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THE EFFECT OF ALCOHOLS ON THE CARBONIC ACID DEHYDRATION REACTION

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The work upon which this report is based was supported in part by funds provided by the United States Department of the Interior, Office of Water Resources Research, as authorized under the Water Resources Research Act of 1964.

The research supported under the above project was intended to elucidate the effect of hydrocarbon-like impurities on the carbon dioxide/water system. Because of the importance of this system in natural waters a broad spectrum thermodynamic and kinetic approach was used. Initially we adopted the use of the recently developed ion selective electrodes to study a typical natural water system - aqueous solutions containing Mg^{+2}, Na^{+}, Cl^{-}, HCO_3^{-}/CO_3^{-2}. Measurements were simultaneously made on pH, Na^{+} activity and Mg^{+2} activity. The results have been extensively analyzed and are appended to this report as the manuscript: "The Chemical Interactions in $MgCl_2$ - $NaHCO_3$ Mixtures." We have been invited to present this work at the International Symposium on the Chemistry and Physics of Aqueous Gas Solutions to be held in Toronto next May. It will be published in the proceedings of that symposium.

At the same symposium, we shall also be presenting and publishing a second work entitled: "The Effect of Alcohols on the Carbonic Acid Dehydration Reaction." In this paper we point out the very drastic effect that small concentrations of hydrocarbon-like moities have on the activation parameters of this important dehydration reaction.

The techniques and ideas resulting from the above work are being vigorously applied to other natural water systems.

REFERENCES

Chin-tung Lin and G. Atkinson, "The Chemical Interactions in $MgCl_2$ - $NaHCO_3$ Mixtures

THE EFFECT OF ALCOHOLS ON THE CARBONIC ACID DEHYDRATION REACTION

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Abstract

The carbonic acid dehydration kinetics have been studied by the stopped-flow technique in CH_3OH/H_2O and t-BuOH/H_2O mixtures. Precise values of the activation parameters $\Delta G^{\ddagger}$, $\Delta H^{\ddagger}$, and $\Delta S^{\ddagger}$ have been obtained. CH_3OH has a very minor effect on the dehyration process except in the very low organic range. The addition of t-BuOH has a marked effect on the process with $\Delta H^{\ddagger}$ showing a maximum near $X_o = 0.06$ and $AS^{\ddagger}$ going from negative to positive at the same concentration.

Introduction

The carbon dioxide-water system is extremely important in the full range of natural waters. It is inextricably linked to all living processes in such waters. In the pH range common to most natural waters we can write the important equilibria[1] as

$$\begin{tikzcd} CO_2(g) + H_2 \arrow[r, shift left, "K_s"] & CO_2(aq) \arrow[l, shift left] \arrow[r, shift left, "K_D"] & H_2(O_3(aq) \arrow[l, shift left] \arrow[d, shift left] \\ & & H^+(aq) + HCO_3^-(aq) \arrow[u, shift left, "K_a"'] \end{tikzcd}$$

It has been known for many years that only a small fraction of the dissolved CO_2 is available as carbonic acid. In fact, Raman data on the CO_2/H_2O system show that the bulk of the CO_2 has a vibrational spectra almost identical to gaseous CO_2. The energy of activation for the dehydration/hydration step is very large reflecting its slow rates.

Although reasonable qualitative explanations of this slow process have been advanced, a quantitative description is missing. The radical banding change needed to go from CO_2 to the protonated $CO_2{}^{-2}$ ion is the commonly advanced explanation. However, we also know from the existence of solid CO_2 clathrate hydrates and the above mentioned Raman data, that the dissolved CO_2 exists in a "hole" in the water structure.[2]

In an earlier paper[3] in this series we examined the effect of simple salts such as NaCl and LiBr on the kinetics and thermodynamics of the CO_2 hydration process. The effects noticed were very small. In addition the effect of changing H_2O to D_2O was shown to be explicable in terms of classical isotope effects.

In this paper we will examine the effect of CH_3OH and t-BuOH on the dehydration kinetics. We have chosen these simple alcohols for two reasons. First, the properties of alcohol-water mixtures have been exhaustively studied by almost every known experimental techique.[4] Secondly, the alcohols serve as simple starting models for the hydrocarbons that are increasingly polluting our natural waters. We have chosen two alcohols with greatly different hydrophobic/hydrophilic ratios so that a tentative view of the relative importance of this factor could be obtained.

Experimental

The data to be discussed were obtained using the stopped-flow technique. The experimental details are discussed in ref. 3. Basically, solutions containing $H^+(aq)$ and $HCO_3{}^-(aq)$ together with an acid-base indicator are mixed. The protonation reaction takes place during the mixing time so the rate process observed directly is the dehydration process characterized by k_2.

$$H_2CO_3(aq) \underset{k_1}{\overset{k_2}{\rightleftharpoons}} CO_2(aq)$$

The temperature of the reaction is controlled to ±0.10° by a thermostatted mixing chamber block. The solutions used were made up by weight from reagent grade chemicals. Tables I and II summarize the k_2 data obtained in the CH OH/H O mixtures. Tables III and summarize the k_2 data obtained in the t-BuOH/H_2O mixtures. Fig. 1 shows the entropy of activation plotted against mole fraction organic.

Discussion of Results

If we examine the full range of the CH_3OH/H_2O data we note that $\Delta G^\ddagger$ exhibits a very shallow minimum while $\Delta H^\ddagger$ shows a maximum in the range $X_o = .15-.20$. The net result is a "roller coaster" effect in $\Delta S^\ddagger$. This type of effect has been seen previously in solvolysis kinetics observed over wide solvent mixture ranges. Focusing on the low CH_3OH range we note an abrupt change in $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ below $X = .02$. the overall increase, however, is less than 20%.

The t-BuOH/water data present much more marked effects. Unfortunately the X_o range covered is smaller because of the very low solubility of $NaHCO_3$ in t-BuOH/H_2O mixtures above $X_o = 0.3$. $\Delta G^{\ddagger}$ is essentially constance over the concentration range covered. $\Delta H^{\ddagger}$, however, shows a maximum at $X_o \approx .06$ with an increase of over 40% over the pure H_2O value. There is again some slight evidence of a "roller coaster" effect. $\Delta S^{\ddagger}$ shows a maximum and actually changes sign going from ~ -8eu in pure water to +9eu at the maximum.

The effect seen in the t-BuOH/H_2O system in very similar to those observed in organic solvolysis reactions in mixed solvetn. A recent review by Hyne[5] admirably describes his own work as well as that of Arnett and others. In a typical solvolysis reaction, for example, t-BuCl in some mixed solvent, we have the following activation process.

$$RX \overset{\Delta H^{\ddagger}}{\rightleftharpoons} R^{\delta+}\text{---}X^{\delta-} \longrightarrow$$

where we are going from a relatively non-polar initial state to a highly polar or pseudo-ionic transition state. In such systems $\Delta H^{\ddagger}$ commonly shows a minimum when plotted against X_o. But Arnett has noted that for the solvolysis of dimethyl-t-butylsulfonium salts and similar compounds, a maximum in $\Delta H^{\ddagger}$ is observed. In these cases we are commonly going from a highly polar and/or hydrogen bonded initial state to a transition state wehere the charge is more dispersed.

In the case at hand

$$H_2CO_3 \overset{\Delta Z^{\ddagger}}{=\!=} [H_2CO_3]^{\ddagger} \longrightarrow (O_2(aq)$$

the initial state is quite polar and, obviously, hydrogen bonded to the surrounding waters. Analogy would seem to lead to the belief that the transition state was significantly less polar. It should be noted that CO_2 itself is quite non-polar. So our overall process goes from a highly polar, hydrogen bonded initial state to a non-polar final state which seem to hydrogen bond feebly, it at all.

Hyne and Arnett have had some success in breaking down the activation parameters in the following fashion

$$\Delta Z^{\ddagger} = \overline{Z}_t - \overline{Z}_i$$

where $\overline{Z}_t$ = "parameter" of solution for the transition state
$\overline{Z}_i$ = "parameter" of solution for the initial state.

By modeling the initial state, then, it is possible to ascertain how much of the solvent effect on $\Delta Z^{\ddagger}$ is due to change in solvent effect on

References

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Table I

Dehydration Rate Constant in CH_3OH/H_2O

X_{CH_3OH}	T (°C)	k_2 (sec^{-1})
0.003	5.0	2.76
0.003	20.0	11.9
0.003	38.5	49.3
0.010	5.0	2.51
0.010	20.0	12.7
0.010	38.5	50.0
0.060	5.0	2.88
0.060	20.0	14.4
0.060	38.5	57.5
0.14	5.0	3.32
0.14	20.0	16.0
0.14	38.5	69.0
0.30	5.0	3.65
0.30	20.0	17.3
0.30	38.5	74.2
0.80	5.0	2.75
0.80	20.0	10.1
0.80	38.5	33.2

Table II

Activation Parameters of Dehydration in CH_3OH/H_2O

X_{CH_3OH}	E_A (Kcal)	$\Delta G^{\ddagger}$ (Kcal)	$\Delta H^{\ddagger}$ (Kcal)	$-\Delta S^{\ddagger}$ (e.u.)
.003	14.36 ±0.008	15.7_6	13.7_6	6.7_1
.010	15.05 ±0.17	15.7_5	14.4_6	4.3_2
.060	15.05 ±0.16	15.6_7	14.4_5	4.0_7
-14	15.18 ±0.10	15.5_9	14.5_9	3.3_4
.30	15.06 ±0.10	15.5_4	14.4_7	3.5_9
.80	12.37 ±0.09	15.9_0	11.7_8	1.3_8

Extra significant figures are carried on all activation parameters so that round-off errors do not trouble other workers.

Table III

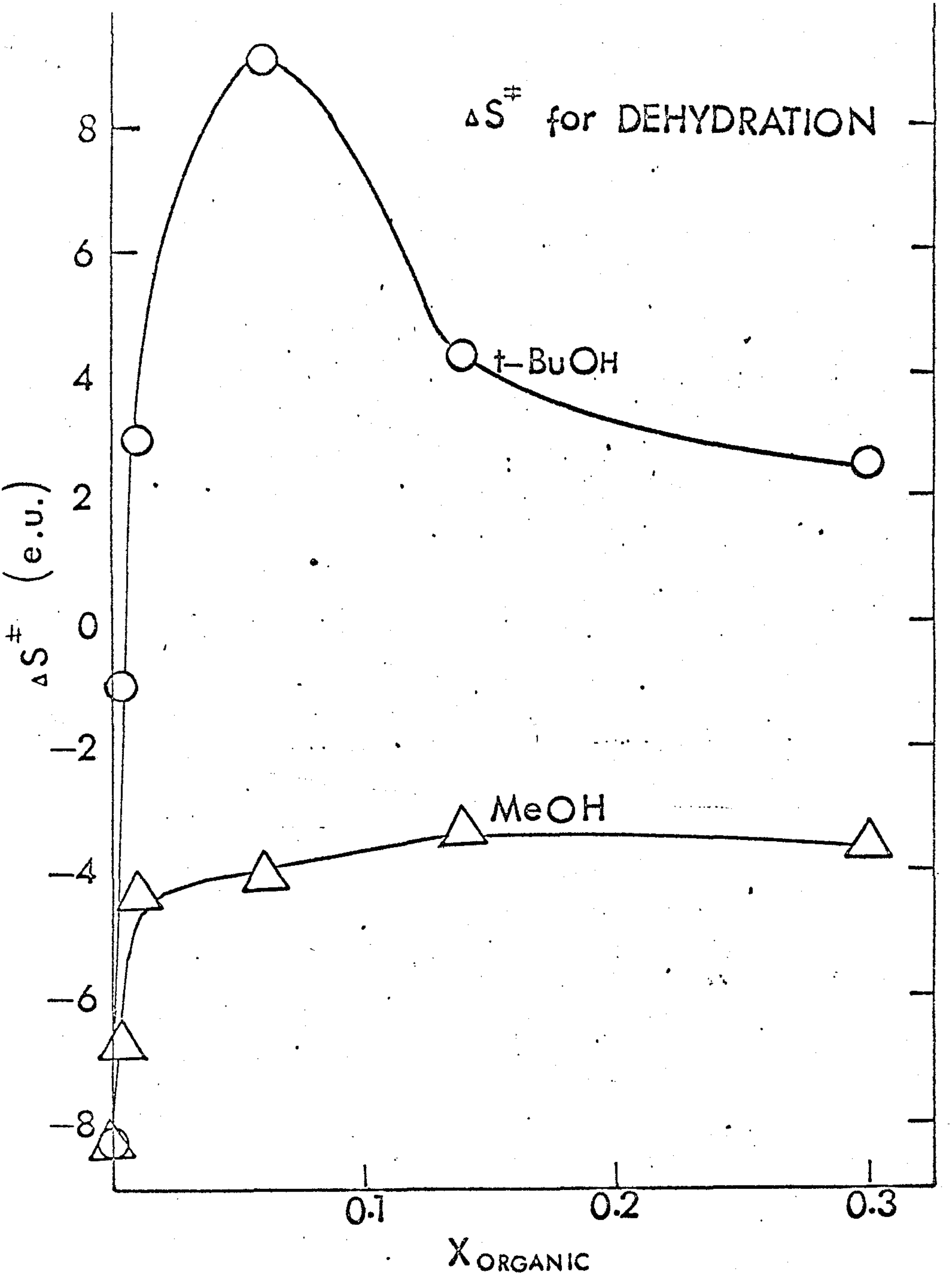
Dehydration Rate Constant in t-BuOH/H_2O

$X_{t\text{-}BuOH}$	T (°C)	k_2 (sec^{-1})
0.003	8.5	4.35
0.003	17.0	12.3
0.003	25.5	23.1
0.010	8.5	3.85
0.010	17.0	9.96
0.010	25.5	23.2
0.060	8.5	3.56
0.060	17.0	9.76
0.060	25.5	25.7
0.14	8.5	3.72
0.14	17.0	8.73
0.14	25.5	23.5
0.30	8.5	3.14
0.30	17.0	8.47
0.30	25.5	20.3

Table IV

Activation Parameters of Dehydration in $t\text{-}BuOH/H_2O$

$X_{t\text{-}BuOH}$	E_A (Kcal)	$\Delta G^\ddagger$ (Kcal)	$\Delta H^\ddagger$ (Kcal)	$\Delta S^\ddagger$ (e.u.)
0.003	15.89 ±0.32	15.5_9	15.2_9	1.0_1
0.010	17.09 ±0.34	15.6_2	16.5_0	-2.9_6
0.060	18.86 ±0.38	15.5_7	18.2_7	-9.0_7
0.14	17.53 ±0.36	15.6_3	16.9_4	-4.3_8
0.30	17.78 ±0.36	16.4_4	17.1_9	-2.5_3


ΔS‡ for DEHYDRATION
t-BuOH
MeOH
ΔS‡ (e.u.)
8
6
4
2
0
−2
−4
−6
−8
0.1
0.2
0.3
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the initial state and how much on the transition state. For the (non-polar)→(polar) cases, the initial state effect was shown to be dominant. But in the cases where the transition was seemingly (polar)→(less polar), effect on both initial and transition states seemed important. Unfortunately no good data is available on the heats of solution H_2CO_3. We are attempting to analyze some data on the thermodynamics of H_2CO_3 dissociation in these terms but have not finished the process yet. In addition there is little good data on the thermodynamics ob carboxylic acids that might serve as useful model compounds. The solvent effects are most marked in the low X_o range which typically was not examined in any detail.

It is possibly worthwhile to speculate briefly about the marked change in $\Delta S^\ddagger$ in the t-BuOH/H_2O system. We go from a negative $\Delta S^\ddagger$ to a positive $\Delta S^\ddagger$ in a very narrow X_o range. The X_o range is the same in which all of the properties of the t-BuOH/H_2O system show very marked extrema. The most popular explanation of these marked effects involves very strong H_2O clustering around the strongly hydrophobic t-Butyl group. The clustering may be more closely related to the well-characterized clathrate hydrate structure than a more normal pure water structure. This "cage" effect has a very pronounced dependence on X_o in the low X_o region because of the rather large numbers of H_2O molecules needed per cage. The change from negative to positive $\Delta S^\ddagger$ is most simply interpreted in terms of the very high degree of order around the initial state-he hydrated H_2CO_3 molecule.

It is unfortunate that no more data is available on the kinetics of hydrogen bonding acids in mixed solvents. Both the temperature and solvent effects seem very pronounce. These large kinetic effects could serve as a very useful probe of the changes in solvent character in such systems.

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The Chemical Interactions in $MgCl_2$ - $NaHCO_3$ Mixtures

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Abstract

The chemical interactions of Mg^{+2} with carbonate and bicarbonate in the presence of the Na^+ ion have been studied as a function of temperature ranging from 0-30°C and of ionic strength varying from 0.15 to 0.64 M. In the case of $MgCO_3$ ion pair formation, a constant enthalpy of reaction was observed in the temperature range investigated. In the case of $MgHCO_3^+$ ion pair formation, the association constant shows a minimum around 20°C. Within experimental error, the effect of ionic strength on the ion pair formation processes is in line with the Debye-Hückel theory in its extended form. The $NaCO_3^-$ and $NaHCO_3$ ion pair formation constants in the absence of the Mg^{+2} ion have been determined at 20°C. The values are 0.5 M^{-1} with an ionic strength of 0.36 M and 4.4 M^{-1} at 0.19 M, respectively. The calculations were based on the EMF measurements using the glass and the ion-selective electrodes.

Introduction

Sodium and magnesium ions are the two major cations found in seawater, and carbon dioxide is one of the primary gases which dissolves in seawater.[1] The chemical interactions between the two cations and the ionic species of the carbonic acid have been subjected to some study in recent years. However, the discrepancies in the reported formation constants are serious (see Table 4). A systematic study of these reactions as a function of temperature and ionic strength has not been made. Furthermore, by fixing the ionic strengths of the solution, the uncertainties introduced by the activity coefficients (e.g. $\gamma_{MgHCO_3^+}$) at higher ionic strengths are essentially eliminated. The application of ion-selective electrodes to chemical problems until recently has been confined largely to analytical work. In 1966, Thompson and Ross[2] used the electrodes to determine the percentages of calcium and magnesium[3] ions in seawater. Their results agreed well with the data calculated for the chemical model of seawater. Later these electrodes were employed by Leyendekkers to measure the activity coefficients for the system Ca(II) - Na(II) - Cl(I) - water[4] and by Nakayama to investigate the formation of calcium bicarbonate and carbonate ion pairs.[5] The association reactions of $SO_4^=$ with Mg^{+2} and Ca^{+2} have also been studied by this technique.[6] While some workers reported that the technique failed to generate reliable results.[7] The purposes of this investigation are to use ion-selective electrodes to study some complex ionic interactions common in seawater and to discuss some of its limitations and advantages.

The results of the present study indicate that a set of reasonably good association constants can readily be obtained from the direct measurements of ionic activities with due attention paid to the calibration and standardization of the reference solutions. The most serious inherent limitations are that the technique requires closely matched reference solutions and quick measurements. A closely matched reference solution could reduce the errors in parameters such as the activity coefficients of specified ions and the liquid-junction potentials of the media to minimum. Quick measurements have to be made as a result of the variation of the electrode potential readings by several millivolts a day.

As it will be seen later, the problem of electrode potential variation can best be resolved if the electrode potential of a test solution is directly compared to that of a closely matched reference solution which is measured right after or before the test solution. And then the Nernst slope can be used to correct for the difference in electrode potentials to evaluate the ionic activities for the test solution. The Nernst slopes tested by these electrodes are in excellent agreement with theoretical values. This is because the Nernst equation is generally checked in a wide range of pure electrolyte concentrations. The errors caused by the electrode instability with respect to time thus appear to be insignificant. Employing this procedure an independent study on the well established $MgSO_4$ association by this method shows that the results compare favorably with those obtained by other techniques.[8]

Experimental

A. Reagents

Analytical reagent NaCl (Malliuckrodt), reagent grade $NaHCO_3$ (99.7-100.3% purity, Merck) and $MgCl_2 \cdot 6H_2O$ (Merck) were dried and used in the experiments along with certified NaOH and HCl solution (N/10, Fisher). The concentrations of NaCl and $NaHCO_3$ were determined from weight and the concentrations of filtered magnesium chloride were standardized with EDTA titrations. Stock solutions were prepared for NaCl and $MgCl_2$ and were subsequently diluted to the desired concentrations with deionized distilled water. A known volume of NaOH or HCl was added to adjust the pH values of the solutions. The weighed amounts of $NaHCO_3$ were introduced freshly for each determination.

B. Method

The pH and electrode potential measurements were made using an Orion model 801 digital pH/mv meter equipped with Thomas glass and the Orion ion-selective electrodes.

A single junction reference electrode (Orion Model 90-01) in conjunction with the glass and divalent ion-selective electrodes were used to measure the respective activities for the H^+ and the Mg^{+2} ions. This reference electrode gives a quicker response than does a saturated KCl calomel electrode in the measurements of magnesium activities. Both the conventional calomel electrode and the recommended double-junction electrode were tested as a reference for the sodium electrode. No significant difference between these two reference electrodes was observed and the more convenient calomel electrode was selected to determine the sodium ion activities. The reaction cell made for the study requires 200 ml of fresh solutions for each measurement. The cell was enclosed by mounting the electrodes and the thermometer (1/10°C per division) in the holes on the cap of the cell. The solutions were gently stirred and the data were taken generally within one hour after the solution was prepared. The pH meter was standardized at each temperature against a NBS standard Buffer (0.008695 m KH_2PO_4 + 0.03043 m Na_2HPO_4). The errors in pH measurements resulting from the liquid junction potential differences between the various media have been corrected and will be discussed later. The temperatures were controlled within ± 0.1 at 0, 10, 20 and 30°C for solutions at 0.15 M. At 20°C, the ionic strength of the solutions was regulated at 0.15, 0.35 and 0.64 M. For solutions at 0°C and 0.64 M ionic strength, the filling solution (Orion 90-00-01) in the single junction reference electrode was replaced with a solution of 3 M KCl saturated with $AgNO_3$. The ion-selective electrodes have been calibrated in pure NaCl and $MgCl_2$ solutions with known concentrations in the same range as the test solutions. Using the activity coefficients furnished in the Orion Manual, the experimental Nernst slopes are within 0.7 - 3% of the theoretical values. The readings from the magnesium electrode stabilized much more quickly than those from the sodium electrode. The experimental error in the sodium electrode measurements was found primarily coming from the drift observed in the electrode potentials. During the course of measurement, the pH values remain fairly constant and the reproducibility is within ± 0.05 pH units. This implies that the rate of CO_2 loss from the solution is slow enough so that accurate data can be obtained under the present experimental conditions.

Results

A. Potentiometric Calibrations of Standard Solutions

The electrode potential versus solution composition was calibrated for each temperature and ionic strength. The calibration was made in three solution systems.

a. Pure NaCl and pure $MgCl_2$ solutions

As described in the experimental section, the electrode pairs were checked with respect to the Nernst equation in these solutions. The typical results are shown in Table 1a and Figure 1a. The errors in the electrode potential measurements are generally within ± 0.2 mv. At 0°C, the errors for the magnesium electrode increased to ± 0.3 mv.

b. Mixtures of NaCl and $MgCl_2$ solutions

Case 1 A constant NaCl concentration with varying $MgCl_2$ concentrations. Case 2 A constant $MgCl_2$ concentration with varying NaCl concentrations.

The compositions of the standard solutions are closely matched to those of the test solutions. The purposes of the experiments were two-fold. The first is to try to obtain a linear relationship between the electrode potentials and the activities of the specific ion in question in the presence of the other ion. The second is to determine the point at which the relationship breaks down as the ratio of the specific ion concentration over the other cation concentration decreases. The tests are essential in view of the fact that the ion-selective electrode is selective only if the coexistent foreign cation concentration is below a certain relative level. The experimental data are presented in Table 1b. The results in this table gave a Nernst slope for Na^+ ion of 59.4 mv. The plot indicates that the sodium electrode is essentially free from the Mg^{+2} ion interference. A plot (Fig. 1b) of the magnesium electrode potentials versus its activities based on the data from Table 1b indicates that a linear variation holds down almost to 0.004 molar magnesium ion concentration. A positive departure from the line begins to appear for the first two pairs of data. The linear function does not necessarily possess a theoretical Nernst slope; rather it shows experimentally that as a result of the presence of the sodium ion, the theoretical slope for the $MgCl_2$ solutions (29 mv at 20°C) was reduced proportionally to a lower value (27.5 mv), in a certain narrow range of $MgCl_2$ concentrations. This is because the relative electrode potential contribution from the sodium ion increases as the magnesium ion concentration decreases. It is worth noticing that the apparent interference of the Na^+ ion on Mg^{+2} electrode potentials decreases as the latter is measured in a constant NaCl media. At higher ionic strengths and lower temperatures, the slopes obtained experimentally for the Mg^{+2} ion are usually several millivolts below the theoretical Nernst values.

c. Mixtures of the NaCl and $MgCl_2$ solutions with a 20% or less Variation in the NaCl concentration

The free sodium ion concentrations in the test solutions are generally several percent less than those in the standard reference solutions due to the complexation of the sodium ion with bicarbonate and carbonate. The potentiometric calibrations are used to establish the experimental conditions under which the apparent electrode potentials of the magnesium ion remain constant regardless of the small change in the NaCl concentrations. Part of the results are tabulated in Table 1c. An analysis of the data in the left part of this table shows that a Nernst type linearity holds for all the concentration pairs except the one at $MgCl_2$ equal to 0.02 M, and the effects of NaCl on the magnesium potentiometric readings are within the experimental errors. With higher $[Na^+]/[Mg^{+2}]$ ratios, the data in the right part indicate that the linearity is poor and the apparent NaCl effects on the magnesium electrode potentials are obvious as shown in Fig. 1c.

B. The Activity Coefficients

The activity coefficients for the Mg^{+2} ion are sometimes calculated from the quotient of $\frac{\gamma_\pm^3 (MgCl_2)}{\gamma_\pm^2 (KCl)}$. The mean activity coefficients for $MgCl_2$, KCl, NaCl and HCl have been tabulated by Harned and Owen.[9] These measured values for $\gamma_{\pm(NaCl)}$ and the calculated values for $\gamma_{Mg^{+2}}$ from the above quotient differ somewhat from those listed in the Orion Manual at 25°C. This may be due to the fact that the assumptions used in various equations to arrive at the values for the activity coefficients are not necessarily the same or valid. Nevertheless, the Nernst plots in the pure NaCl or the pure $MgCl_2$ solutions yield satisfactory results by using the activity coefficients listed in the manual. Subsequently, the same coefficients are employed to convert the measured activities to the corresponding concentrations. Therefore, the errors, if any, involved in the activity coefficients are essentially eliminated in the concentration terms which are paramount in the evaluation of the association constants. The temperature effects on the sodium and magnesium activity coefficients are not considered. The values in Harned and

Owen's tables indicate that $\gamma_{\pm(NaCl)}$ varies less than 1.5% in a 30° range. The mean activity coefficients for the Mg^{+2} ion as a function of temperature are not available. The calculated values for the Ba^{+2} ion from the ratios of $\frac{\gamma_{\pm}^{3}(BaCl_2)}{\gamma_{\pm}^{2}(NaCl)}$ show that their variations with the temperature are not significant in terms of the present procedure of evaluating the association constants.

Recently it has been reported that the mean activity coefficients of pure electrolytes are different from those in mixed electrolytes. In the present study, since the test solution was matched closely to the reference solution and both HCO_3^- and Cl^- ions are singly charged, they have a similar hydration radius. The difference may greatly be narrowed. Furthermore, in view of the serious discrepancies between the various association constants reported in the literature, all these simplifications seem justified.

C. Potentiometric Measurements in Test Solutions

a. The $NaCO_3^-$ Ion Pair Formation

The reactions between the sodium ion and the carbonate ion were studied at high pH's. At these pH values, the reactions due to the bicarbonate ion are not important. To eliminate the instrumental errors, the sodium electrode was recalibrated just before the measurements were made. The experimental conditions and results are shown in Table 2a. In this table, the total sodium ion concentration is kept constant. The potentiometric readings increase as the concentrations of $NaHCO_3$ decrease; a clear indication of decreased amount of $NaCO_3^-$ formed at the lower $NaHCO_3$ concentrations.

b. The $NaHCO_3$ Ion Pair Formation

NaCl was added to maintain a constant ionic strength for the reaction system. The high $NaHCO_3$ concentrations are necessary as a result of weak interactions. The data are summarized in Table 2b.

c. The $MgHCO_3^+$ and $MgCO_3$ Ion Pair Formation

As shown in Table 3, between two reaction solutions, a standard reference was made. Using this reference point and the Nernst slopes determined experimentally, the concentrations of the cations in the reaction solutions can be evaluated. The instrumental instability is normally within ± 0.2 mv. The results presented in Table 3 were collected on different days and the inner solutions of the electrodes have been refilled during the course of measurements. The changes in the Na^+ ion concentrations due to ion pair reactions are not large enough to allow the simultaneous solutions for the association constants of $NaCO_3^-$ and $NaHCO_3$ as a function of temperature and ionic strength.

The studies were repeated at 0, 10, and 30°C. The errors in the slope at 0°C as seen in Figure 5 are higher than those at other temperatures. This is because the readings are less stable at this temperature. At 20°C two systems with higher ionic strengths were studied. The ionic strengths were raised by increasing both sodium and magnesium concentrations. At $I = 0.64$ M the variation of pH's is greatly retarded possibly caused by the formation of $Mg(OH)_2$ ppt at a lower pH value. The highest point in Figure 7 represents a supersaturated solution with a very slight ppt. formed at the end of the measurements. Thus the slope obtained from Figure 7 should not be regarded as a definite number. Only the intercept means a significant value.

d. The Liquid Junction Potential Approximation

The commonly available buffer solutions have an ionic strength up to 0.1 molar concentration. With the reaction solutions having a much higher ionic strength, the correction for the liquid junction potential becomes necessary in light of the sensitivity of the calculations to the pH values.

Jordan[11] has used the mixture of H_2O-CH_3CN-HCl with a HCl concentration of 2×10^{-3} M to define the acidity scales in the mixed water-acetonitrile buffer solutions. In our study, we started with a 0.1 M NaCl solution and adjusted its pH to 10.922 or ($[OH^-] = 1.091 \times 10^{-3}$). The ionic strengths of the solution were then regulated to higher values by the successive additions of NaCl to the same solution. The pH values measured with the glass and the single junction electrode pair were recorded at each ionic strength. The volume increases in the solution brought about by the added NaCl were corrected. The hydroxide ion has a concentration of 10^8 fold higher than the hydrogen ion concentration. Therefore the calculated pH values converted from the OH^- concentrations are more accurate than those based on the H^+ concentrations. In the calculations the OH^- ion in terms of mole numbers was assumed unchanged. The difference between pH_{obs} and pH_{calc} after corrected for the ionic strength effects was believed to be resulting from the change of the liquid junction potential from one medium to the other. The results (Table 4) obtained agree reasonably well with those reported recently by Hansson[12] using a cell type no. II through a different approach in an effort to set new pH scales and standard buffers for seawater.

Treatment of Data and Discussion

A. The $NaCO_3^-$ Ion Pair Formation

The association constant for the $NaCO_3^-$ formation was evaluated as follows

$$K_1 = \frac{[NaCO_3^-]}{[Na^+]\,[CO_3^=]} \tag{1}$$

with $[NaCO_3^-] = [Na_T] - [Na^+]$ and $[CO_3^=] = [NaHCO_{3_T}] - [NaCO_3^-]$

In this equation, Na_T and $NaHCO_{3_T}$ designate the total sodium and carbon concentrations; the rest are the free ion concentrations. A quick iteration generates a value of $4.2 \pm 0.8\ M^{-1}$ for K_1 at 0.19 ± 0.01 M ionic strength. This value parallels to that of $6.1\ M^{-1}$ corrected from $18.52\ M^{-1}$ reported by Garrels and Thompson[13] at 25°C and infinite dilution. The activity coefficients used for correction are listed in Tables 2 and 5, and the $\gamma_{HCO_3^-}$ value was assumed for $\gamma_{NaCO_3^-}$. Other literature values are $3.55\ M^{-1}$ [14] and $2.22\ M^{-1}$ [15] at 25°C and infinite dilution.

The above treatment excludes the reaction between the Na^+ and the $NaCO_3^-$ ions to form Na_2CO_3. With the inclusion of Na_2CO_3 ion pair formation the mass balance equations are modified to

$$[Na_T] = [Na^+] + [NaCO_3^-] + 2[Na_2CO_3] \tag{2}$$

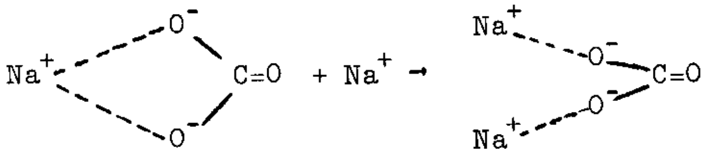
$$[CO_{2_T}] = [CO_3^=] + [NaCO_3^-] + [Na_2CO_3] \tag{3}$$

Rearranging the above equations and defining a new equilibrium relationship, $[Na_2CO_3] = K_2\,[Na^+]\,[NaCO_3^-]$, equation (2) divided by equation (3) yields

$$A = \frac{[Na_T] - [Na^+]}{[CO_{2_T}]} = \frac{K_1[Na^+] + 2K_1K_2[Na^+]^2}{1 + K_1[Na^+] + K_1K_2[Na^+]^2}$$

or $$1 + K_1X + K_1K_2Z = 0; \quad X = \frac{A-1}{A}[Na^+] \text{ and } Z = \frac{A-2}{A}[Na^+]^2 \qquad (4)$$

A plot of eq (4), however, yields negative and unreasonable values for both K_1 and K_2; an implication of non-existence of the Na_2CO_3 ion pairs under the present conditions. From the electrostatic and statistic viewpoints, it seems logical to expect that the bond breaking and formation process as shown below is highly unfavorable



B. The $NaHCO_3$ Ion Pair Formation

At pH values around 8, the concentrations of $NaCO_3^-$ are very small compared to those of $NaHCO_3$. Using the K_1 value obtained to correct for residual $NaCO_3^-$ concentrations, the association constant for $NaHCO_3$ evaluated through a set of straightforward mass balance equations is 0.5 ± 0.1 M^{-1} at 0.36 ± 0.01 M ionic strength. To extrapolate this value to infinite dilution, it (0.99 M^{-1}) stands at the midway point between the values of 0.59 M^{-1} and 1.45 M^{-1} at 25°C reported by Garrels[16] and Nakayama[14] respectively. However, it should be noted that the errors in these simple Na^+ ion pair formations determined by the sodium electrode are considerable.

C. The $MgHCO_3^+$ and $MgCO_3$ Formation Reactions.

The magnesium ion pair formation in the mixture of NaCl and $MgCl_2$

gives rise to more complicated equations

$$\begin{tikzcd}
 & & MgHCO_3^{+} \arrow[r, shift left] \arrow[r, leftarrow, shift right] \arrow[d, shift left] \arrow[d, leftarrow, shift right] & MgCO_3 + H^{+} \arrow[d, shift left] \arrow[d, leftarrow, shift right] \\
 & & Mg^{+2} & Mg^{+2} \\
 & & + & + \\
CO_2 + H_2O \arrow[r, shift left] \arrow[r, leftarrow, shift right] & H_2CO_3 \arrow[r, shift left] \arrow[r, leftarrow, shift right] & H^{+} + HCO_3^{-} \arrow[r, shift left] \arrow[r, leftarrow, shift right] & 2H^{+} + CO_3^{=} \\
 & & + & + \\
 & & Na^{+} \arrow[d, shift left] \arrow[d, leftarrow, shift right] & Na^{+} \arrow[d, shift left] \arrow[d, leftarrow, shift right] \\
 & & NaHCO_3 & NaCO_3^{-} + H^{+}
\end{tikzcd} \tag{5}$$

Na_2CO_3 was excluded as explained previously. The other possible species, $Mg(HCO_3)_2$ was eliminated on the basis of the relative errors calculated from a charge balance equation. The charge balance equation was not used in the data treatment to avoid the gross errors in the Na^+ ion measurements reflected in the determination of the much lower free magnesium ion pair concentrations.

The mass balance equations for the above reactions are

$$[Mg_T] = [Mg^{+2}] + [MgHCO_3^{+}] + [MgCO_3] \tag{6}$$

$$[Na_T] = [Na^{+}] + [NaHCO_3] + [NaCO_3^{-}] \tag{7}$$

$$[CO_{2_T}] = [H_2CO_3] + [HCO_3^{-}] + [CO_3^{=}] + [Mg_T] - [Mg^{+2}] + [Na_T] - [Na^{+}] \tag{8}$$

The equilibrium relationships give

$$Y = \frac{[MgHCO_3^{+}] + [MgCO_3]}{[Mg^{+2}][HCO_3^{-}]} = K_{1s} + \frac{K_{2s}}{K_{2a}(H^{+})} \tag{9}$$

with $K_{1s} = \dfrac{[MgHCO_3^{+}]}{[Mg^{+2}][HCO_3^{-}]}$, $K_{2s} = \dfrac{[MgCO_3]}{[Mg^{+2}][CO_3^{=}]}$

$$K_{1a} = \frac{[H_2CO_3]}{[H^+][HCO_3^-]} \quad \text{and} \quad K_{2a} = \frac{[HCO_3^-]}{[H^+]\,[CO_3^=]}$$

By plotting Y versus $1/[H^+]$, the concentration quotient association constants for the magnesium bicarbonate and carbonate formation are readily obtained through a quick iteration process. The constant ionic strengths were made possible by the keeping of the pH values lower than 9 and the sodium ion concentrations several times higher than the magnesium concentrations. The ionic strength of the solution was evaluated from

$$I = \tfrac{1}{2}\{[Mg^{+2}] \times 4 + [CO_3^{-2}] \times 4 + [Na^+] + [Cl^-] + [HCO_3^-] + [NaCO_3^-] + [MgHCO_3^+]\}$$

as explained in Table 3, the errors reflected on the stability constants for $MgCO_3$ and $MgHCO_3^+$ association are negligible as the average ionic strength was used for calculation. The typical experimental results are given in Table 3 and the least squares plots for the various systems are shown in Figures 2-7.

Eq (a) could be rearranged to yield the thermodynamic association constants.

$$\frac{Y}{X} = K_{1s}^{\circ} + \frac{K_{2s}^{\circ}}{K_{2a}^{\circ}} \frac{\gamma_{MgHCO_3^+}}{a_{H^+}} \quad ; \quad X = \frac{\gamma_{Mg^{+2}} \cdot \gamma_{HCO_3^-}}{\gamma_{MgHCO_3^+}} \qquad (10)$$

Where K_{1s}°, K_{2s}° and K_{2a}° represent the previously defined values extrapolated to infinite dilution. This equation was abandoned because the activity coefficients for $MgHCO_3^+$ are not available and the constants evaluated this way are strongly dependent on the activity coefficients chosen for the various ions involved.

The association constants for the carbonic acids, H_2CO_3 and HCO_3^-, and the activity coefficients used in the calculation are collected in Table 5.

Table 6 shows the various association constants obtained and their extrapolated values as compared to the literature values; some of them are in good agreement with the results in this work. Greenwald[16] used a $KHCO_3$ concentration close to the $NaHCO_3$ concentration in our study and no $Mg(HCO_3)_2$ formation was observed. The stability constants at 20°C have a sequence of $K_{MgCO_3} \gg K_{NaCO_3^-} \gtrsim K_{MgHCO_3^+} > K_{NaHCO_3}$. The magnitudes of the constants imply that these ion pair formations are electrostatic in nature with the exception for $MgCO_3$. Although the thermodynamic data do not distinguish the inner ion pair from the outer sphere, the kinetic studies[17] have concluded the formation of the magnesium bicarbonate ion pair to be controlled by the loss of the inner sphere water molecules.

A least squares plot was applied to the $MgCO_3$ system to generate a value of -4.3 Kcal/mole for the enthalpy of reaction and a value of -1.7 e.u. for the entropy of reaction at 20°C and 0.15 M ionic strength. Extrapolated to infinite dilution, a considerable positive ΔS may reflect partially the increased disorder of the solution upon charge neutralization. In the case of $MgHCO_3^+$, a minimum value for the association constants was observed around 20°C. So is the case for its acid association constant defined as $K_{1s}{}^a = [MgHCO_3^+]/[MgCO_3][H^+]$. The qualitative plots are for the latter two cases and the best fit for the $MgCO_3$ system shown in Fig. 8. The temperatures at which the acid association constants have minimum values have been well documented by Harned and his workers[18] for the carbonic and some of the other acids. A theoretical interpretation has been put forth by Gurney[19] to relate the 'minimum temperature' which gives a minimum association constant to the electro- and non-electro-forces involved in the chemical bonding. The shift of a positive enthalpy of reaction for the formation of $CoCl^{+2}$ and $FeBr^{+2}$ to the negative value for that of $CoBr^{+2}$ and $FeOH^{+2}$ was also interpreted on the basis of a lower minimum temperature for the first two systems and a higher one for the latter two.[19,20] Owing to the experimental difficulties, the temperature range in the present study is limited to a 30° change. In the study of the $CaHCO_3^+$ ion pair formation in the range of 10° to 90°C, Bauman and Almon[21] were able to observe a minimum temperature at 13°C with a much less drastic change in the association constants with respect to the temperature as compared to the magnesium bicarbonate system. A systematic study of the possible ion pair formations for $NaSO_4^-$, $NaCO_3^-$, KCO_3, KSO_4^-, $KHCO_3$ and $NaHCO_3$, as a function of temperature may produce new information on the non-constancy of the enthalpy of reaction. The results at 20°C and the three ionic strengths are shown in Fig. 9. The theoretical values at 0.35 M and 0.64 M were extrapolated based on the values at 0.15 M. The activity coefficients used for correction are in Table 5 and those for HCO_3^- were assumed for $MgHCO_3^+$. The errors involved in obtaining the association constant for $MgCO_3$ at 0.64 M clearly manifests themselves in the theoretical curve in Fig. 9. The rest of the three points are not too far away from the values corrected from those at 0.15 M. The limited ionic strength study, however, does show that the specific sodium ion effects on the magnesium bicarbonate and carbonate formations are not noticeable in the present study.

Acknowledgement

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Table 1a

The Typical Electrode Potentials versus the Pure NaCl or $MgCl_2$ Concentrations* at 20°C

NaCl (M)	mv (Na^+)	$MgCl_2$ (M)	mv (Mg^{+2})
0.03	35.2	0.002	-0.1
0.05	48.9	0.004	6.5
0.10	64.9	0.010	16.2
0.20	81.2	0.020	22.7
0.30	91.0	0.040	29.4
0.40	98.4	0.100	38.9

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*In these solutions, the pH values were adjusted around 7.

Table 1b

The Typical Electrode Potentials versus the NaCl Concentrations in the Presence of a Constant $MgCl_2$ Concentration ($MgCl_2$ = 0.02 M) or versus the $MgCl_2$ Concentrations in the Presence of a Constant NaCl Concentration (NaCl = 0.11 M) at 20°C

NaCl (M)	mv (Na^+)	$MgCl_2$ (M)	mv (Mg^{+2})
0.002	$-30._4$	0.002	0.4
0.050	$48._3$	0.004	6.6
0.080	$59._3$	0.010	15.6
0.090	$62._8$	0.020	22.7
0.095	$64._1$	0.040	29.6
0.100	$65._2$	0.100	38.8

Table 1c

The Electrode Potentials versus $MgCl_2$ Concentrations in a Mixture of NaCl and $MgCl_2$ with Small Variations in NaCl Concentrations.

$MgCl_2$ (M)	NaCl (M)	mv (Mg^{+2})	$MgCl_2$ (M)	NaCl (M)	mv (Mg^{+2})
0.10	0.400	72.1	0.05	0.650	67.5
0.08	0.400	69.2	0.04	0.650	66.3
0.06	0.400	67.1	0.03	0.650	64.3
0.04	0.405	63.1	0.02	0.650	61.6
0.02	0.400	57.8	0.01	0.650	57.8
0.08	0.350	69.1	0.02	0.500	61.6
0.04	0.320	62.9	0.03	0.550	63.5
			0.05	0.550	66.6

Table 2

The Sodium Electrode Potential Measurements at 20°C

A.

$NaHCO_{3_T}$ (M)	$NaOH_T$ (M)	$NaCl_T$ (M)	pH*	mv (Na^+)	C_{Na^+} (M)
0.08	0.100		12.25_0	$74._9$	0.151
0.07	0.090	0.020	12.24_0	$75._1$	0.153
0.06	0.080	0.040	12.22_8	$75._8$	0.155
0.05	0.070	0.060	12.14_8	$76._0$	0.157
0.04	0.055	0.085	12.11_4	$76._8$	0.162
0.03	0.045	0.105	11.96_7	$77._7$	0.169

B.

$NaHCO_{3_T}$ (M)	$NaOH_T$ (M)	$NaCl_T$ (M)	pH*	mv (Na^+)	C_{Na^+} (M)
0.10		0.30	8.1	$97._0$	0.380
0.20		0.20	8.1	$96._2$	0.366
0.30		0.10	8.1	$95._5$	0.359
0.40			8.1	$94._7$	0.346

*$pH = pH_{obs} + \Delta pH$; pH_{obs} was the measured value and ΔpH was a correction factor (see text).

A. Ionic strength = 0.19 ± 0.01 M, $\gamma_{Na^+} = 0.729$

B. Ionic strength = 0.36 ± 0.01 M, $\gamma_{Na^+} = 0.710$

Table 3

Experimental Conditions and Concentration Calculations for the $MgCl_2$-$NaHCO_3$ System at 20°C and 0.15 ± 0.01 Ionic Strength

No.[f]	$MgCl_{2_T}$ (M)	$NaHCO_{3_T}$ (M)	$NaCl_T$ (M)	HCl_T (M)	$NaOH_T$ (M)	pH_{obs}[a]	Na^+ (M)	mv(Na^+)	Mg^{+2} (M) x 10^2	mv(Mg^{+2})	Y[b]
1	0.02	0.096			0.014	8.87_6	0.1012	$66._3$	0.9725	16.7	14.6
Ref	0.01		0.110			~7.6	0.110	$68._0$	1.00	17.3	(14.4)[e]
2	0.02	0.098			0.012	8.76_7	0.1012	$66._3$	1.000	17.2	13.2
3	0.02	0.100			0.010	8.69_4	0.0992	$66._9$	1.047	15.2	11.9
Ref	0.01		0.110			~8.5	0.110	$69._9$	1.00	14.7	
4	0.02	0.100	0.003		0.007	8.54_5	0.1022	$67._6$	1.129	16.2	9.5
5	0.02	0.100	0.0015		0.0085	8.62_0	0.1040	$65._0$	1.116	14.9	9.6
Ref	0.01		0.110			~8.7	0.110	$66._6$	1.00	13.9	
6	0.02	0.100	0.005		0.0050	8.40_6	0.1033	$64._7$	1.212	15.9	7.8
7	0.02	0.100	0.0065		0.0035	8.33_6	0.1080	$67._2$	1.433	15.6	4.4
Ref	0.02		0.110			~8.7	0.110	$67._6$	2.00	19.4	
8	0.02	0.100	0.001			8.05_5	0.1067	$66._9$	1.488	15.9	3.8
9	0.02	0.100	0.0065		0.0035	8.36_3	0.1080	$67._2$[c]	1.284	19.0	6.3
Ref	0.02		0.110			~8.7	0.110	$67._6$[d]	2.00	24.2	
10	0.02	0.100	0.010			8.047	0.1067	$66._9$[d]	1.460	20.5	4.1

Table 3 continued

No.[f]	$MgCl_{2_T}$ (M)	$NaHCO_{3_T}$ (M)	$NaCl_T$ (M)	HCl_T (M)	$NaOH_T$ (M)	pH_{obs} [a]	Na^+ (M)	mv(Na^+)	Mg^{+2} (M) x 10^2	mv(Mg^{+2})	Y [b]
11	0.02	0.100	0.01	0.0025		7.93_1	0.1067	$66._9$ [d]	1.460	16.4	4.2
Ref	0.02		0.11			~9.0	0.110	$67._6$ [d]	2.00	20.0	
12	0.02	0.100	0.01	0.0050		7.63_4	0.1067	$66._9$ [d]	1.543	16.9	3.4 (3.2)[e]

[a] $pH = pH_{obs} + 0.005$ (see text)

[b] Y was defined as $[Mg_T] - [Mg^{+2}]/[Mg^{+2}]\,[HCO_3^-]$ (see text)

[c] same as No. 7

[d] Taken from No. 8 and its reference; at pH < 8, readings were less stable, no measurements were made for Na^+ ion activity to assure quick measurements. In view of the weak $NaHCO_3$ association, the error introduced was negligible.

[e] The iterated ionic strengths for the most basic solution (run No. 1) and the most acid solution (run No. 12) are 0.140 and 0.159 M respectively. The Y values regenerated based on these ionic strengths as shown in brackets are well within the experimental errors of those evaluated based on 0.15 M. The difference in Y's for run No. 12 may partially be accounted for by the ionic strength variation from 0.150 M to 0.159 M.

[f] For each system, an average of two out of ten runs had errors significantly larger than the standard deviation and were redetermined. Only these redetermined points along with other points are shown in Figures 2 - 6.

Table 4

The Liquid Junction Approximation: The pH measurements as a Function of Ionic Strength at 20°C

NaCl (m)	NaCl (m)	pH_{obs}	γ_{OH^-} (a)	pOH_{obs} (b)	OH^- (a) $M \times 10^3$	pH_{cal} (b)	$\Delta pH = pH_{cal} - pH_{obs}$
0.100	0.1002	10.92_2	0.766	3.078	1.091	10.922	0
0.200	0.2009	10.88_6	0.726	3.114	1.089	10.898	0.012
0.300	0.3020	10.85_6	0.705	3.144	1.086	10.884	0.028
0.500	0.5045	10.80_9	0.691	3.191	1.081	10.873	0.064
0.700	0.7080	10.77_5	0.685	3.225	1.076	10.867	0.092

(a) H.S. Harned and B.B. Owen, The Physical Chemistry of Electrolytic Solution, 3rd, Reinhold publishing Corporation, New York, 1958, p. 729.

(b) $[OH^-] = [a_{OH^-}/\gamma_{OH^-}]_{NaCl = 0.1 M}$ x volume correction for ionic strength higher than 0.1 M.

$pOH_{obs} = 14 - pH_{obs}$; $pH_{cal} = 14 - pOH_{cal} = 14 + \log [\gamma_{OH^-} \times OH^-]$

Table 5

The Acid Association Constants Corrected for H_2CO_3 and HCO_3^- at Various Temperatures and Ionic Strengths Together with the Various Activity Coefficients Involved in the Calculations

Temp. (°C)	0°	10°	20°	30°	20°	20°	Reference
Ionic str. (M)	0.15	0.15	0.15	0.15	0.35	0.64	
$K_{a1} \times 10^{-6}$	2.10	1.60	1.31	1.16	1.25	1.18	a
$K_{a2} \times 10^{-10}$ (M^{-1})	1.58	1.16	1.00	0.725	0.718	0.610	b
γ_{H^+}	0.774	0.770	0.764	0.760	0.734	0.719	c
$\gamma_{HCO_3^-}$			0.715		0.712	0.683	d
$\gamma_{CO_3^=}$			0.348		0.258	0.213	d
$\gamma_{Mg^{+2}}$			0.363		0.292	0.265	e
γ_{MgCO_3}					1.04	1.1	f

a H.S. Harned and R. Davis, jun, J. Amer, Chem. Soc., 65 2030 (1943).

b H.S. Harned and S.R. Scholes, jun, J. Amer. Chem. Soc., 63, 1706 (1941).

c Extrapolated values, H.S. Harned and B.B. Owen, The Physical Chemistry of Electrolytic Solutions 3rd , Reinhold Publishing Corporation New York, 1958.

d Values are at 25°C; A.C. Walker, O.B. Bray and J. Johnson, J. Amer. Chem. Soc., 49, 1235 (1927).

e Values are taken from the Orion manual. These values are higher than those obtained from $\gamma_{Mg^{+2}} = \dfrac{\gamma_{\pm}^{3}(MgCl_2)}{\gamma_{\pm}^{2}(KCl)}$

f R.M. Garrels and M.E. Thompson, Amer. J. Sci., 260, 57 (1962).

Table 6

The Association Constants obtained for $K_{1s} = \frac{[MgHCO_3^{+}]}{[Mg^{+2}][HCO_3^{-}]}$, $K_{2s} = \frac{[MgCO_3]}{[Mg^{+2}][CO_3^{=}]}$ and $K_{1s}^{a} = \frac{[MgHCO_3^{+}]}{[MgCO_3][H^{+}]}$ in this work and Those Appearing in the Literature

Temp (°C)	Ionic Str. (M)	$K_{1s}(M^{-1})$	$K_{2s}(M^{-1})$	$K_{1s}^{a}(M^{-1} \times 10^{-8})$	α[b]	Reference
0°	0.15 ± 0.01	7.35	367.0	3.17	0,9548	This work
10°	0.15 ± 0.01	4.05	339.3	1.38	0.9915	This work
20°	0.15 ± 0.01	2.35	225.9	1.04	0.9764	This work
30°	0.15 ± 0.01	2.53	165.8	1.10	0.9938	This work
20°	0.35 ± 0.013	2.33	130.1	1.29	0.9464	This work
20°	0.64 ± 0.02	1.99	~90[a]	~1.4[a]	0.7036	This work
20°	→ 0	7.00	1.8×10^{3}	0.97		This work[c]
~22°	~0.15	5.88		3.16		d
~22°	~0.15	2.70		1.00		e
~22°	→ 0	7.24		0.72		e
25°	→ 0	8.91		0.72		e
25°	varied	5×10^{3}				f
25°	→ 0	14.4				g
28.4°	varied	No ion pair formation				h
20°	0.1		152			i
25°	→ 0		2.5×10^{3}			g
25°	0.72	1.62	112.3			j

a Theoretical values estimated from Fig. 9. The experimental values could not be accurately evaluated based on an insufficient number of datum points.

b Correlation coefficient for eq (9).

Table 6 contd.

c Values obtained using the activity coefficients in Table 5. The values for K_{1s} and K_{2s} at infinite dilution would be about 25% higher if $\gamma_{Mg^{+2}} = \frac{\gamma^3_{\pm(MgCl_2)}}{\gamma^2_{\pm(KCl)}}$ was assumed and $\gamma_{\pm(MgCl_2)}$ and $\gamma_{\pm(KCl)}$ in Harned and Owen's Tables were used.

d I. Greenwald, J. Biol. Chem., 141, 780 (1941).

e Values corrected and reported in P.B. Hostetler, J. Phys. Chem., 67, 720 (1963).

f R. Näsänen, Z. Phys. Chem., 190 A, 183 (1942).

g R.M. Garrels and M.E. Thompson, Amer. J. Sci., 260, 57 (1962).

h F. Halla and R. Van Tassel, J. Phys. Chem., 62, 1135 (1958).

i J. Raaflaub, Helv. Chim. Acta., 43, 629 (1960).

j J.E. Hawley, Ph.D. Thesis, Oregon State University, 1973.

Figure Captions

Fig. 1a - A plot of electrode potentials versus activities of NaCl or $MgCl_2$ pure electrolyte at 20°C.

Fig. 1b - A plot of electrode potentials versus Na^+ activities in 0.02 M $MgCl_2$ solution or versus Mg^{+2} activities in 0.11 M NaCl solution at 20°C.

Fig. 1c - Plots of electrode potentials versus Mg^{+2} activities in the NaCl-$MgCl_2$ mixtures at 20°C. X for points having NaCl $\geq$ 0.55 M O for points having NaCl $\leq$ 0.405 M.

Fig. 2 - A plot of $\dfrac{[Mg_T] - [Mg^{+2}]}{[Mg^{+2}][HCO_3^-]} = Y$ versus $\dfrac{1}{[H^+]} \times 10^{-8}$ at 20°C and 0.15 M ionic strength.

Fig. 3 - A plot of Y versus $1/[H^+] \times 10^{-8}$ at 30°C and 0.15 M ionic strength.

Fig. 4 - A plot of Y versus $1/[H^+] \times 10^{-8}$ at 10°C and 0.15 M ionic strength.

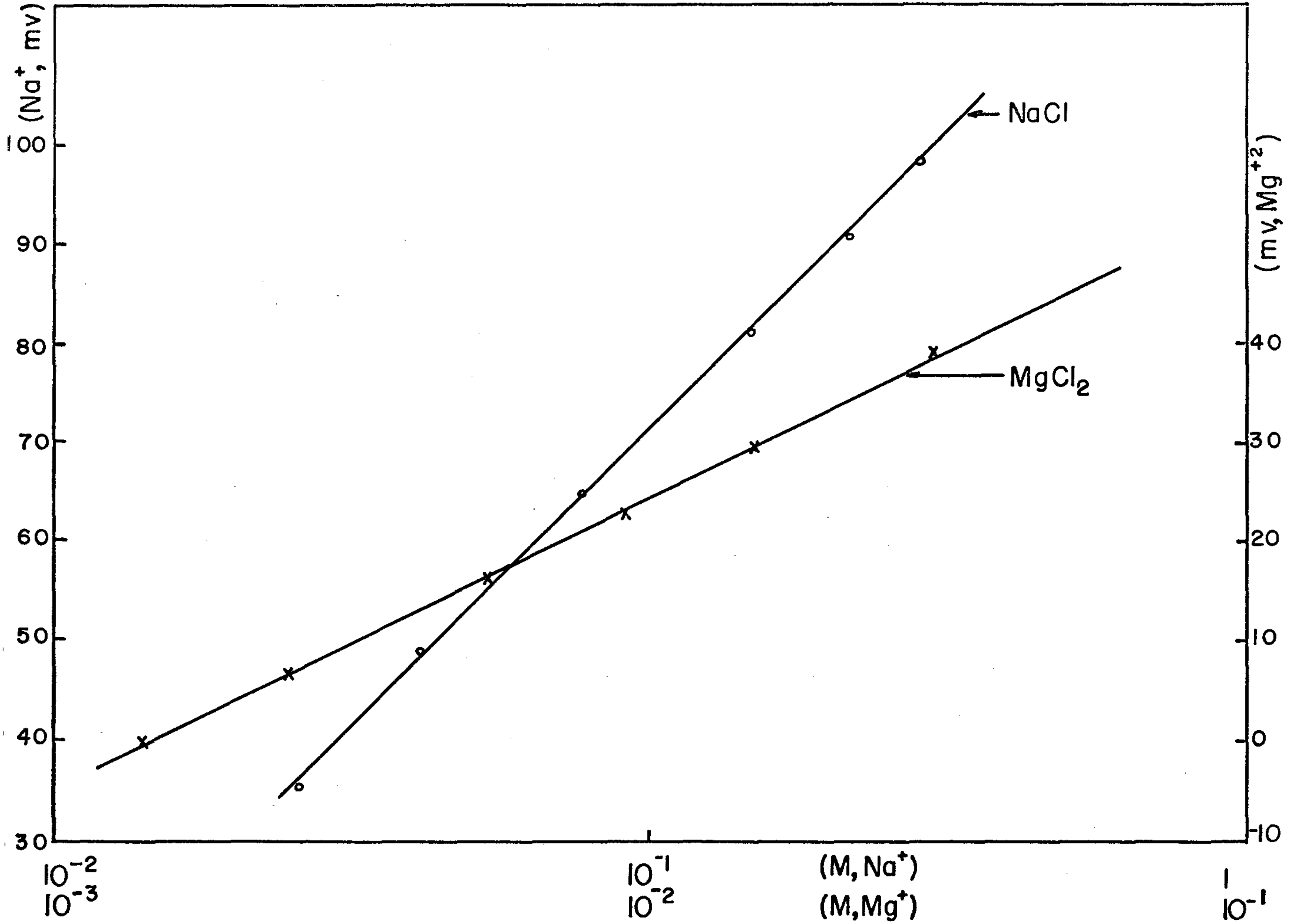
Fig. 5 - A plot of Y versus $1/[H^+] \times 10^{-8}$ at 0°C and 0.15 M ionic strength.

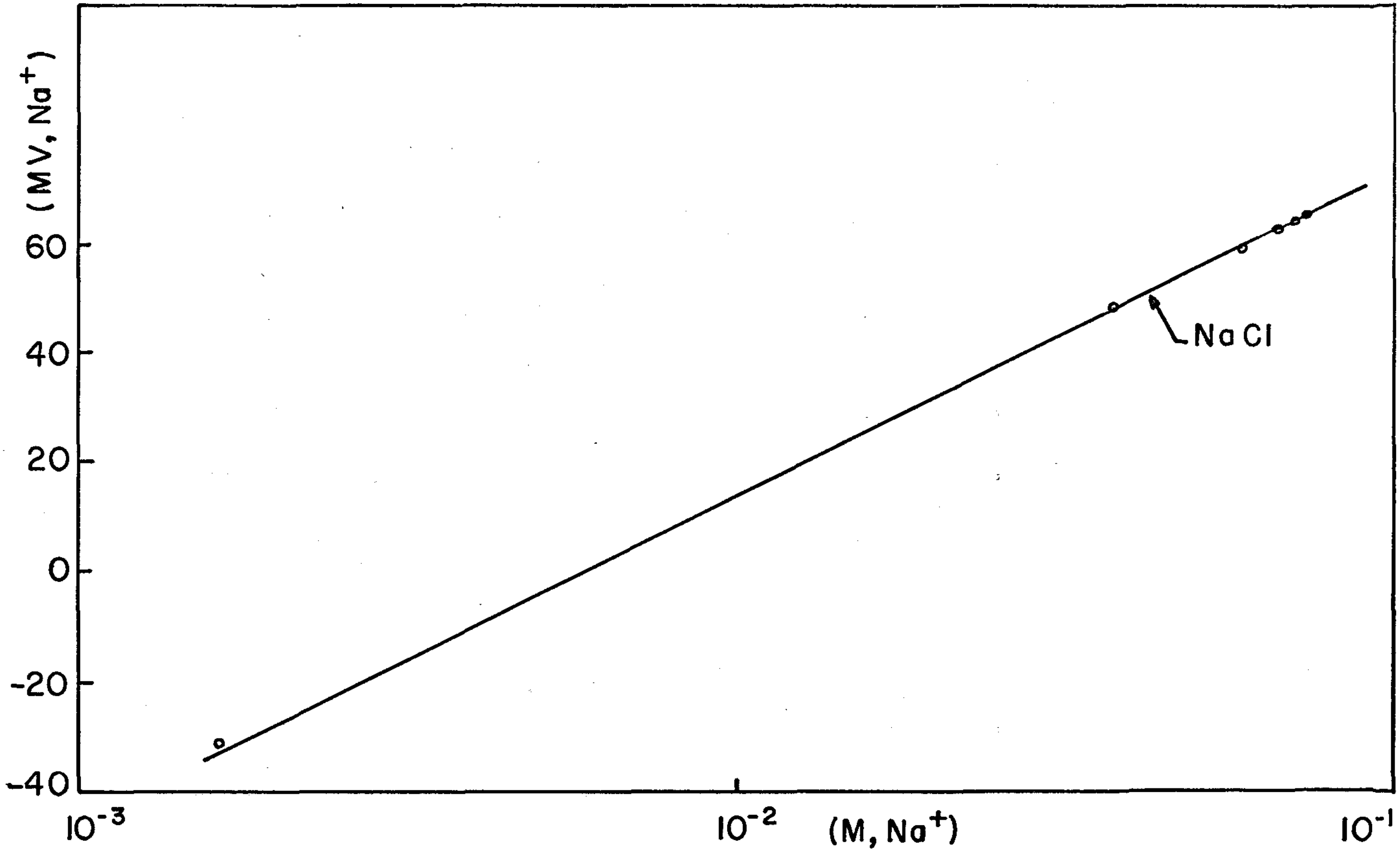
Fig. 6 - A plot of Y versus $1/[H^+] \times 10^{-8}$ at 20°C and 0.35 M ionic strength.

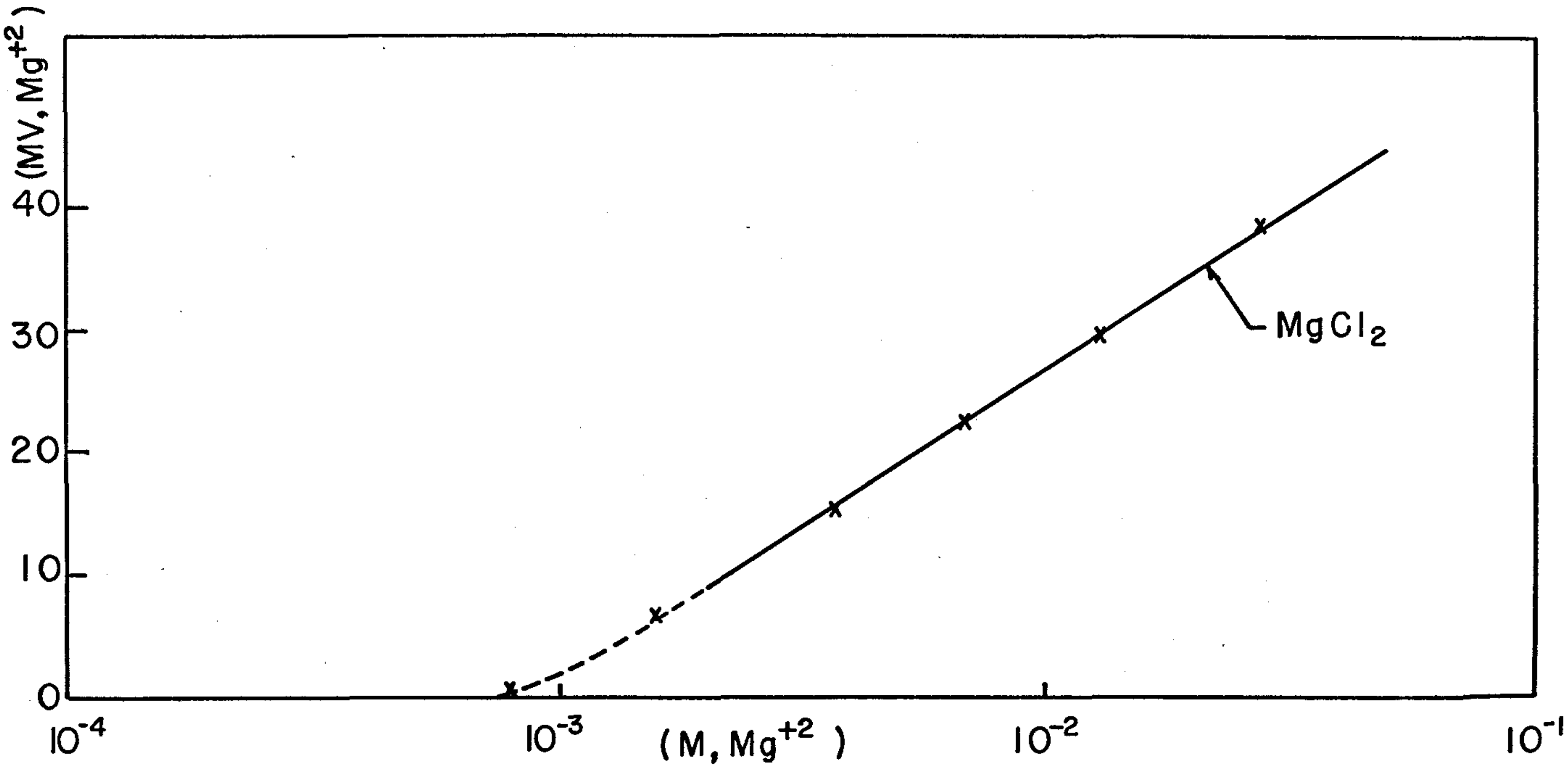
Fig. 7 - A plot of Y versus $1/[H^+] \times 10^{-8}$ at 20°C and 0.64 M ionic strength.

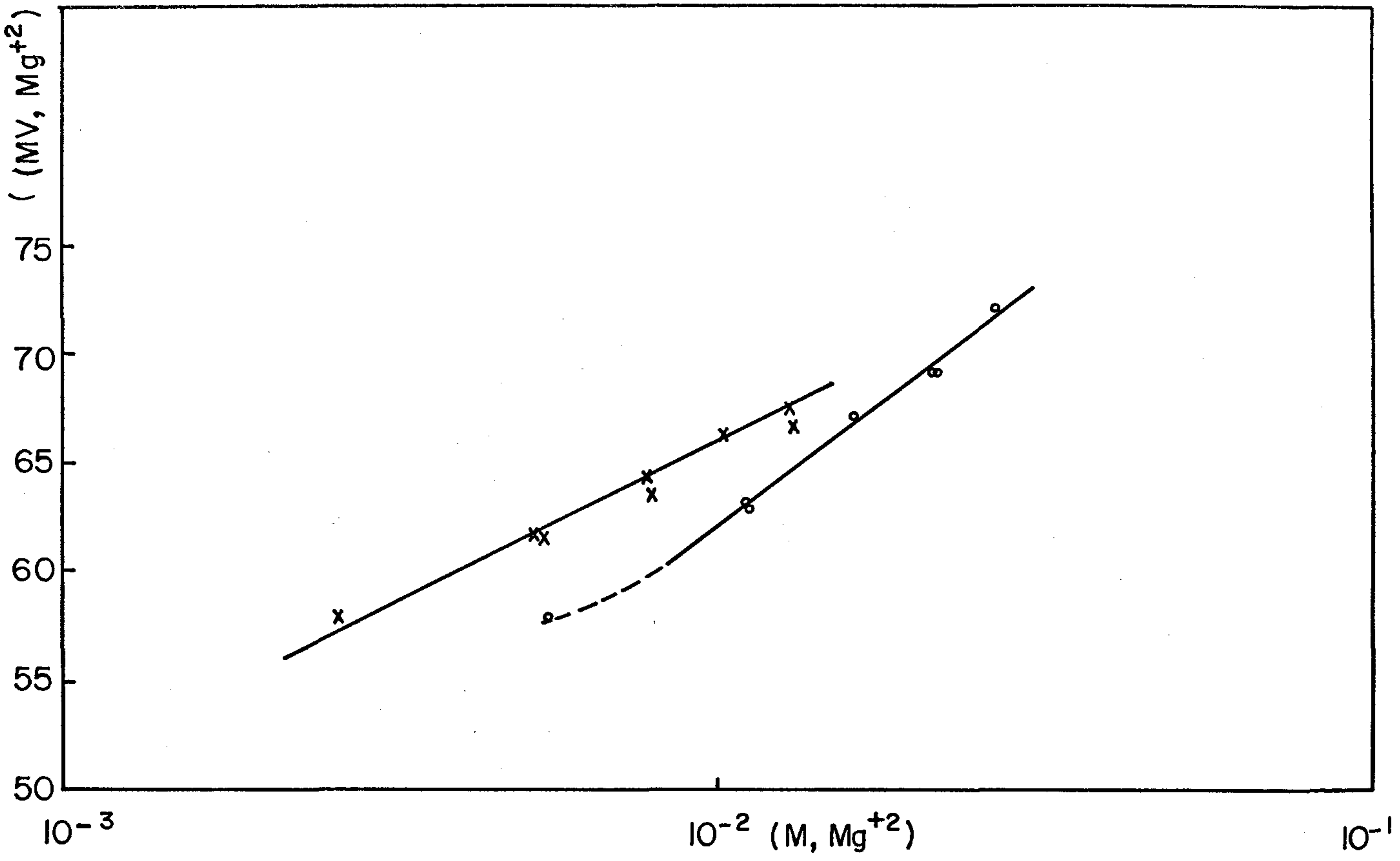
Fig. 8 - Plots of log K versus 1/ Temp. $\times 10^{-3}$ for the association reaction of $Mg^{+2} + CO_3^{=} \rightleftarrows MgCO_3$, $Mg^{+2} + HCO_3^- \rightleftarrows MgHCO_3^+$ and $MgCO_3 + H^+ \rightleftarrows MgHCO_3^+$.

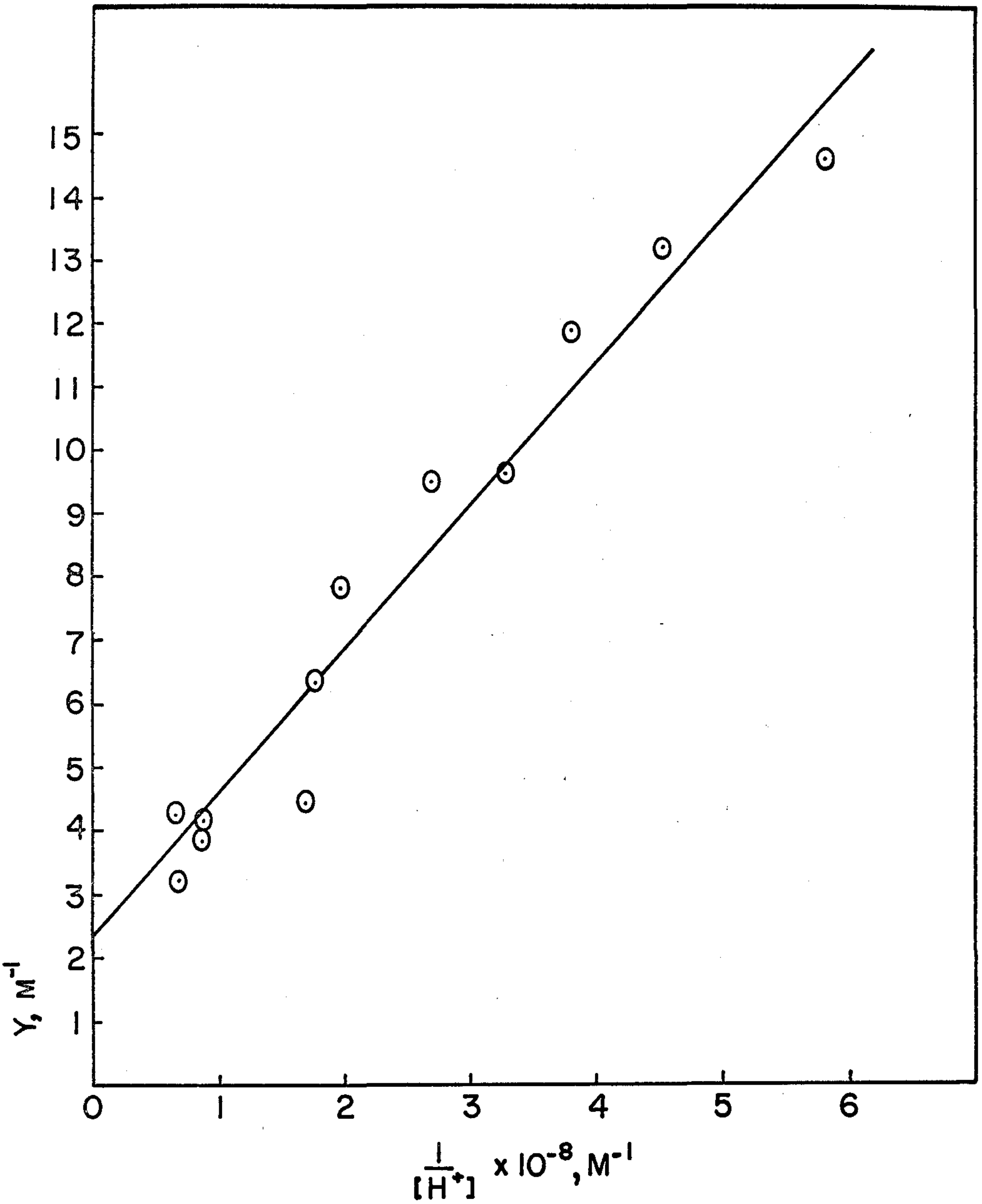
Fig. 9 - Plots of log K versus ionic strength for the reactions of $Mg^{+2} + CO_3 \rightleftarrows MgCO_3$ and $Mg^{+2} + HCO_3^- \rightleftarrows MgHCO_3^+$. (•) Experimental values; (Δ), theoretical values based on the points at 20°C and 0.15 M ionic strength.

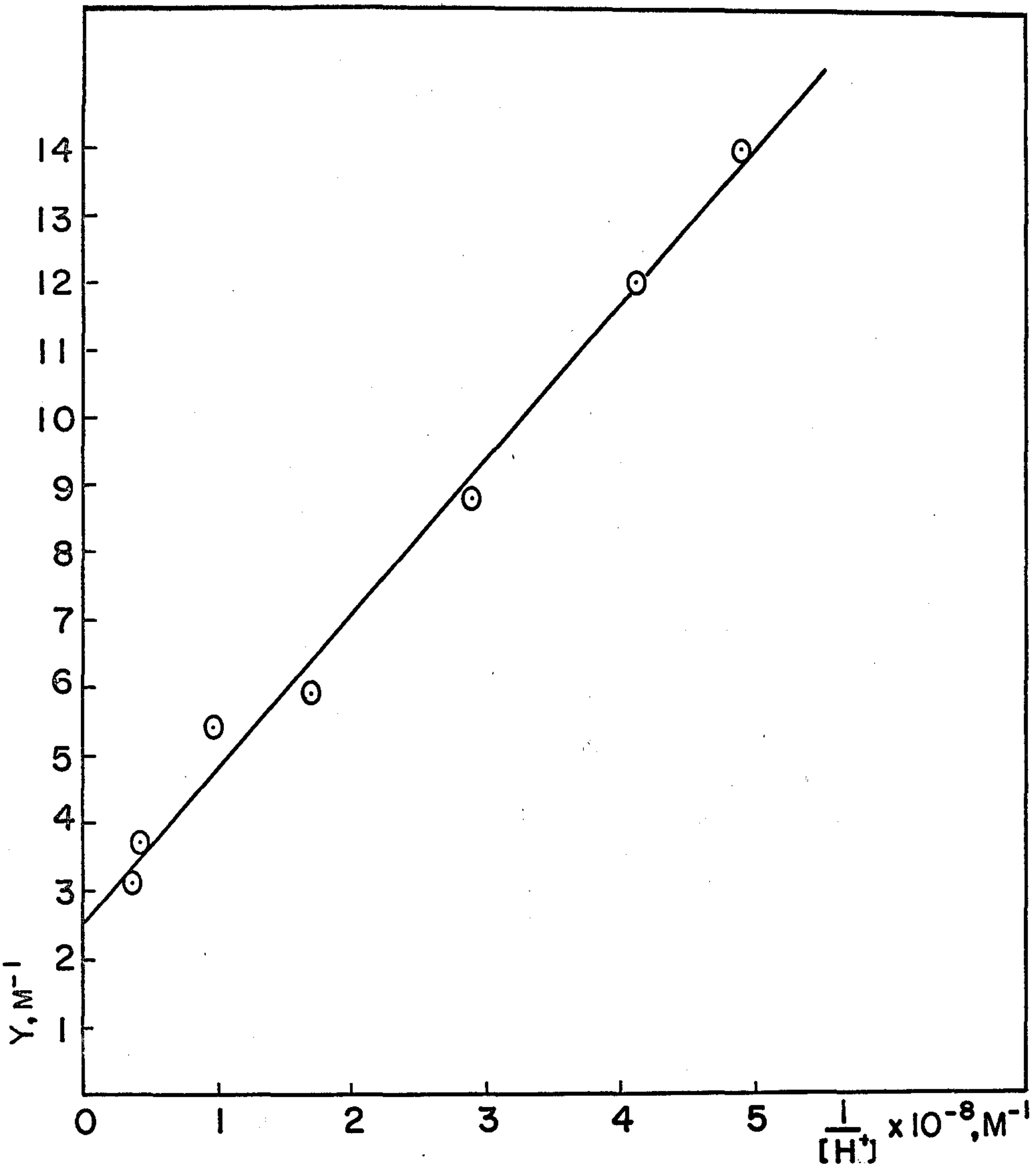

(Na$^+$, mv)
100
90
80
70
60
50
40
30
(mv, Mg^{+2})
40
30
20
10
0
-10
NaCl
MgCl$_2$
10^{-2}
10^{-3}
10^{-1}
10^{-2}
(M, Na$^+$)
(M, Mg$^+$)
1
10^{-1}


(MV, Na$^+$)
60
40
20
0
-20
-40
Na Cl
10^{-3}
10^{-2}
(M, Na$^+$)
10^{-1}

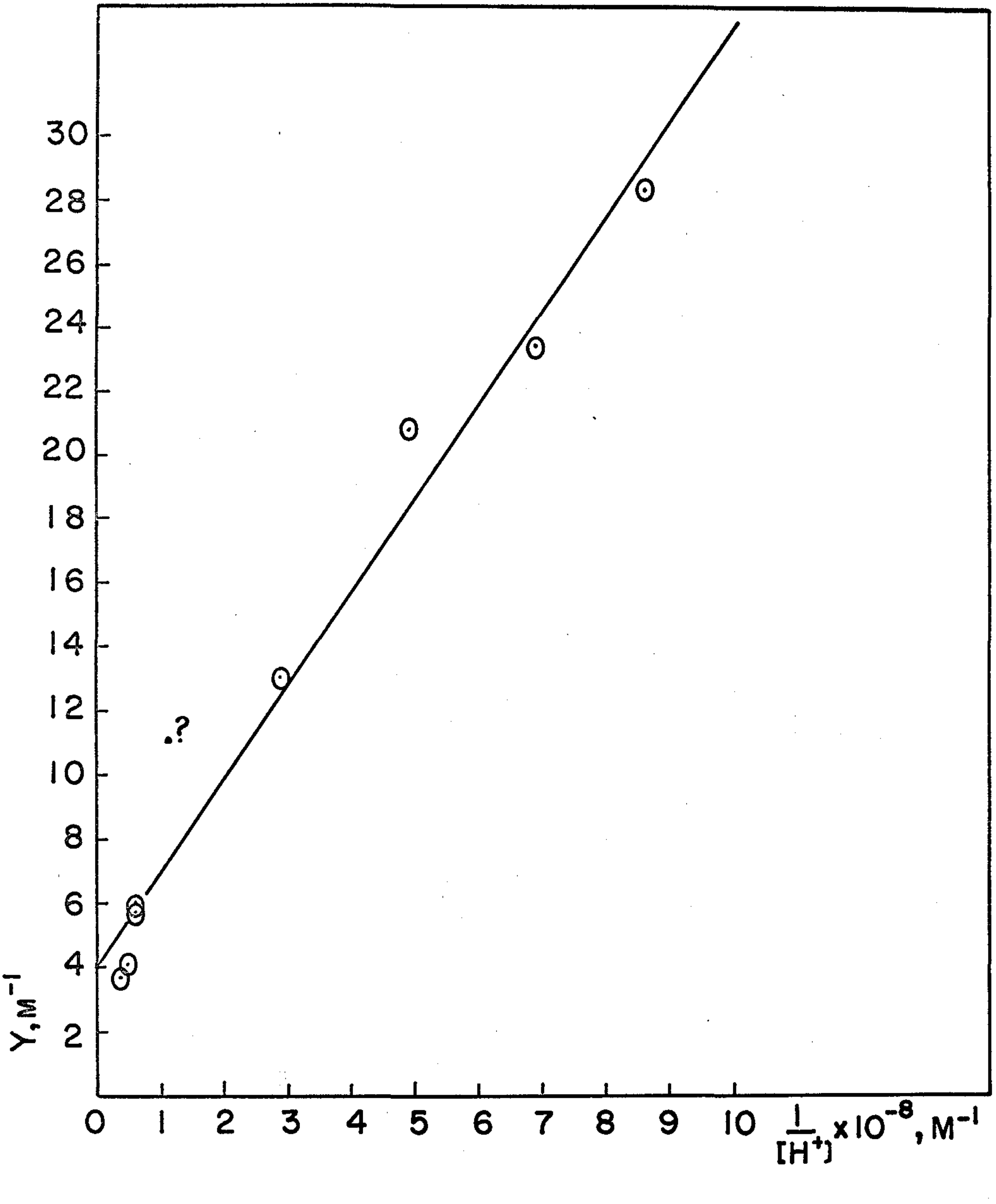

(MV, Mg+2)
40
30
20
10
0
10-4
10-3
(M, Mg+2)
10-2
10-1
MgCl2

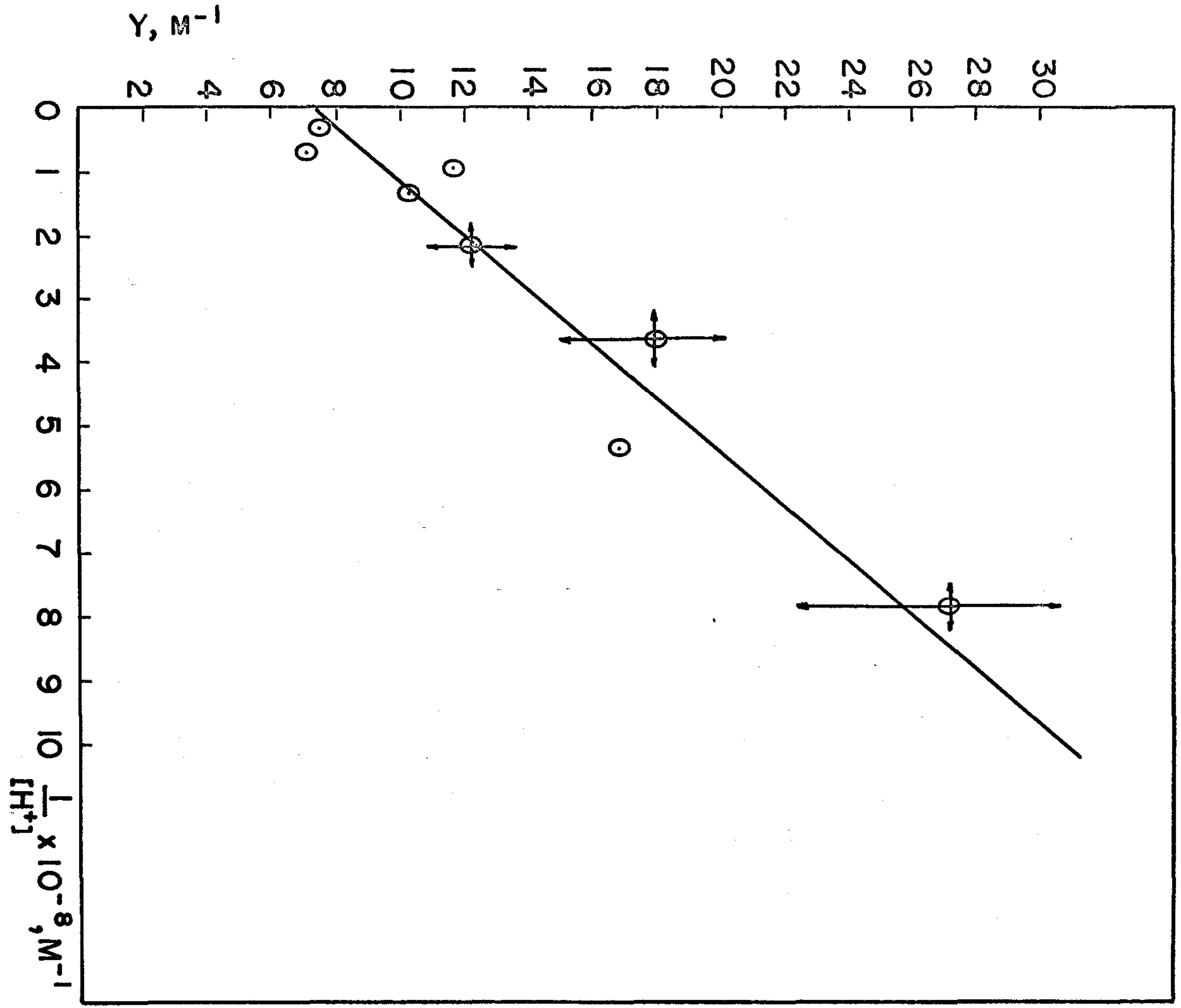

((MV, Mg+2)
75
70
65
60
55
50
10−3
10−2 (M, Mg+2)
10−1

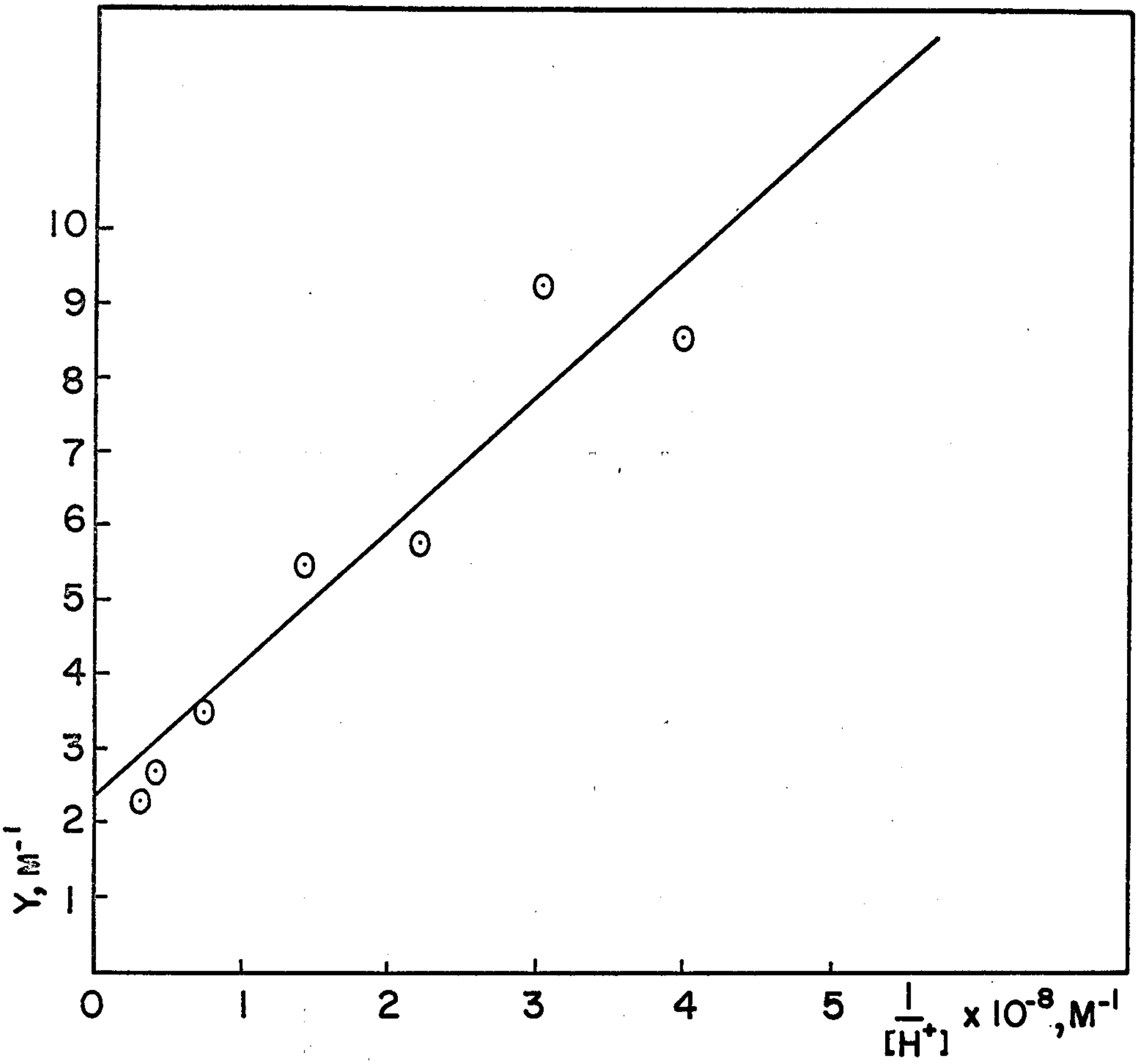

Y, M^{-1}
1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
0
1
2
3
4
5
6
$\frac{1}{[H^+]} \times 10^{-8}, M^{-1}$

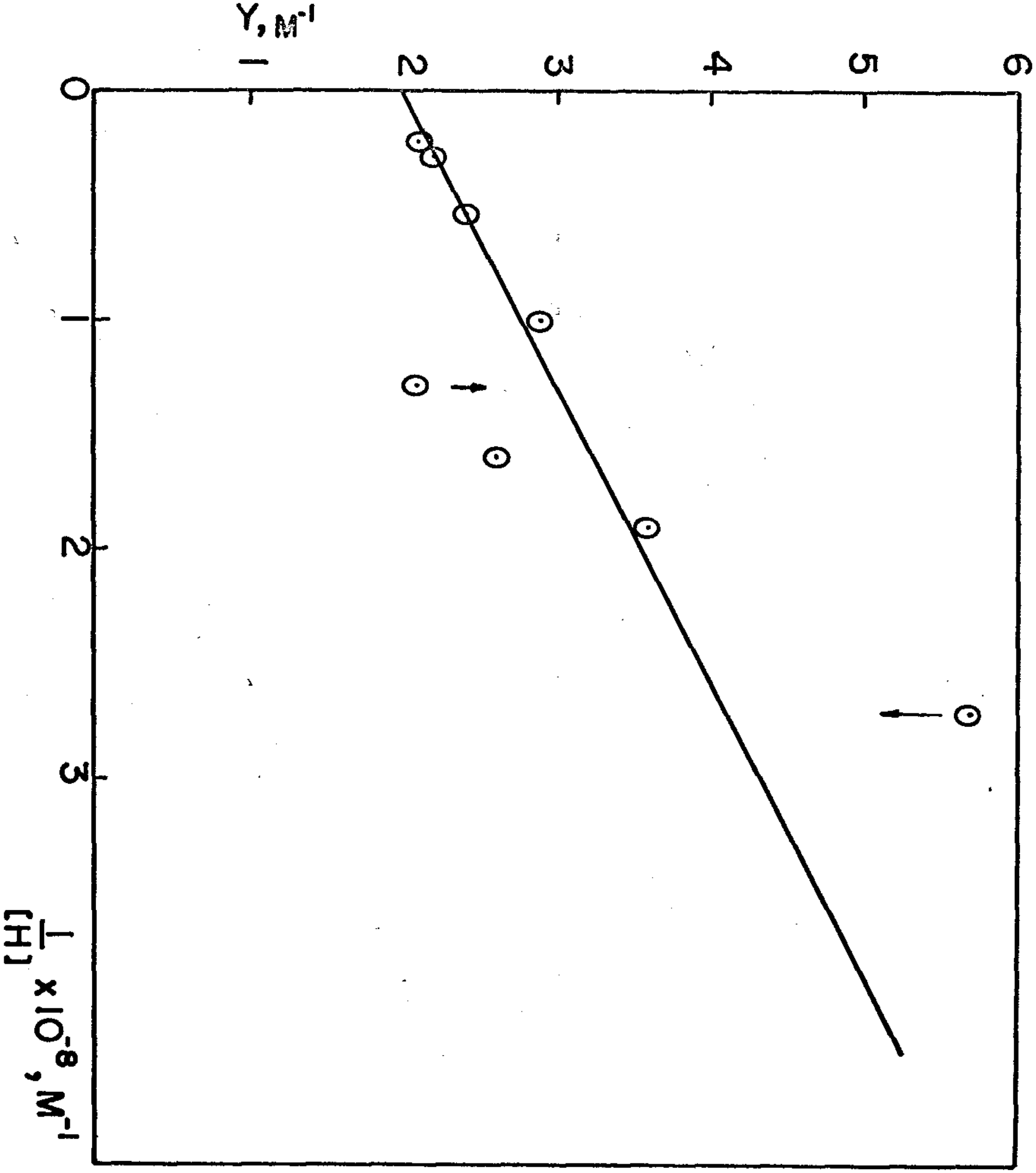


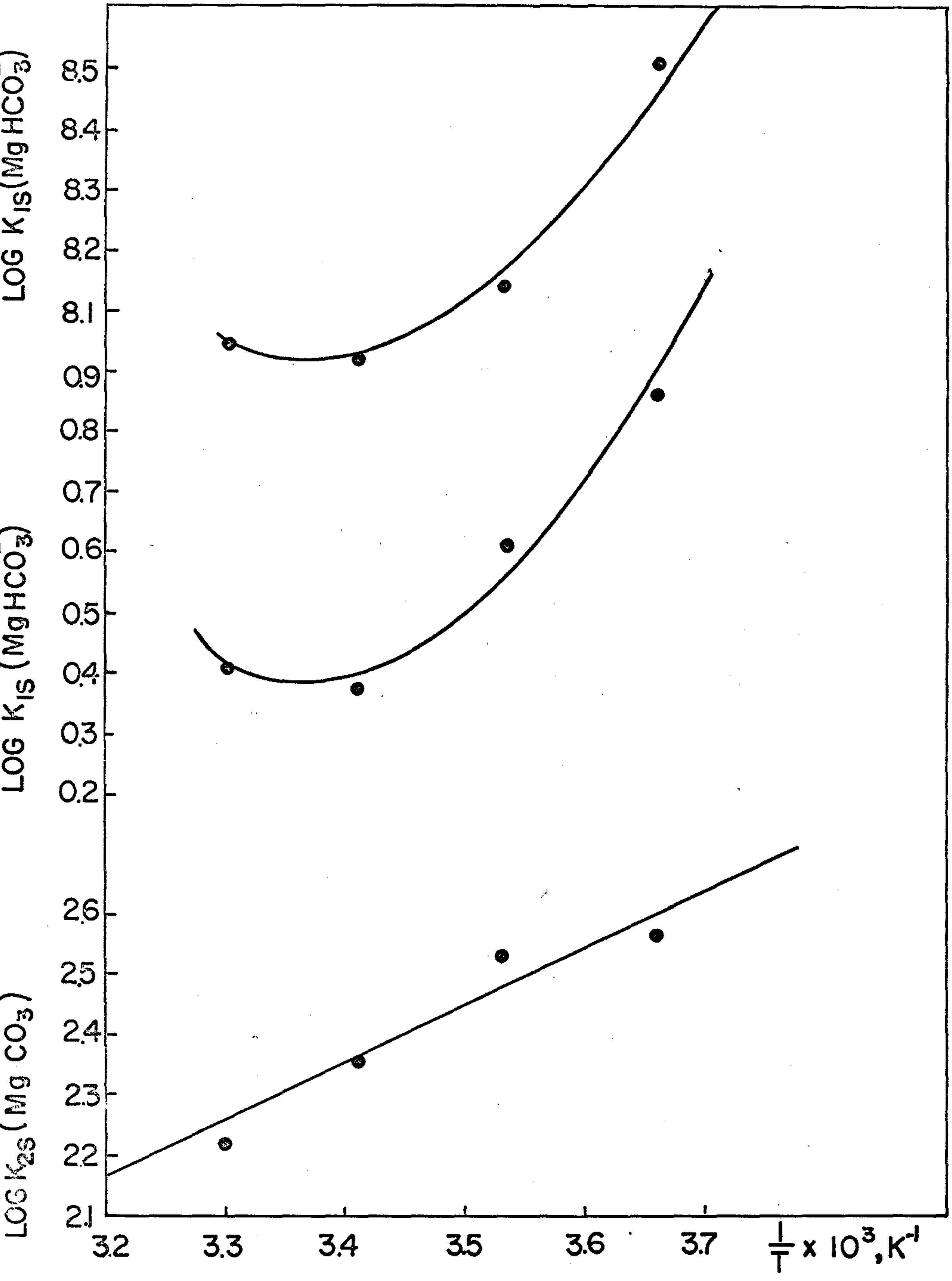
Y, M^{-1}
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
1
2
3
4
5
$\frac{1}{[H^+]} \times 10^{-8}, M^{-1}$


Y, M^{-1}
2
4
6
8
10
12
14
16
18
20
22
24
26
28
30
0
1
2
3
4
5
6
7
8
9
10
$\frac{1}{[H^+]} \times 10^{-8}, M^{-1}$
?


Y, M^{-1}
2
4
6
8
10
12
14
16
18
20
22
24
26
28
30
0
1
2
3
4
5
6
7
8
9
10
$\frac{1}{[H^+]} \times 10^{-8}, M^{-1}$


Y, M^{-1}
1
2
3
4
5
6
7
8
9
10
0
1
2
3
4
5
$\frac{1}{[H^+]} \times 10^{-8}, M^{-1}$


Y, M^{-1}
0
1
2
3
4
5
6
0
1
2
3
$\frac{1}{[H]}$ x 10^{-8}, M^{-1}


LOG K_{1S}^{a} (Mg HCO_3^-)
8.5
8.4
8.3
8.2
8.1
0.9
0.8
0.7
LOG K_{1S} (Mg HCO_3^-)
0.6
0.5
0.4
0.3
0.2
2.6
2.5
2.4
LOG K_{2S} (Mg CO_3)
2.3
2.2
2.1
3.2
3.3
3.4
3.5
3.6
3.7
$\frac{1}{T} \times 10^3, K^{-1}$

RESEARCH PROJECT TECHNICAL COMPLETION REPORT
OWRR PROJECT NO. A-045-OKLA

THE EFFECT OF HYDROCARBON-POLLUTION ON THE CARBON DIOXIDE-WATER SYSTEM

SUBMITTED TO
THE OKLAHOMA WATER RESOURCES RESEARCH INSTITUTE
OKLAHOMA STATE UNIVERSITY
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RESEARCH PROJECT

TECHNICAL COMPLETION REPORT

The Effect of Hydrocarbon-Pollution on the Carbon Dioxide-Water System

OWRR Project No. A-045
Agreement No. 14-31-001-3836
July 1, 1972 to June 30, 1974

submitted by:

Gordon Atkinson
Principal Investigator

The University of Oklahoma
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