Equilibrium and response curve analyses on the adsorption of CaCl2 and Ca(NO3)2 using a retardation resin
by Jeffrey Edward Rehor

A thesis submitted in partial fulfillment of the requirements for the degree of MASTER OF SCIENCE in Chemical Engineering
Montana State University

Abstract:
Equilibrium constants were determined for the adsorption of CaCl2 / Ca(NO3)2, CdCl2, and ZnCl2 by Bio-Rad Laboratories' AG11A8 bifunctional resin. The equilibrium constants were found to decrease with rising temperature for CaCl2 but increase for Ca(NO3)2/ CdCl2, and ZnCl2.

Experimental response curves were also generated for CaCl2 and Ca(NO3)2 by injecting a concentrated pulse into a column packed with the resin. These response curves were analyzed using the method of weighted moments to estimate an equilibrium and rate parameter. Both of these parameters showed maximum values at 20°C.

The experimental curves were compared to curves generated from a model of the system. The best fit between the theory and the experimental data occurred at 10°C while the agreement at 20°C and 50°C was not quite as good.

The equilibrium parameter was also estimated directly from the equilibrium constant to yield a comparison.

A wide discrepancy between the two values was found.

STATEMENT OF PERMISSION TO COPY

In presenting this thesis in partial fulfillment of the requirements for an advanced degree at Montana State University, I agree that the Library shall make it freely available for inspection. I further agree that permission for extensive copying of this thesis for scholarly purposes may be granted by my major professor, or, in his absence, by the Director of Libraries. It is understood that copying or publication of this thesis for financial gain shall not be granted without my written permission.

Signature Jeffrey Edward Rihor

Date May 25, 1982

EQUILIBRIUM AND RESPONSE CURVE ANALYSES ON THE ADSORPTION OF $CaCl_2$ AND $Ca(NO_3)_2$ USING A RETARDATION RESIN

by

JEFFREY EDWARD REHOR

A thesis submitted in partial fulfillment of the requirements for the degree

of

MASTER OF SCIENCE

in

Chemical Engineering

Approved:

Robert L. Nickelson
Chairperson, Graduate Committee

Head, Major Department

Michael Malone
Graduate Dean

MONTANA STATE UNIVERSITY
Bozeman, Montana

May, 1982

ACKNOWLEDGEMENTS

The author wishes to thank the staff and fellow graduate students of the Chemical Engineering Department at Montana State University for the help provided in this research project.

A special thanks goes to Dr. Robert Nickelson for his continual guidance and supervision of this research.

Thanks also go to Elizabeth Hartz for the aid in writing the computer programs.

TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

ABSTRACT

Equilibrium constants were determined for the adsorption of $CaCl_2$, $Ca(NO_3)_2$, $CdCl_2$, and $ZnCl_2$ by Bio-Rad Laboratories' AG11A8 bifunctional resin. The equilibrium constants were found to decrease with rising temperature for $CaCl_2$ but increase for $Ca(NO_3)_2$, $CdCl_2$, and $ZnCl_2$.

Experimental response curves were also generated for $CaCl_2$ and $Ca(NO_3)_2$ by injecting a concentrated pulse into a column packed with the resin. These response curves were analyzed using the method of weighted moments to estimate an equilibrium and rate parameter. Both of these parameters showed maximum values at 20°C.

The experimental curves were compared to curves generated from a model of the system. The best fit between the theory and the experimental data occurred at 10°C while the agreement at 20°C and 50°C was not quite as good.

The equilibrium parameter was also estimated directly from the equilibrium constant to yield a comparison. A wide discrepancy between the two values was found.

INTRODUCTION

Several recent investigations have studied the desalination of water using retardation resins (1,9,10). Very little research, however, has been done using inorganic salts other than sodium chloride. The applications of retardation resins to the removal of other ions would seem to be numerous and important.

The most significant applications may be in the area of pollution control. Concern has grown about the quantity of chemicals which have been released into our waterways. As restrictions on effluent quality increase the need for alternate methods to remove a variety of ions will be necessary. Another possible use will be the recovery of valuable products from plant effluents. There are also processes involving substances such as mercury and cadmium where such a recovery is valuable for both of these reasons (2,3).

The retardation resins have properties that make them unique when compared with the usual ion exchange resins that have been used in the past. The ion exchange resins work on the principle that an ion present on fresh resin is removed in exchange for an ion in the treated solution. For example, in the simple water softening process, sodium ions on the resin are released as calcium ions are removed from the water. To reuse the ion exchange resin it must be chemically treated to replace the ions removed so it is restored to its original form.

Retardation resins, on the other hand, have both positive and negative sites that satisfy each other until some ionic substance is present. Then both anions and cations are adsorbed into the resin. Regeneration can be accomplished by contacting the resin with pure water. The rate of regeneration can usually be increased by heating the water prior to contact with the resin.

Very little information is available on the mechanism of adsorption on the retardation resin. Equilibrium and rate data are available only for sodium chloride. There are many unanswered questions about the effects the valency state of the ions, the ionic radius, and the interaction between different anions and cations have on the adsorption equilibrium and rate.

EXPERIMENTAL PROGRAM

The experimental program can be divided into two independent experiments. The first of these is an equilibrium measurement. The objective of this experiment is to estimate the equilibrium constants for the adsorption of inorganic chemicals from aqueous solutions using a specific resin.

The second part is an experimental generation of response curves from pulse injections of inorganic species into a packed column. The objective here is to obtain both an equilibrium and rate parameter. These two parameters will be estimated using the method of weighted moments to numerically integrate the experimental response curves. By substituting both of these parameters into the theoretical model of the system a theoretical response curve can be generated.

Several different chemical species at varied temperatures will be investigated. The inorganic chemicals to be used are: $CaCl_2$, $Ca(NO_3)_2$, $CdCl_2$, and $ZnCl_2$. The operating temperatures are 10^oC, 20^oC, and 50^oC.

EXPERIMENTAL MATERIALS AND EQUIPMENT

To perform the equilibrium analysis the only required materials and equipment are the resin and the conductivity probe with its associated electronics. The pulse response experimentation requires one additional item, namely the glass column. Each of these items will now be discussed in detail.

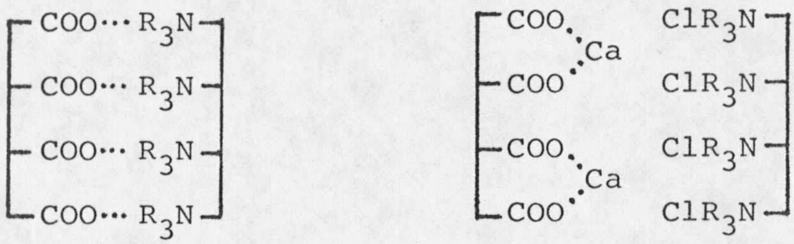
Column

The column used for this experimentation is jacketed and made by Bio-Rad Laboratories. The inside diameter is 0.7 cm and the bed length is 15.0 cm.

Resin

The resin used in this research is Bio-Rad Laboratories' AG11A8. They produce this type of resin by polymerizing acrylic acid inside another of their resins, AG-1X8 or Dowex 1. The result is a styrene divinylbenzene, cross-linked polymer lattice, with paired anion and cation exchange sites. This resin is referred to as bifunctional because of its ability to adsorb both anions and cations. A simplified structure of the resin in its completely cleansed form is shown in Figure 1a. When the resin is brought into contact with the ionic solution, the inorganic substance is adsorbed without an exchange.

This is represented in Figure 1b. The resin has a moisture content of 40% and the particle size is 50-100 mesh. (4)



(a) (b)

FIGURE 1: AG11A8 RESIN (a) BEFORE ADSORPTION
(b) AFTER ADSORPTION

Conductivity Probe

The concentrations in the liquid phase were measured using a conductivity probe. A sketch of the probe assembly is shown in Figure 2. The design is similar to a design described by Lamb et. al. (5). The probe measures the electrical conductivity of a very small volume of fluid surrounding the tip of the probe. A brief description of the principles of the conductivity probe follows:

The most important "sections" of the probe are the two electrodes. One of these is a point electrode

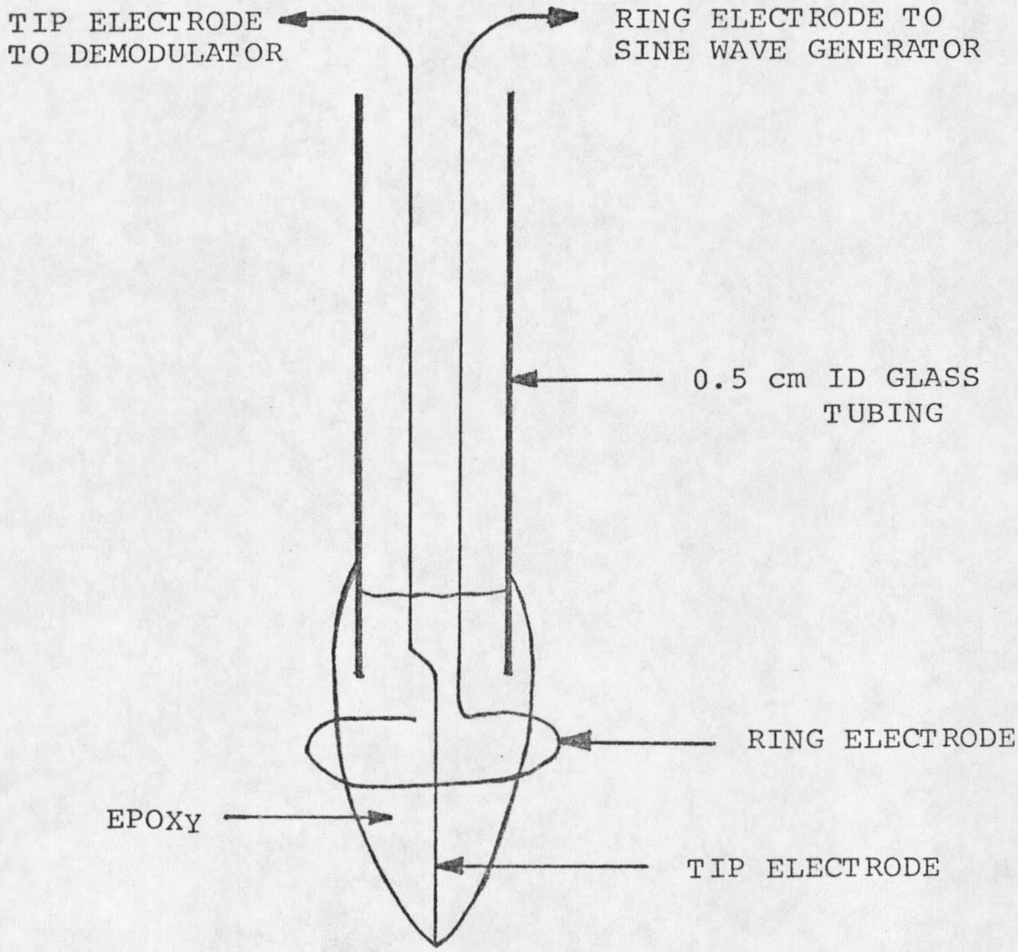


FIGURE 2: CONDUCTIVITY PROBE

located at the tip of the probe while the other is a ring electrode located approximately one centimeter above the tip. The tip consists of the cross-sectional area of an exposed face of platinum wire with a diameter of 0.01 cm. The ring electrode is approximately three centimeters of 0.015 cm platinum wire. The sizes are not important as long as the tip electrode is much smaller than the ring electrode.

An a.c. voltage source is then connected to the ring electrode. The result is an electric field in the electrolyte surrounding the ring. The current between the two electrodes is a function of the resistance of the electrolyte between them. The current that enters the tip is proportional to the conductivity of the fluid at the tip.

When the probe is placed in a nonhomogeneous fluid the changes in conductivity of the fluid alter the impedance of the probe. This causes variations in the amplitude of the input carrier wave. So the signal exiting the probe is an amplitude modulated sine wave. This signal must be processed in order to give a usable result. First the signal leaving the probe is amplified. Next it is demodulated by rectifying it. Finally the signal is run through a low pass filter to remove the carrier wave and all other high frequencies. Figure 3 shows a block diagram of the signal processing components and a typical signal at each point.

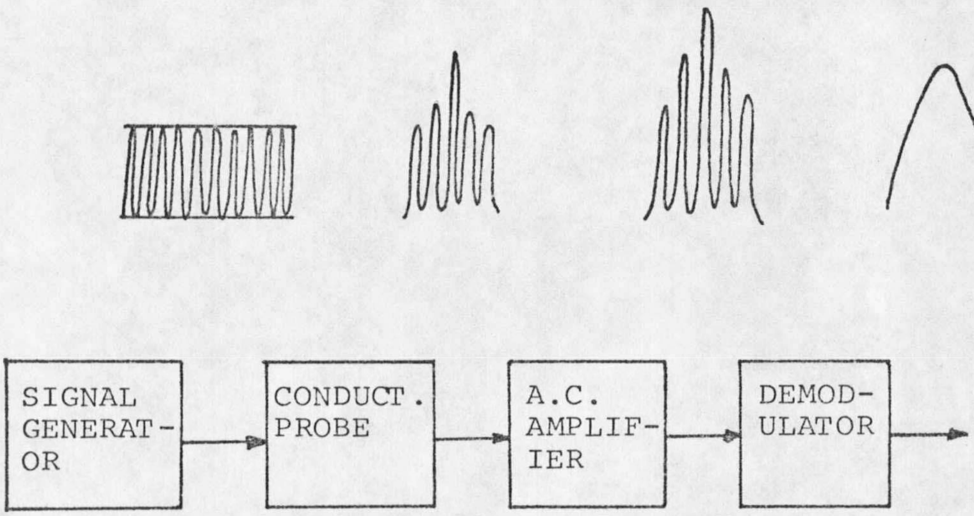


FIGURE 3: SIGNAL PROCESSING BLOCK DIAGRAM

Electronics

The sine wave generator used is the Heathkit model IG-18 Sine-Square Audio Generator. A signal of .3V with a frequency of 5 kHz was output. A Heathkit model IP-17 high voltage power supply was used to send a 25V signal to the demodulating system. The demodulator was constructed by Arthur McCready in 1977 for use in his doctorate project. The details on the demodulator can be found in his thesis (6). The output voltages were measured using a Hewlett Packard model 3440A digital voltmeter. Finally the response curves were plotted using a Hewlett Packard 7030AM X-Y recorder.

EXPERIMENTAL PROCEDURE

Before any experimentation was done the resin was given a thorough rinsing. This was accomplished using a 2.5 cm by 70 cm glass column. The column was filled generally halfway with resin. Distilled water was then pumped through the packed bed at a flow rate of about 12.0 liters/day for 72 hours. After the rinsing cycle was completed air was blown through the column to remove any excess moisture. A small sample of the rinsed resin was then weighed and allowed to dry in order to check the moisture content. This moisture content was found to be 40%. The resin was then placed in a tightly sealed jar for use in the experimentation.

Equilibrium Analysis

The entire experimentation to determine the equilibrium constants was performed in two small beakers. Five grams of the wet resin was carefully weighed into one of the beakers. Fifty milliliters of distilled water was then added to each beaker. The beaker with only water was used to construct a calibration curve between concentration and voltage. A small volume, on the order of 0.5 ml, of the inorganic solution to be tested was added to each beaker. The concentration of this addition was .2M. A magnetic stirrer kept the resin and solution properly mixed. The extent of the adsorption was monitored using the conductivity probe. In general thirty minutes was allowed for the adsorption to reach equilibrium. At this point a final voltage reading was taken. This procedure was repeated until a total of three milliliters of the inorganic chemical were added.

Trials were made at temperatures of $10^{o}C$, $20^{o}C$, and $50^{o}C$. The trials at $10^{o}C$ and $50^{o}C$ required two specializations. First a constant temperature bath was used to alleviate any temperature fluctuations. A second difference was how the final voltage reading was taken. After the adsorption reached equilibrium the liquid was drained from the resin. This liquid was then either warmed or cooled to room temperature. It was at this temperature that the final voltage reading was taken. After the reading the liquid was returned to the adsorption beaker. The calibration curve was also prepared at room temperature.

Pulse Responses

A simplified sketch of the system used to perform the pulse responses is shown in Figure 4. The first step was to pack the column. The best technique for accomplish-

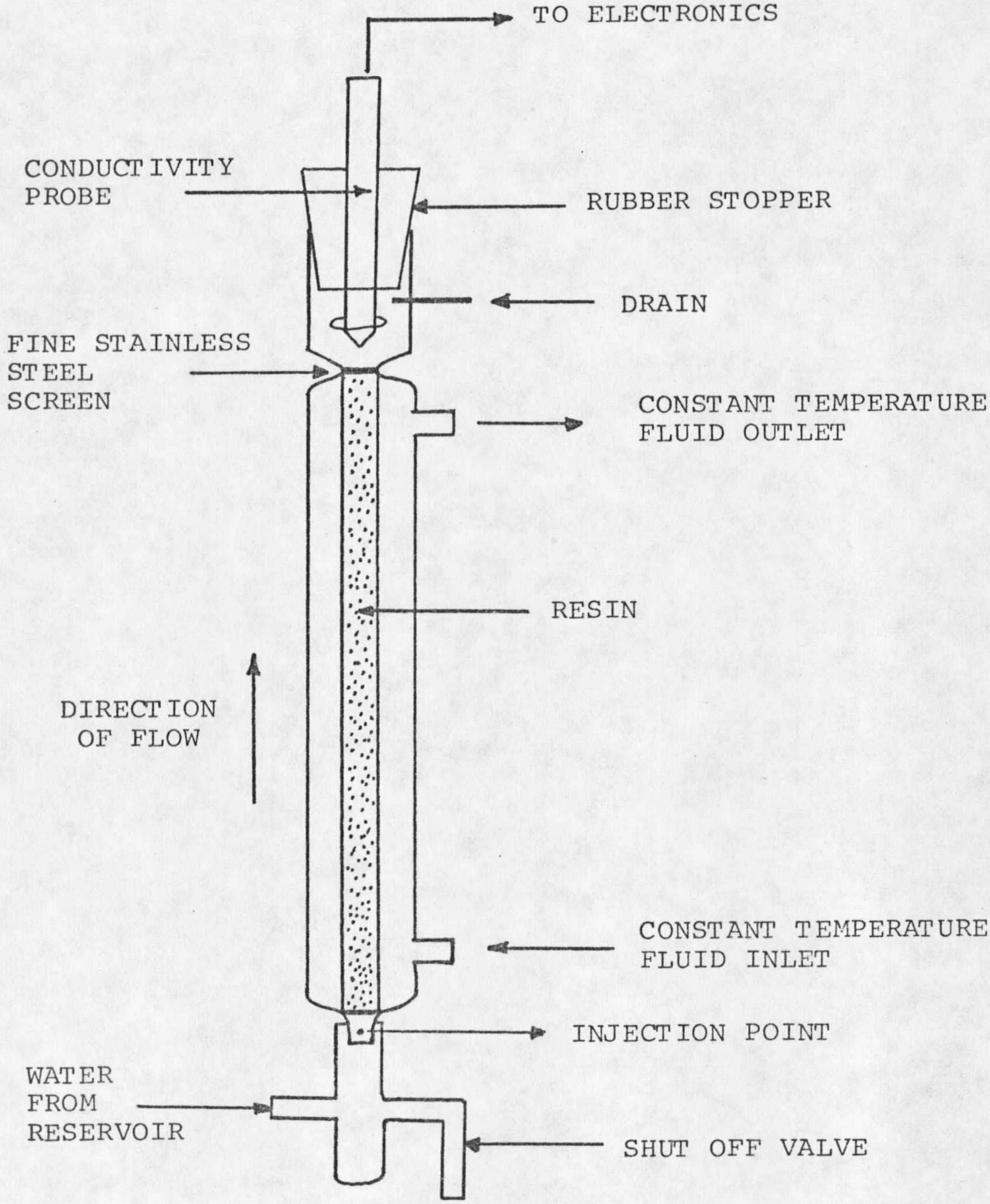


FIGURE 4: PACKED COLUMN ASSEMBLY

ing this was to form a slurry of resin and water and pour this mixture into the column. This step must be done carefully to prevent air bubbles from forming in the bed. As soon as this step was completed the valve at the base of the column was opened which allowed distilled water to flow through the system. The flow rate was kept as close to 1.0 ml/min as possible. The system was allowed to run in this manner for thirty minutes. This time allowed for the stablization of the flow rate and also the flushing out of any soluble impurities in the system.

The next step was to inject a sample of the inorganic compound. The concentration of this impulse was generally 4M. The volume of the impulse was 2 μl. The recorder was started 50 seconds after the injection. This was useful since the recorder had a maximum limit on the time axis of 20 minutes. Therefore delaying the start by 50 seconds allowed more of the tail on the response curve to be sketched.

After the run was completed the used resin was discarded. The final step was to use the conductivity probe to take voltage readings on samples of known concentrations in order to construct a calibration curve between voltage and concentration. This calibration curve is needed to convert the response curves from voltage versus time to concentration versus time.

There is one more step that had to be done prior to each run whether it was an equilibrium analysis or a pulse response. This was an electro-treatment of the probe tip. The treatment was necessary to help alleviate the drifting of the voltage readings. The drift was caused by the formation of scale on the tip electrode. Prior to each run the following steps were performed. First the tip was rubbed with emery cloth to remove the buildup of scale. Next a voltage of approximately +2V was applied for 10 seconds to the probe. The current flowing from the ring electrode to the tip formed an oxide layer on the tip. This oxide layer is far less susceptible to drifting, thus increasing the accuracy of the readings.

A MODEL OF THE ADSORPTION SYSTEM

Solid phase diffusion is most often the rate controlling step in liquid adsorption processes. Simplifications developed recently by Liaw et. al. (7) and Rice (8) for step responses in packed columns make it possible to determine a solution for impulse responses when both film and solid phase diffusions are important. These simplifications will now be briefly discussed. Liaw et. al. solved the combined transport equation:

$$\frac{\partial q}{\partial t} = \frac{D_s}{r^2} \frac{\partial}{\partial r}\left(r^2 \frac{\partial q}{\partial r}\right) \qquad \text{(I-1)}$$

This was paired with a non-dispersive convection equation for the fluid phase:

$$V \frac{\partial C}{\partial z} + \frac{\partial C}{\partial t} = -\left(\frac{\partial \bar{q}}{\partial t}\right)/\eta \qquad \text{(I-2)}$$

where:

$$\bar{q} = \frac{3}{R^3} \int_0^R q r^2 \, dr \qquad \text{(I-3)}$$

Next they assumed the solid phase composition profiles are always parabolic with respect to the radial coordinate, or simply:

$$q(r,z,t) = a_0(z,t) + a_2(z,t) r^2 \qquad \text{(I-4)}$$

This assumption leads to a simplified conservation relationship:

$$\frac{\partial C}{\partial x} + K\frac{\partial C}{\partial \theta} + \xi\frac{\partial C}{\partial x\ \partial \theta} = 0 \qquad \text{(I-5)}$$

where K is the equilibrium constant and ξ is the combined transfer resistance defined as:

$$\xi = R\left(\frac{K}{3k} + \frac{R}{15D_S}\right) \qquad \text{(I-6)}$$

Equation (I-5) can be solved by a LaPlace Transformation with a step change at the inlet. This solution was shown by Liaw et. al. to be:

$$\frac{C}{C_O} = \frac{1}{p}\exp\left(\frac{-Kpx}{1+\xi p}\right) \qquad \text{(I-7)}$$

where p is the LaPlace transform variable.

Rice (8) showed that equation (I-7) had a closed form inversion which is tabulated as a J function:

$$J(s,\tau) = \frac{C(x,\theta)}{C_O} = 1 - \int_0^s \exp(-\tau-\beta)\, I_O(\sqrt{4\tau\beta})\, d\beta \qquad \text{(I-8)}$$

where:

$$s = \frac{Kx}{\xi} \qquad \text{and} \qquad \tau = \frac{\theta}{\xi}$$

The impulse response is simply the derivative of the J function with respect to time. This produces:

$$\frac{C_i(x,\theta)}{C_o} = \sqrt{\frac{s}{\theta\xi}}\ \exp(-s-\frac{\theta}{\xi})\cdot I_1(\sqrt{4s\theta/\xi}) + \delta(\theta) \qquad \text{(I-9)}$$

where C_o is taken to be the impulse strength. $\delta(\theta)$ has meaning only at the column entrance where s=0.

It is much easier to arrive at the impulse response in the LaPlace domain by directly using equation (I-7). This produces an impulse response of:

$$C_i = \exp(\frac{-Kpx}{1+\xi p}) \qquad \text{(I-10)}$$

Later when the method of weighted moments is discussed, equation (I-10) will be very important in the determination of Kx and ξ.

EXPERIMENTAL RESULTS AND DISCUSSION

Equilibrium Analysis

The first step in processing the raw experimental data is to convert the voltage readings into concentrations using a calibration curve. A typical calibration curve is shown in Figure 5. Each voltage reading has its corresponding concentration value read off of the calibration curve. This step produces all of the liquid phase concentrations.

Next the concentration of the inorganic species in the resin must be calculated. This concentration is denoted by Q and can be shown to be:

$$Q = \frac{VC_o - (V + V_m)C}{W} \cdot \rho_p \qquad \text{(II-1)}$$

where:

$$\rho_p = \rho_s(1 - \epsilon_p) \qquad \text{(II-2)}$$

ρ_s represents the dry compressed particle density and ϵ_p is the internal void fraction. For Bio-Rad's AG11A8 resin, ρ_p was found to be 0.66 grams/ml. (9)

Values for C and Q for all the equilibrium analyses are given in Appendix A. The solid phase concentration, Q is then plotted versus the equilibrium liquid concen-

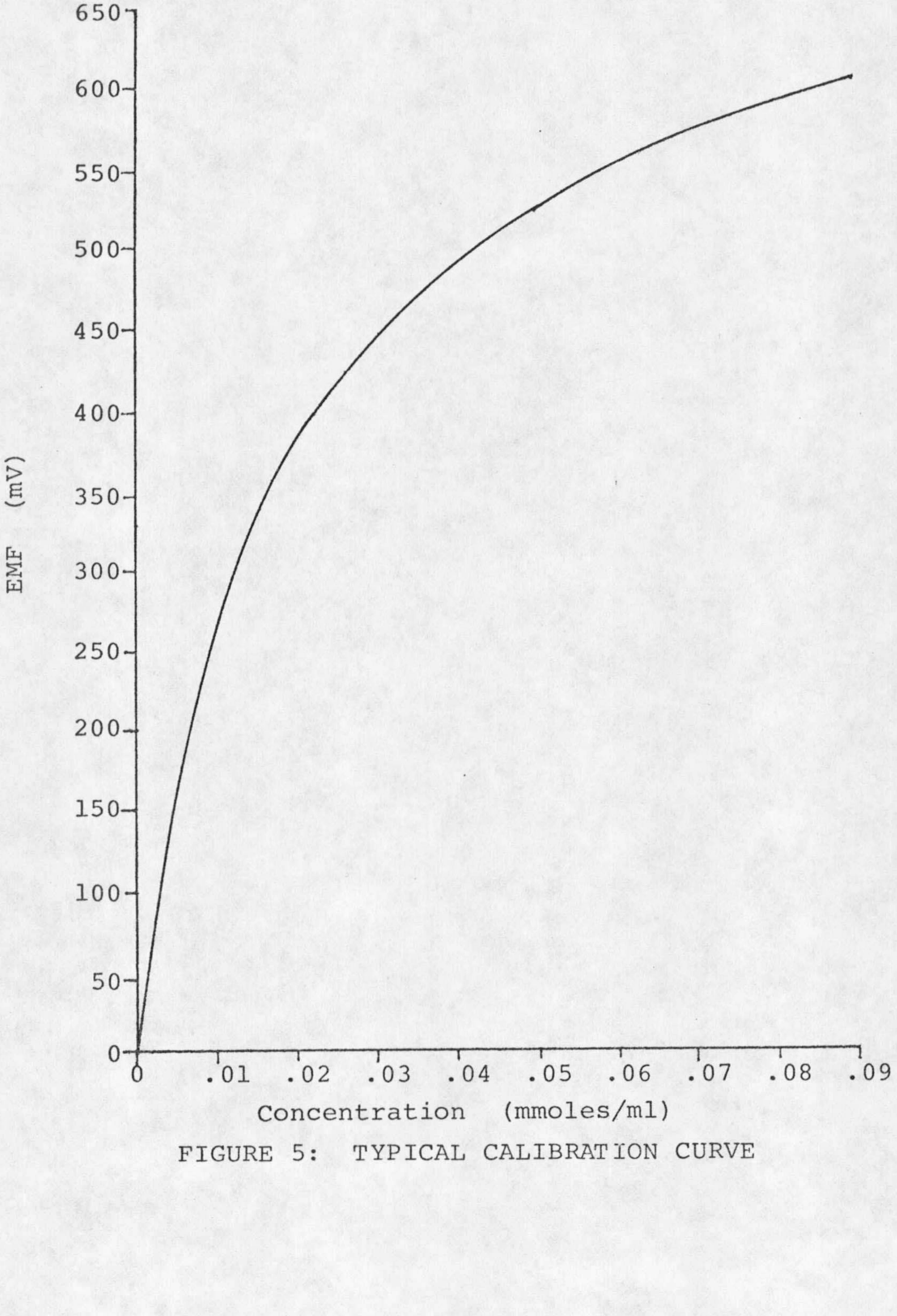


FIGURE 5: TYPICAL CALIBRATION CURVE

tration, C. The slopes on these curves is K, also known as the equilibrium constant.

The equilibrium graphs are shown for $CaCl_2$, $Ca(NO_3)_2$, $CdCl_2$, and $ZnCl_2$ in Figures 6-9, respectively. The data points at concentrations less than 0.02 mmoles/ml are the least accurate due to fluctuating voltage measurements. The best line through the points was found simply by using a straightedge. This line was drawn so that it always included the best data point, the origin. The equilibrium constants found from these graphs are summarized in Table I.

Three equilibrium data points were also taken using NaCl. The reason for doing this was as a comparison to results from previous research. Table II summarizes the values for the equilibrium liquid and solid phase concentrations, C and Q, repectively. Also included are values of Q for both rinsed and unrinsed AG11A8 resin determined by Rice and Foo. (10)

As can be noted from Table II the experimental values for Q are somewhat lower than those suggested by Rice and Foo. Part of this difference is simply due to differences in batches of resin and the degree of rinsing.

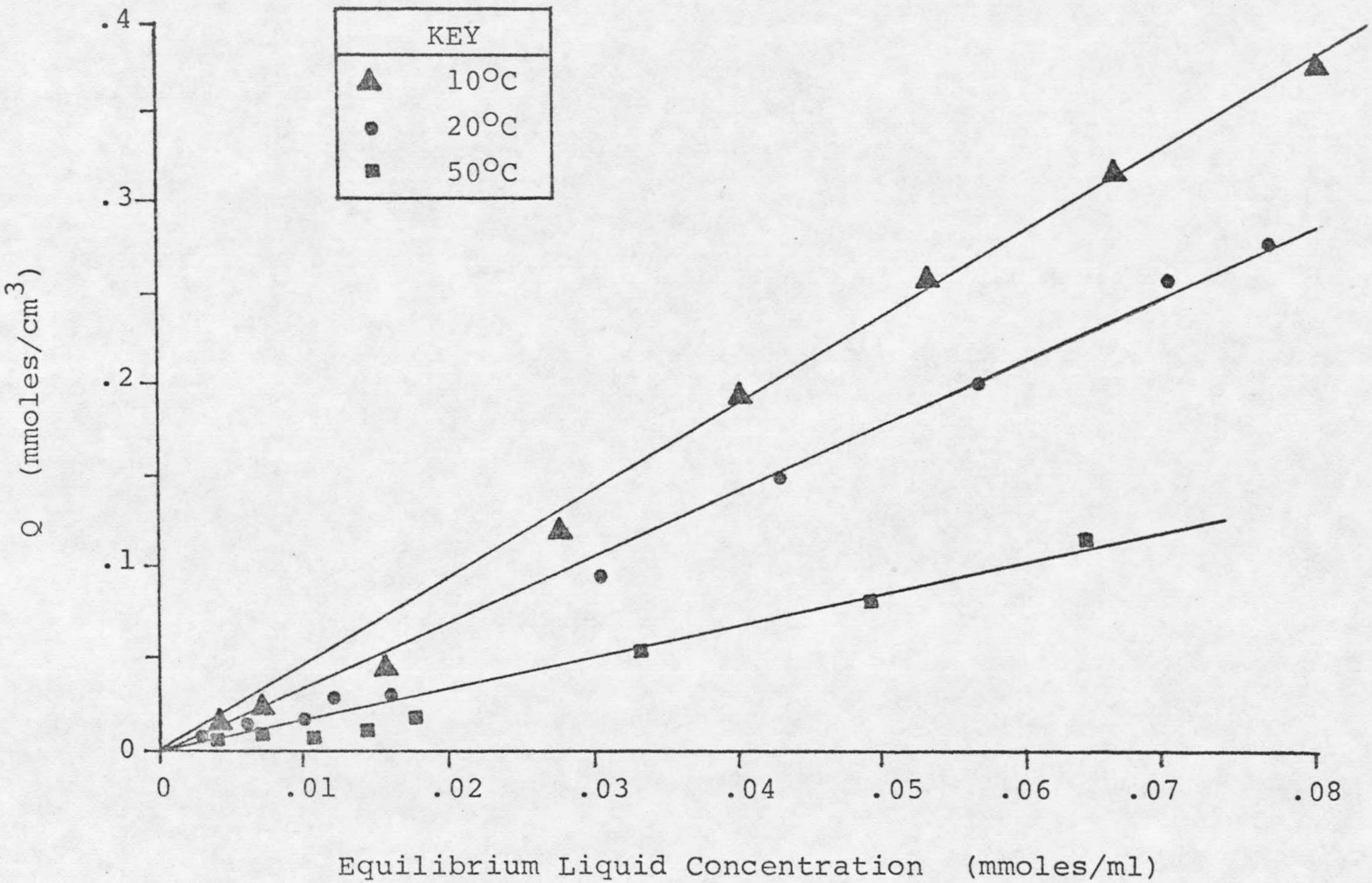


FIGURE 6: $CaCl_2$ EQUILIBRIUM CURVES

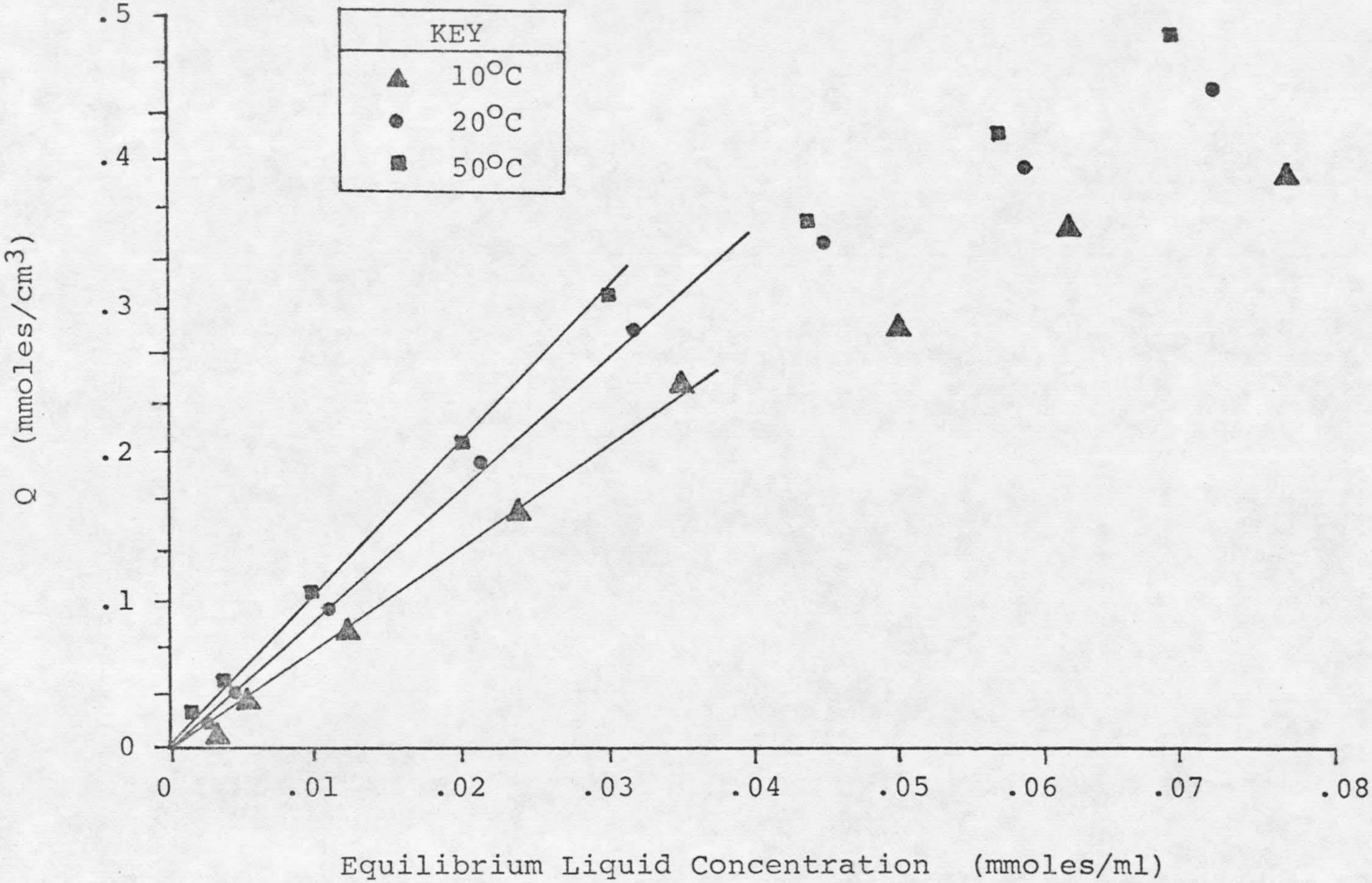


FIGURE 7 : $Ca(NO_3)_2$ EQUILIBRIUM CURVES