CATION EXCHANGE IN A CARBONACEOUS ION EXCHANGER

Harold Frederic Walton*
Northwestern University, Evanston, Illinois

Introduction.—The distribution of a pair of cations between a solution and a solid ion exchanging body such as a zeolite has been studied by many investigators and for different materials. Generally speaking, true equilibrium has not been reached in these studies, for the distribution has been different according to the direction from which it was approached, but the rather definite pseudo-equilibrium can be represented empirically by the equation

$$\left(\frac{C_1}{C_2}\right)_{\text{solid}} = K \cdot \left(\frac{C_1}{C_2}\right)^{p}_{\text{solution}} \quad \ldots\ldots(1)$$

where K and p are constants, p being less than one (Rothmund and Kornfeld, Z. Anorg., *103*, 129, 1918).

In one or two cases (e.g., Moller, Koll. Beih., *46*, 1, 1937), true equilibrium was reached, and, at the same time, the mass action law was obeyed, p in the above equation being one. This raises the question whether p will not always be unity for a true equilibrium. To answer this question was one of the aims of the present investigation.

A new type of exchanger made from bituminous coal by treatment with sulfuric acid or sulfur trioxide has come into use in recent years. Such a material is "Zeo-Karb", manufactured by the Permutit Company. This was chosen for investigation because the great speed of its ion exchange reactions would favor approach to equilibrium and also because of its technical importance and the fact that exchanges involving the hydrogen ion can be performed with it. The exchanges first studied were calcium-sodium and sodium-hydrogen.

Experimental Method.—The Zeo-Karb was first ground to 40-80 mesh. Portions were saturated with calcium, sodium, and hydrogen ions by passing solutions of calcium and sodium chlorides and of hydrochloric acid, and were then washed and air-dried. Weighed samples were shaken with 50-200 cc portions of solutions containing the chloride of the other cation which was to participate in the exchange. Control experiments showed that no observable change occurred between 6 and 72 hours of shaking, so that after 12 hours the supernatant solution was withdrawn and analyzed.

It was necessary to know the saturation capacity or "ultimate exchange" of the Zeo-Karb. This was found for the calcium Zeo-Karb by digestion with concentrated sulfuric acid and analysis of the resulting solution, also by leaching out the calcium by dilute acid. The sodium Zeo-Karb was first saturated with hydrogen ions, and these displaced by potassium ions and titrated.

It was also desirable to know whether the extent of swelling of the material in water would change with ionic exchange, since Graf (Koll. Beih., *46*, 229, 1937) showed that the swelling of casein had a marked effect on the ion exchange. Tests showed that the volume of the Zeo-Karb varied by one to two per cent at the most during the ion exchanges studied.

RESULTS

(a) *The Calcium-Sodium Exchange.*—The data obtained by agitating pure sodium Zeo-Karb with calcium chloride solution, and pure calcium Zeo-Karb with sodium chloride solution, are given in fig.1. The data are plotted according to the equation

$$\left(\frac{(Ca^{++})}{(Na^{+})^2}\right)_{\text{Solid}} = K \cdot \left(\frac{{}^{A}Ca^{++}}{A^2{}_{Na^{+}}}\right)^{p}_{\text{solution}} \quad \ldots\ldots(2)$$

A being the activity calculated by the simple Debye-Hückel theory.

The index p for exchanges in the N/25 solution was 0.82-0.84. The distance apart of the two curves, however, shows that true equilibrium was not attained,

---

* Former Research Chemist, The Permutit Company.

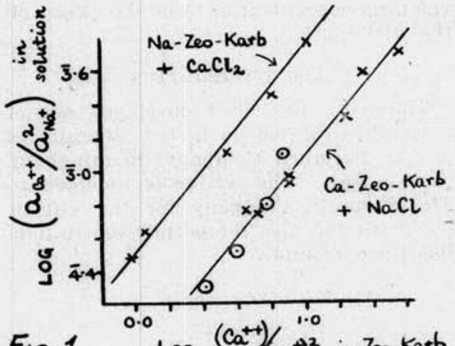

FIG. 1.

Fig. 1.—*Units*: Activities in solution milliequivalents per liter. Concentrations in Zeo-Karb, milliequivalents per gram air dried weight.

even though ample time had been allowed in the experiments for the exchange to reach a steady state. To allow a better chance for equilibrium to be approached, some tests were made where samples of Zeo-Karb which had been used in the main series of tests, and so already contained some of the second cation, were shaken with fresh quantities of salt solutions. The points so obtained are shown by crosses in fig. 2. The data obtained starting with sodium Zeo-Karb showed some inclination to approach the mean of the two curves, but the data for calcium Zeo-Karb stuck closely to the original Ca-Zeo-Karb and NaCl curve.

The calcium and sodium Zeo-Karb stocks had been prepared a year previous to making these tests, and might have acquired a permanent set so that they were in reality two different exchange materials. Therefore, a quantity of sodium Zeo-Karb stock was saturated with calcium ions and three tests were immediately made by shaking samples of this material with N/25 sodium chloride solution. The points obtained are shown as circles in fig. 2 and lie very close to the regular Ca-Zeo-Karb+NaCl curve. The conclusion is that the exchange characteristics of Zeo-Karb are conditioned by the ion with which the material was last saturated and do not change until the material is saturated or nearly saturated with another ion. A similar conclusion was reached by Renold (Koll. Beih., *43*, 1, 1935) from his work on synthetic aluminosilicates.

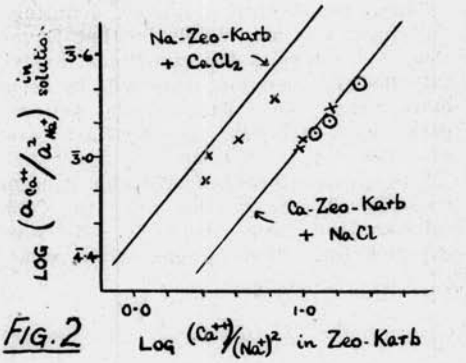

FIG. 2

Fig. 1.—*Units*: Activities in solution milliequivalents per liter. Concentrations in Zeo-Karb, milliequivalents per gram air dried weight.

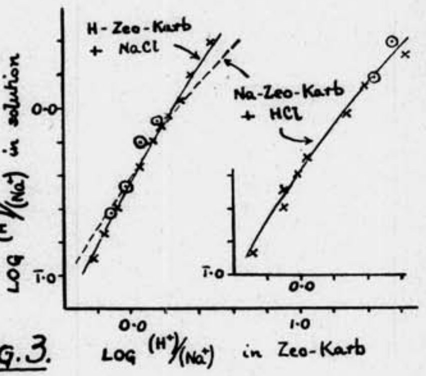

FIG. 3.

The effect of concentration of the solution is seen from fig. 1, the circles referring to N/10 NaCl + Ca-Zeo-Karb. For a given ratio Ca:Na in the exchanger, the simple Ca:Na ratio in the solution is greater in the more concentrated solution, but by plotting activities according to the equation given, a relation is obtained which is independent of the total salt concentration.

(b) *The Sodium-Hydrogen Exchange.*—These results are given in fig. 3. The simple ionic concentration ratios were plotted, these being assumed equal to the acitvity ratios in solution. The curves for Na-Zeo-Karb + HCl and H-Zeo-Karb + NaCl almost coincide, showing a close approach to equilibrium. The index p in Equation 1 is about 0.6, which shows that the mass action law ($p = 1$) is *not* necessarily obeyed for a true equilibrium.

These graphs are, however, definitely not linear. It may easily be that Equation 1 is not valid for exchanges involving the hydrogen ion; this will be seen more clearly when data for the sodium-potassium exchange in Zeo-Karb are available for comparison.

The effect of total concentration is seen from fig. 3; the crosses refer to N/25 solution, the circles to N/10. As was expected for a pair of ions of the same valency, concentration has no effect on the distribution.

ACKNOWLEDGMENTS

The work described developed out of researches carried on in the laboratories of The Permutit Company, Birmingham, New Jersey. The writer is indebted to The Permutit Company for the gift of Zeo-Karb and also for permission to publish these results.