because separation of the bentonite from the supernatant solution was not sufficiently rapid in the more dilute systems. The supernatant solution of the more dilute dispersions had to be separated by filtration through several thicknesses of fine filter paper. In the course of the time-consuming filtration step additional reaction occurred because of CO_2 dissolution and the measured pH prior to the separation step was no longer applicable.

For the computation of pK with Eq. [1] the base remaining in an aliquot sample of each supernatant solution was determined potentiometrically by titration with 0.010 M HCl. The endpoint of each titration was defined by the pH expected for the H_2CO_3 containing solutions.

Assignment of a capacity of 0.18 meq per dry gram of bentonite appeared to yield a reasonable correlation of the data. The ordinate intercept value of the curve drawn leads to an assignment of 9.4 to the intrinsic pK of the $\text{Si}(\text{OH})_4$ constituent of bentonite. This value is in good agreement with a pK assignment of 9.4 published for silicic acid in the literature (6).

iiiiii. Preparation and Examination of Glass Samples

The investigation of the protolytic behavior of two different glass sources (ABS-39 and IBS-Y) was, because of the brief time interval available to this study, much less exhaustive and complete. Only the procedures employed under sections iii. and iiii. were resorted to in the examination of the glasses, which were reduced to a coarse powder before sampling.

The pH data obtained after equilibration of coarsely powdered samples of the less durable ABS-39 glass (12 days) and the more durable ABS-Y Marcoule (ABS-118 Studvick) glass (5 days) in 0.010, 0.10, 1.0 and 5.0 M NaCl solution, respectively, are presented below in Table VI. Samples during this study were stored in a CO₂-free atmosphere to facilitate employment of these extended equilibration periods.

The absence of any sizeable difference in the pH of the two most dilute solutions would appear to indicate that the hydroxylated oxide constituent of these glasses behaves like a two-dimensional charged surface which is impermeable to electrolyte. In the inflexible glass matrix there is no expansion or contraction to change gel volume as electrolyte concentration is changed and had the hydroxylated oxide exhibited three-dimensional gel properties a pH difference of one unit should have been encountered going from the 0.010 M to the 0.10 M NaCl system. The difference in pH values actually observed at the different ionic strengths of the systems under investigation is most probably a consequence of the difference in screening efficiency by the external electrolyte. At high ionic strength the highly charged negative surface of the glass is more effectively screened by the

electrolyte counterions to yield a lower measured pH in solution.

Table VI. Ph Data Obtained During Equilibration of Glass Samples
in NaCl Solutions at Different Concentration Levels

ABS-39 Glass			
Sample	NaCl Conc.	pH _(meas)	pH _(corr)
1	0.010 M	9.214	9.214
2	0.10 M	9.100	9.100
3	1.0 M	8.692	8.82
4	5.0 M	8.175	8.54
ABS-Y Marcoule (ABS-118 Studvick) Glass			
1	6.010 M	8.684	8.684
2	0.010 M	8.672	8.672
3	0.10 M	8.665	8.665
4	0.10 M	8.684	8.684
5	0.10 M	8.732	8.732
6	1.0 M	8.582	8.71
7	1.0 M	8.641	8.77
8	1.0 M	8.535	8.67
9	1.0 M	8.617	8.74
11	5.0 M	7.763	8.12
12	5.0 M	7.784	8.14
13	5.0 M	7.690	8.05

In addition to the pH measurements reported in Table VI potentiometric titration data were obtained with coarsely powdered samples from the two glass sources after careful and complete

protonation of their hydroxylated oxide surface using the procedure employed earlier with the bentonite samples. These data are presented in Figs. 6 and 7.

The data obtained with the ABS-39 glass in Fig. 6 yield a consistent picture. We see that the pH tends to diverge with decreasing ionic strength as the surface charge increases with neutralization of the hydroxylated surface. This result is attributable to the loss in screening efficiency by counterions as the salt concentration increased.

It is interesting to note as well that the pH values of 9.18, 8.94, 8.72 and 8.60 interpolated for the 0.010, the 0.10, the 1.0 and the 5.0 M NaCl systems, respectively, in Fig. 6 after an addition of 0.125 meq of base per gram of glass are not too different from the pH values of 9.214, 9.10, 8.82 and 8.54 obtained from measurements with the glass samples prior to any acid preconditioning.

The data obtained with the ABS-Y Marcoule glass (Fig. 7) do not yield a self-consistent picture. It is apparent that in our preparation of the protonated surface of this glass we managed, in a number of instances, to incorporate excess positive charge on the glass surface, probably as $\text{Si}(\text{OH})_4 \cdot \text{H}^+$ and a number of the pH points measured are, as a result, lower than expected.

Discussion

Both bentonite and glass have hydroxylated metal oxides as an integral component of their chemical composition. In bentonite the predominant hydroxylated oxide is $(\text{H}_4\text{SiO}_4)_n$ as evidenced by the measurement in this research program of an intrinsic pK of approximately 9.4, a value in excellent agreement with the pK value assigned by Busey and Mesmer (6) to the first ionization step in mononuclear silicic acid, H_4SiO_4 . The hydroxylated silica exhibits gel-like properties, the pH of aqueous media in contact with the bentonite being a sensitive function of the ionic strength. With full protonation of the hydroxylated silicon oxide by its careful neutralization with a strong acid, eg., HCl, the potentiometric properties of the bentonite become much less sensitive to the ionic strength of the medium to indicate conversion by the acid treatment of the $\text{Si}(\text{OH})_4$ from a three-dimensional aggregate (gel) to one with two-dimensional (surface-) dominated properties.

The hydroxylated metal oxides of the glasses, however, never appear to exhibit gel-like behavior. In our research program the pH of the aqueous media in contact with the glass was quite insensitive to ionic strength. There was, as the ionic strength of the aqueous medium in contact with the glass was decreased, an increasing positive divergence in the pH values measured as the degree of neutralization in the hydroxylated metal oxide was increased. Indeed this result is typical of two-dimensional charged surface domination of the potentiometric properties of an aqueous medium in contact with it;

upward divergence in pH with lowered ionic strength of the medium at a fixed surface charge is a consequence of less effective screening of the surface charge by the counterions at the lower ionic strength.

The most critical aspect of the pH dependence of aqueous media in contact with bentonite or glass is the sensitivity of the equilibrium between the aqueous medium and the hydroxylated oxide (gel or surface) to the presence of CO_2 in the atmosphere above the solid, solution phases. The dissolution of CO_2 , enhanced by the initial high pH of the aqueous phase, has to lead to increased protonation of the hydroxylated oxide. In turn the increasing presence of carbonate and bicarbonate must lead to preferential withdrawal of carbonate and bicarbonate complexed metal ions (eg rare earths, alkaline earths) from the bentonite and the glass. When both glass and bentonite are in layered contact the effect of CO_2 sorption at the interface is to enhance the above tendencies for reaction. Since the hydroxylated oxide components of the bentonite and glass do not yield the same equilibrium pH to the solution in contact with it the tendency in the presence of CO_2 will, on striving to reach equilibrium, result in attainment of a steady state. The driving force for continued reaction, being enhanced in this way, it is reasonable to expect a more continuously reactive situation at the bentonite, glass interface than with the bentonite or the glass alone in an otherwise similar environment.

To demonstrate the enhancement of reactivity in bentonite and glass that the presence of CO_2 introduces plots of solution pH as a function of time are presented in Fig. 8 for bentonite and glass samples suspended in 0.010 M NaCl. In one set of measurements the

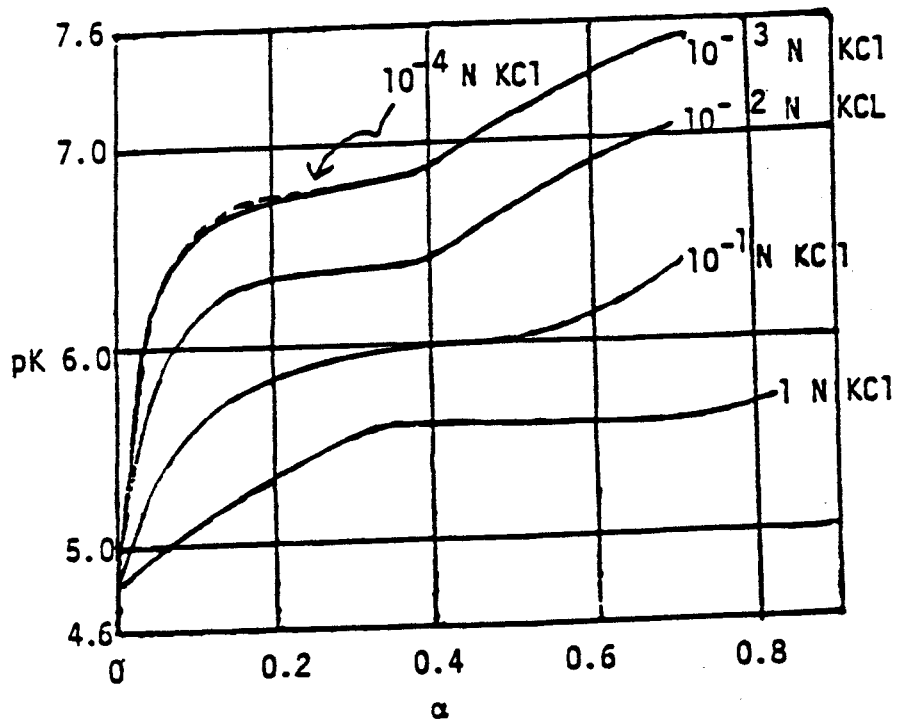
bentonite and glass were contacted with the NaCl in loosely stoppered containers. In the other set of measurements the samples were carefully sealed and stored in a CO₂-free atmosphere. The presence of CO₂ in the equilibrating solution of the loosely stoppered system is documented by the potentiometric titration curve obtained during neutralization of the solution phase with standard HCl at the end of an experiment (Fig. 9). This curve is typical of a NaHCO₃, H₂CO₃ mixture.

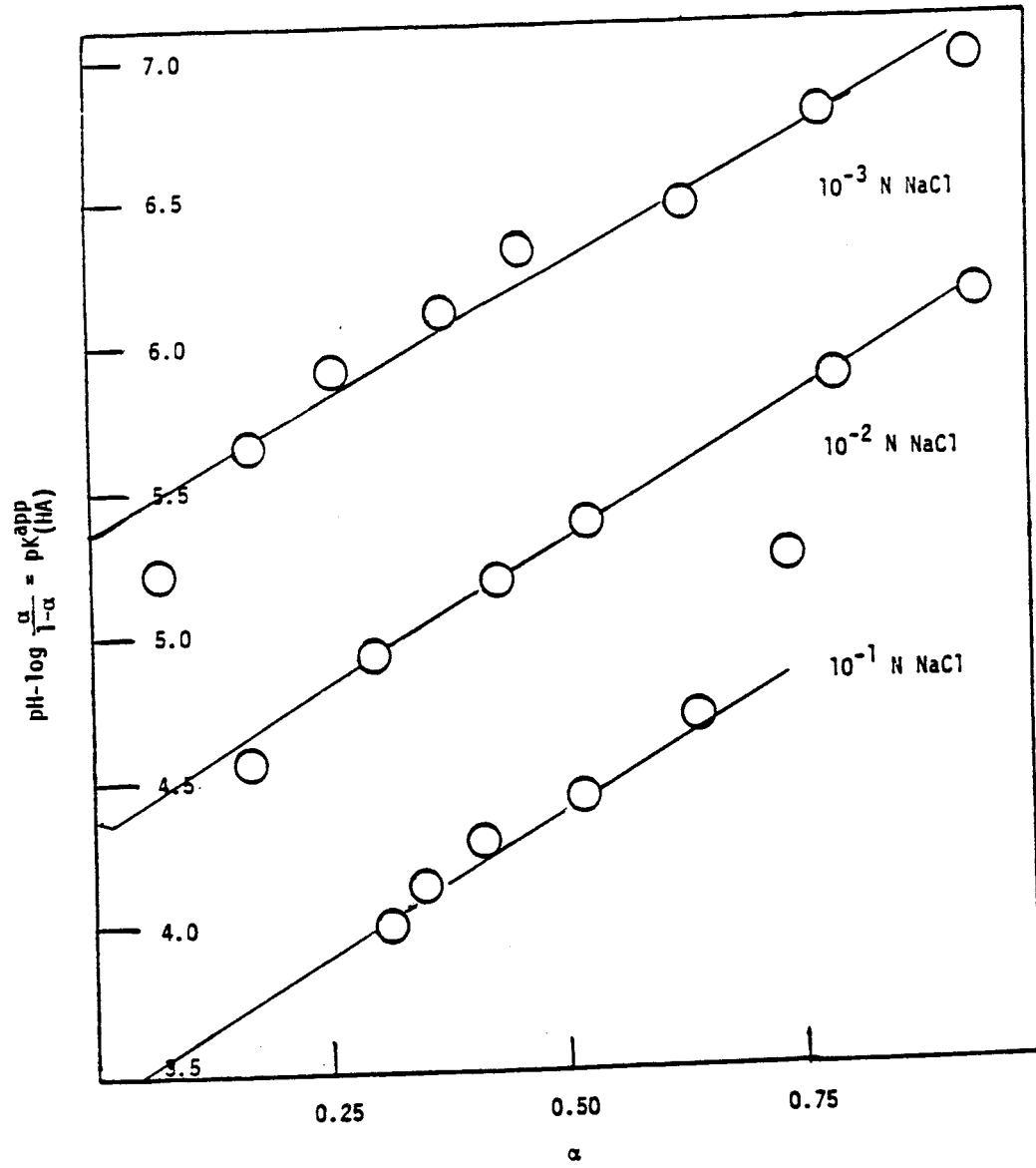
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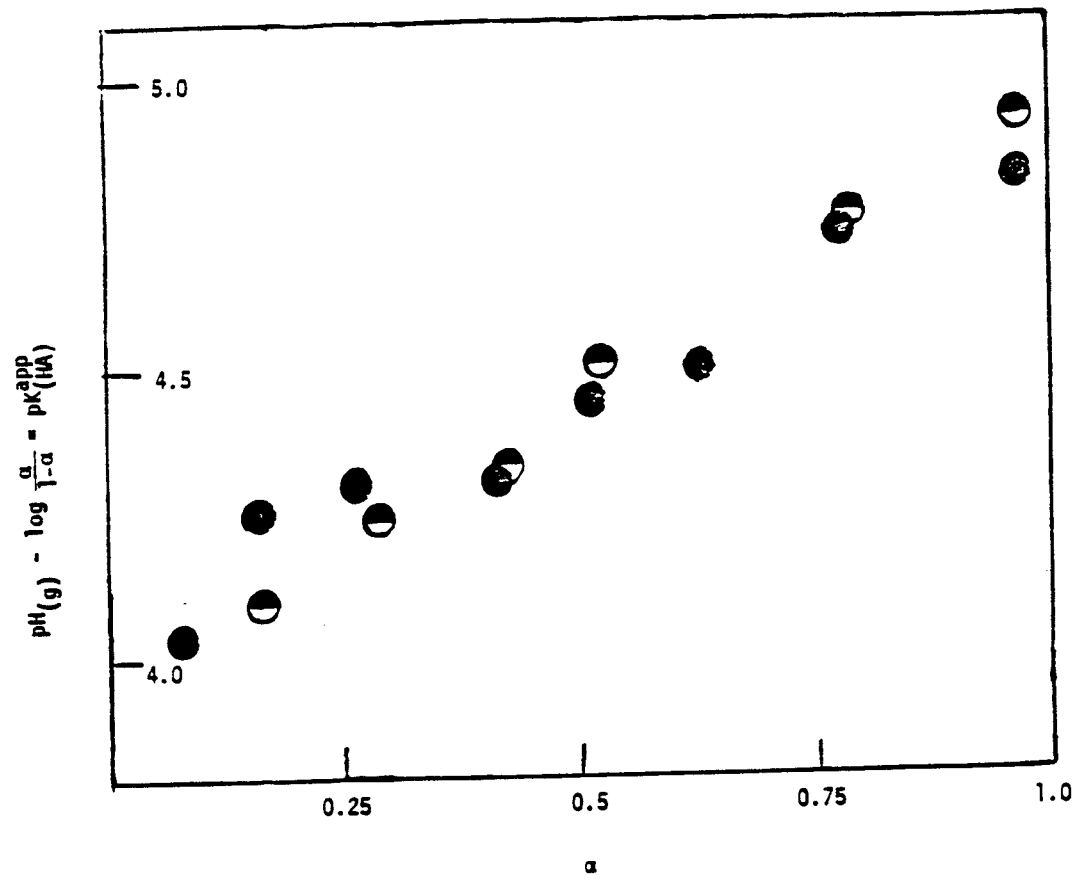
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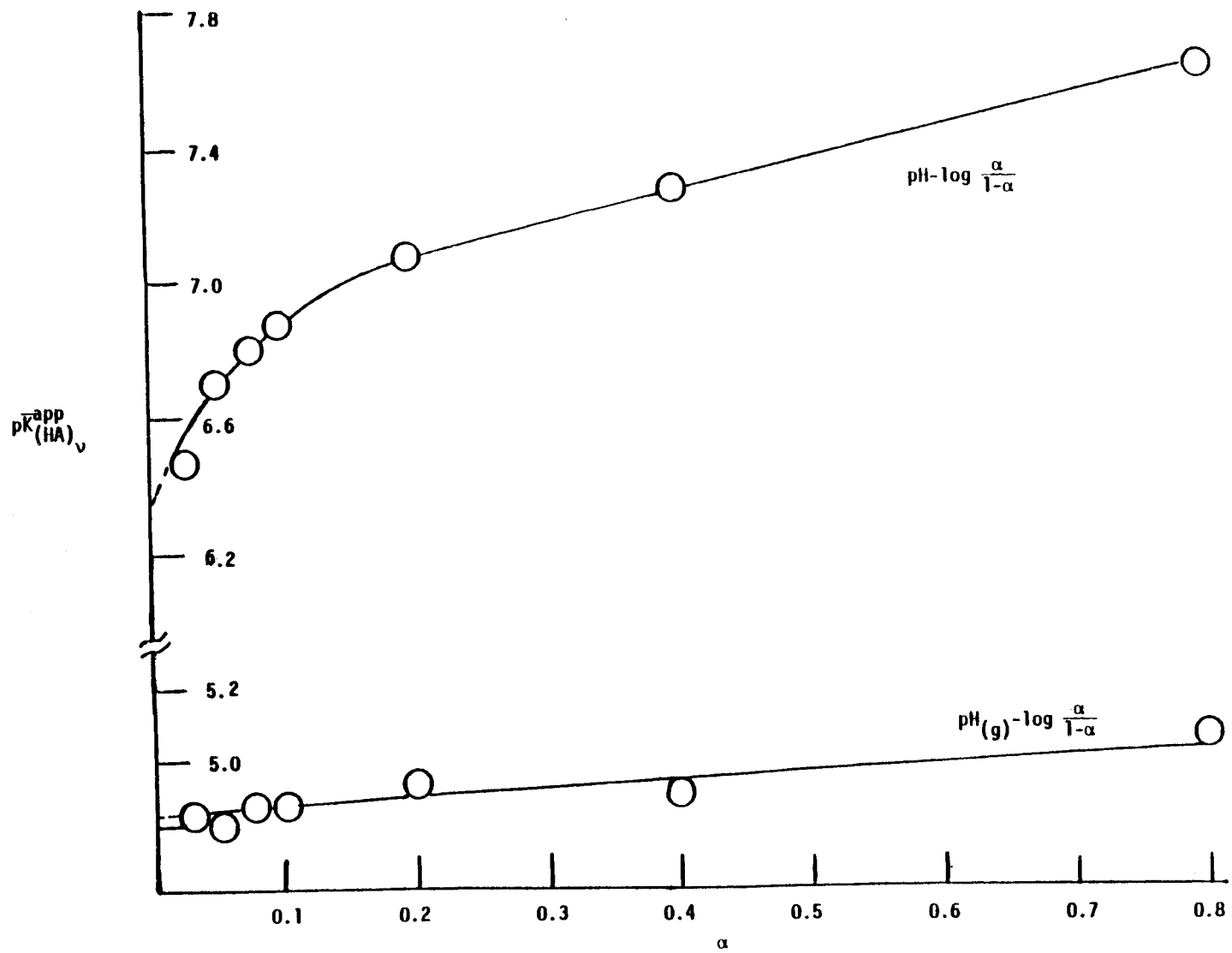
Figure Captions

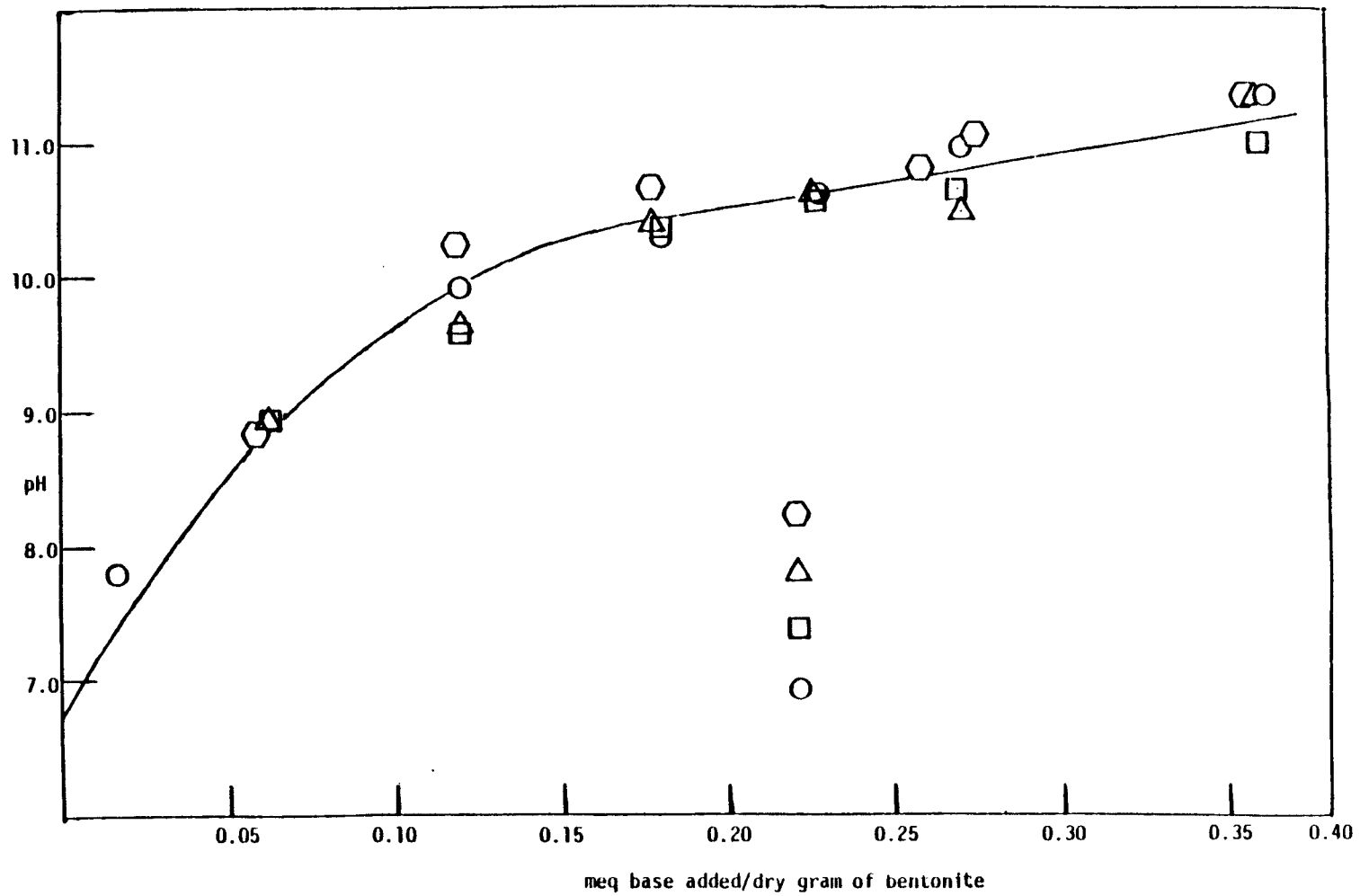
- Figure 1. Potentiometric Titrations of Polymethacrylic Acid with standard KOH. (Polymer Concentration = 0.01 equiv./liter.)
- Figure 2a. Potentiometric Titrations of Sphagnum Peat with standard NaOH.
- Figure 2b. Potentiometric Titrations of Sphagnum Peat with standard NaOH.
(Eq. 6a; 10^{-3} N NaCl; 10^{-2} N NaCl).
- Figure 3. Potentiometric Study of IRC-50 in 0.03 N NaPSS Solution. Titrant is standard NaOH.
- Figure 4. Potentiometric Titration of $[\text{Si}(\text{OH})_4]_n$ Constituent of Bentonite.
- Figure 5. The Apparent pK Versus α Plot of $\text{Si}(\text{OH})_4$ Constituent of Bentonite.
- Figure 6. Potentiometric Titration of ABS-39 Glass Samples.
- Figure 7. Potentiometric Titration of ABS-Y Marcoule Glass Samples.
- Figure 8. The pH of 0.010 M NaCl in Contact with Glass and Bentonite Samples over a 12-Day Period.
- Figure 9. Titration of 0.010 M NaCl Solution Equilibrated with Bentonite to Demonstrate CO_2 Absorption by the Solution.

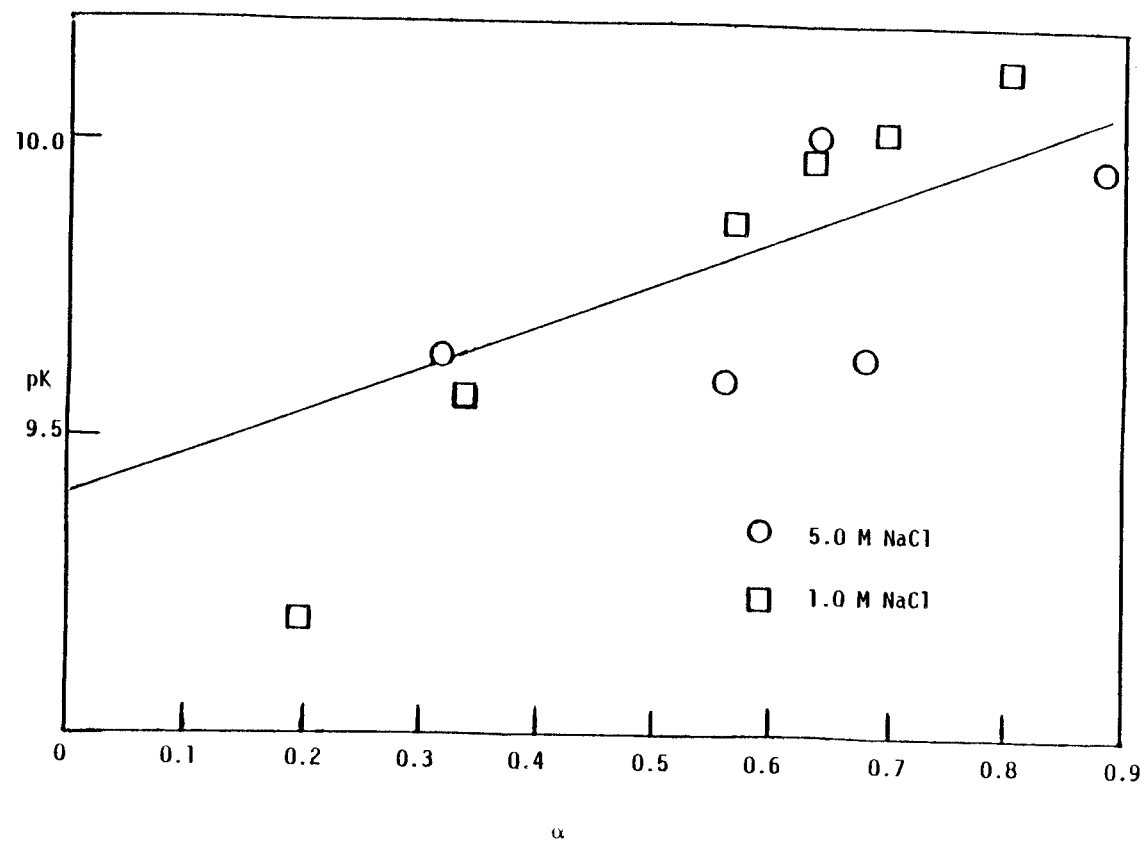


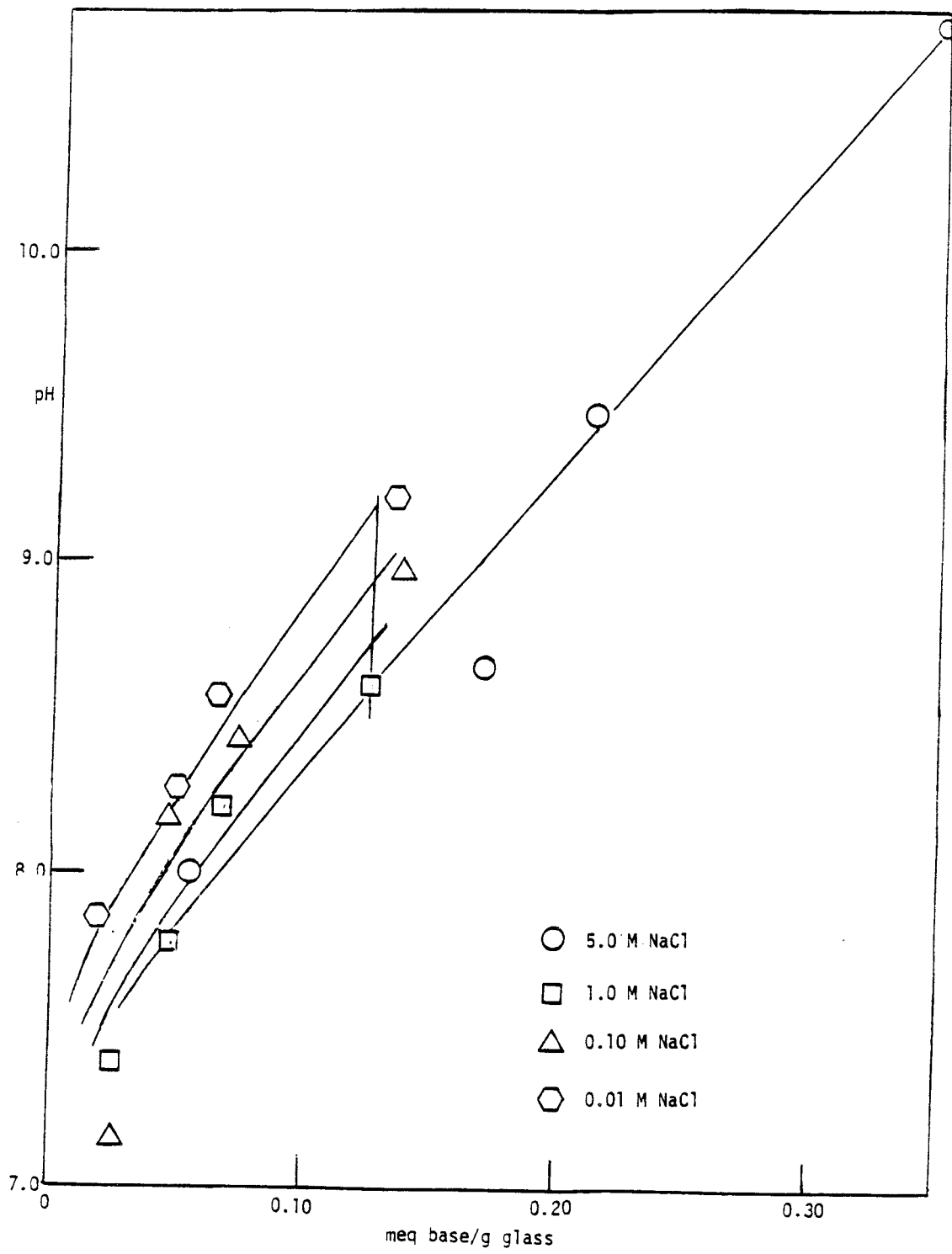


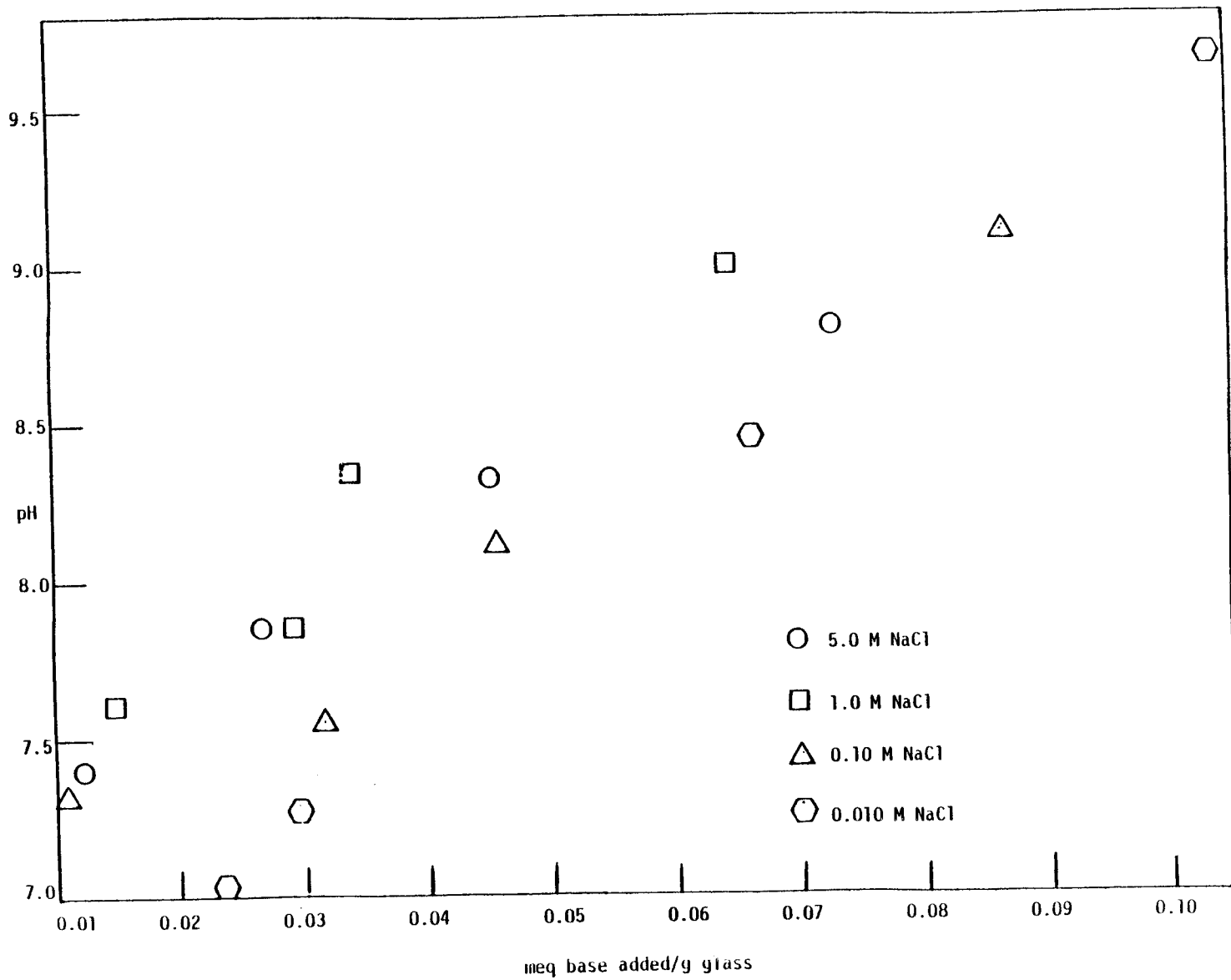


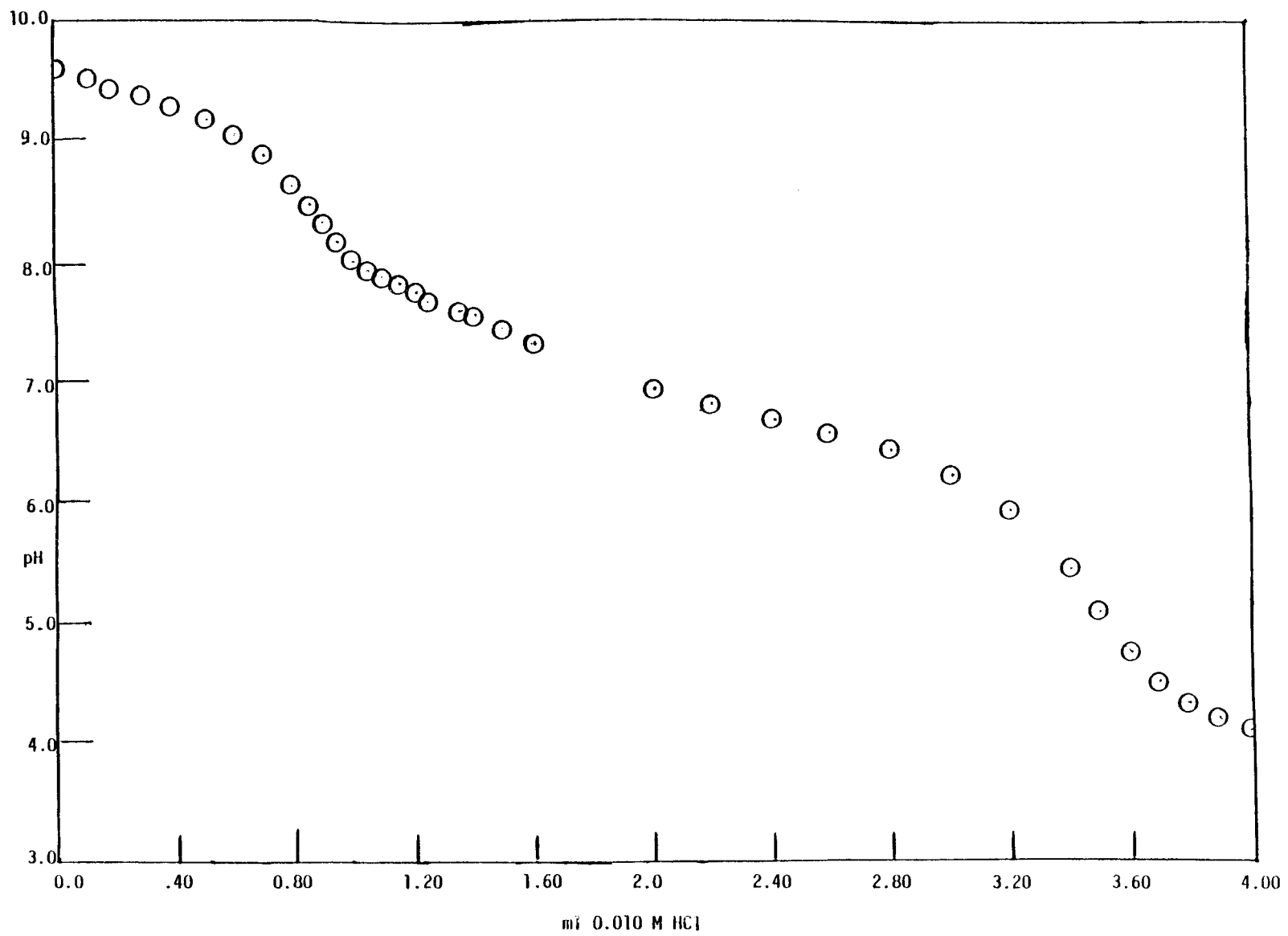


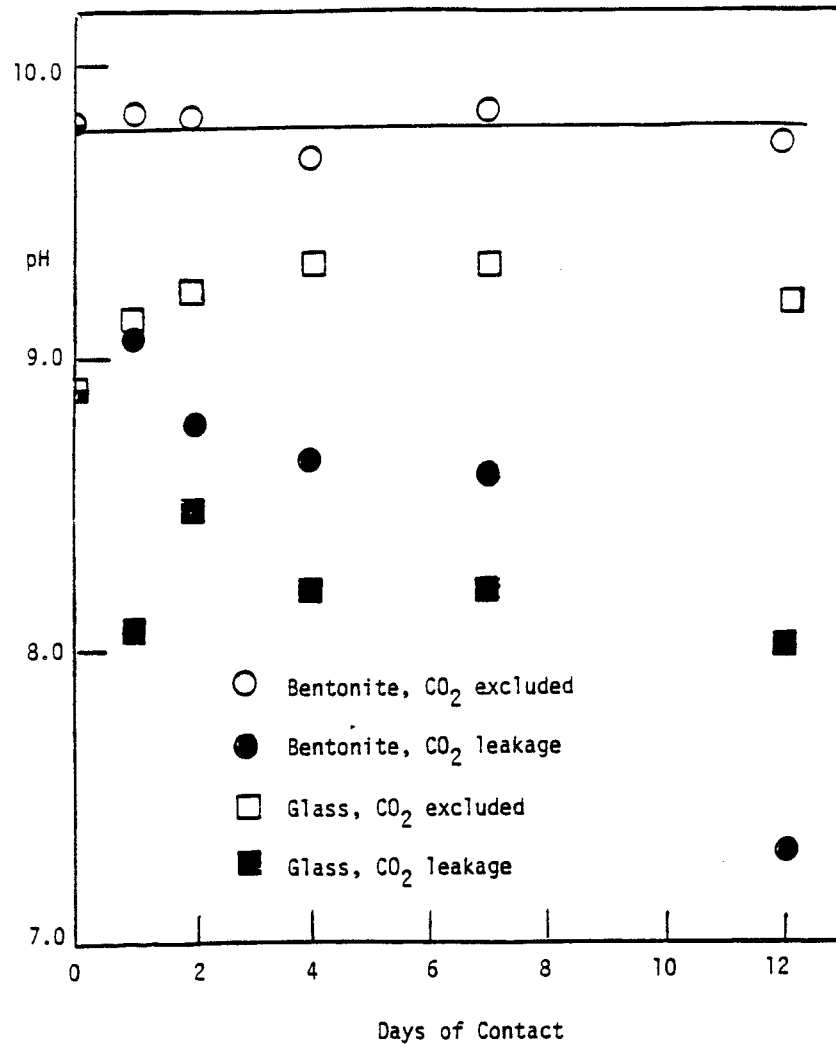












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Department of Inorganic Chemistry

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Division Soil Mechanics, University of Luleå

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