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.

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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

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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.

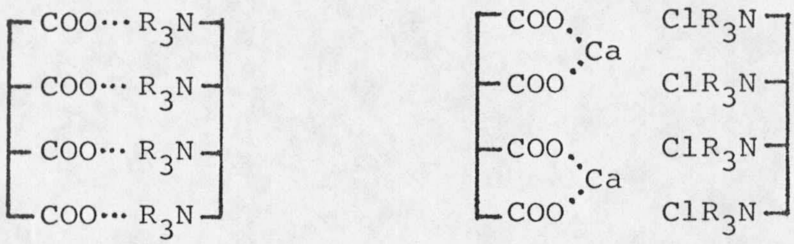
Column

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