

MASS ACTION RELATIONSHIPS OF SOME ZEOLITES IN THE REGION OF HIGH COMPETING CATION CONCENTRATIONS¹

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ABSTRACT

Mass action quotients for the synthetic zeolites Linde 4AXW, 13X, AW-300, AW-400, AW-500, Norton Zeolon and the natural zeolites clinoptilolite and erionite were determined for low cesium or strontium concentrations in the binary systems cesium-sodium, cesium-potassium, cesium-rubidium, strontium-calcium and strontium-sodium. The equilibrium systems cesium-hydrogen and strontium-hydrogen were determined for the zeolites Linde AW-300, Norton Zeolon and clinoptilolite. A portion of the ternary system hydrogen-sodium-cesium was determined for clinoptilolite.

Cesium mass action quotients generally declined in going from cesium-sodium to cesium-rubidium systems. Structural differences between two members of the same zeolite species often resulted in cation exchange equilibria differences as great as those between different species.

The binary curves may be used to determine column loading of the above zeolites.

INTRODUCTION

Considerable interest in the zeolites as cation exchange media has been generated in the atomic energy industry. Several processes using zeolites have been proposed or are in operation. Mercer (1960) studied the use of clinoptilolite for decontamination of condensate wastes containing trace amounts of cesium and strontium radioisotopes. Mathers and Watson (1962) described the disposal of 8200 liters of an intermediate-level waste through an 1800 kg clinoptilolite column. The use of clinoptilolite columns for cesium extraction from Hanford high-level wastes is under consideration (Tomlinson, 1962, and Nelson, *et al.*, 1960). The other cations on the clinoptilolite column, such as sodium, can be preferentially eluted with dilute acid while less than one per cent of the adsorbed cesium is eluted. The cesium remaining on the column is removed at 55° C. with ammonium carbonate. The cesium-ammonium carbonate eluate is then distilled, leaving concentrated, high-purity cesium carbonate. Tuthill, Weth and Abriss at Brookhaven National Laboratory have studied and developed a process for treatment of high-level wastes using clinoptilolite ion exchange columns to remove cesium and strontium (Morgan, *et al.*, 1961).

Several commercially-available, synthetic zeolites are being considered as storage media for fission products such as the above cesium (Tomlinson, 1962). Knoll has shown that synthetic zeolites or clinoptilolite loaded with radioactive cesium or strontium can be heated to 600° C.

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for two hours to remove all zeolitic water before storage, and the radioactive cesium or strontium can be eluted with several agents (Ames and Knoll, 1962).

Despite the interest in the utilization of zeolites for waste decontamination and fission product storage, there are little quantitative data available in the literature on zeolite strontium and cesium exchange equilibria, especially in the region of very high concentrations of competing cations. Process applications involving zeolites cannot be initiated until cesium or strontium exchange equilibria with other cations of interest are known. Consequently, the present study was undertaken to provide the necessary data. Portions of the data from this study, of possible interest to earth scientists, are presented here.

METHODS OF INVESTIGATION

The clinoptilolite used in this study was obtained from the Hector, California, deposits of the Baroid Division of National Lead. The as-received clinoptilolite ore consisted of 85 to 95 per cent by weight pure clinoptilolite, and 5 to 15 per cent by weight unaltered volcanic glass plus quartz and feldspar along with lesser amounts of calcite and montmorillonitic clays (Ames, 1960). Carbonates and clays in the clinoptilolite were removed or destroyed by a ten per cent nitric acid wash prior to use.

The erionite used in this study was from Nevada and contained ten per cent, or less, impurities. Clinoptilolite and erionite purities were estimated by examination of thin-sections and comparison of x-ray diffraction patterns, and average ± 5 per cent of the purity range given for the selected samples used in this study.

Several synthetic zeolites were supplied, as one-sixteenth-inch diameter sodium-based pellets, by the Linde Company of Tonawanda, New York, including 13X, 4AXW, AW-300, AW-400 and AW-500. The Norton Company of Worcester, Massachusetts, supplied one-eighth-inch, hydrogen-based Zeolon pellets.

Table 1 gives the silica-to-alumina ratio of the above zeolites along with their structural types and weight per cent binder for the sodium form.

Zeolites used in the equilibrium experiments were based with saturated chloride solutions of the desired cations. Nitric acid was used in ten per cent solution to hydrogen-base clinoptilolite, Zeolon and AW-300. Fifty-gram portions were placed in 400 ml beakers and appropriate chloride solutions were added. The contacting chloride solutions were changed six times at 45-minute intervals. A seventh and final solution was contacted for two days. Previously-obtained kinetic data indicated

that the above base exchange procedure was adequate (Ames, 1961). Kinetics of coarsely-crystalline, natural zeolites such as stilbite or heulandite are very poor when compared to the synthetic zeolites or those derived from altered tuffs. The equilibrium times involved in the above base exchange procedure would be wholly inadequate for many of the coarsely-crystalline, natural zeolites. Synthetic zeolites and zeolitic altered tuffs are cemented aggregates of crystallites that rarely exceed five microns in size, and for that reason, require a much shorter equilibration time.

After completing the base exchange procedure, the zeolites were thoroughly washed with distilled water until chloride could not be de-

TABLE 1. ZEOLITE PROPERTIES

Zeolite	SiO ₂ /Al ₂ O ₃	Wt. per cent binder	Structural Type
4AXW	2	8	A
4A	2	20	A
13X	2.8	20	Faujasite
AW-300	9-10	25	Mordenite
AW-400	6-7	25	Erionite
AW-500	4-5	25	Chabazite
Zeolon	10	unknown	Mordenite
Clinoptilolite	8-10	5-15	Clinoptilolite
Erionite	6	5	Erionite

tected in the wash water with AgNO₃ solution. All zeolites were checked by x-ray diffraction to assure that no major structural changes had taken place during the exchange.

Cation exchange capacities were determined by a double tracing technique. Weighed, sodium-based samples were contacted with a solution containing 0.1*N* CsCl plus 0.1*N* NaCl plus Cs¹³⁴ to determine cesium removal at 25° C. Cesium-based zeolites were corrected for the cesium-sodium weight differential, then contacted with a solution containing 0.1*N* CsCl plus 0.1*N* NaCl plus Na²² to determine sodium removal onto the same zeolite. Total exchange capacity was assumed to be the sum of sodium plus cesium loading. The solution to zeolite ratios were adjusted to yield statistically reliable Cs¹³⁴ and Na²² counting rates between original and final contacting solutions. Cation exchange capacities for clinoptilolite, AW-300 and Zeolon, determined in the above manner, were substantiated by titration of H⁺-based samples with a standard NaOH solution. Since the exchange capacities as determined by titration were within 5 per cent of the exchange capacity as

determined by the double tracing technique, we must assume that AW-300, Zeolon and clinoptilolite were in fact H^+ -based.

All zeolites were weighed after being water-saturated and oven-dried at $55^\circ C$. Cation exchange capacity determinations were based on the weight of the cooled zeolite after removal from the oven. The weighed zeolites contained the weight per cent H_2O shown in Table 2. At least two days of contact time with shaking were allowed to attain zeolite-solution equilibrium. Other results were obtained in a similar manner.

With the binary cesium-sodium system, for example, two grams of sodium-based zeolite were contacted with 80 ml of solution at $25^\circ C$. The ratios of cesium to cesium plus sodium in the contacting solutions were varied from 1×10^{-1} to 5×10^{-5} , while total solution normality

TABLE 2. ZEOLITE CATION EXCHANGE CAPACITIES

Zeolite	SiO_2/Al_2O_3	Capacity, meq/g	Wt. % H_2O
4AXW	2	3.9	28
4A	2	3.5	22
13X	2.8	3.6	25
AW-500	4-5	2.2	15
AW-400	6-7	2.0	12
AW-300	9-10	1.6	9
Zeolon	10	1.9	12
Erionite	6	2.1	13
Clinoptilolite	8-10	1.7	12

was held constant at 1.0. Four to six zeolite samples with different cesium to cesium plus sodium ratios, in duplicate, were shaken for three days, centrifuged and counted to determine the amount of cesium remaining in the equilibrium solution. Using the exchange capacity, the equivalent fraction of cesium on the zeolite could then be computed by assuming that the cesium removed from the equilibrium solution was adsorbed on the zeolite.

Binary results were plotted as equivalent fraction of strontium or cesium on the zeolite vs. the equivalent fraction of strontium or cesium in the equilibrium solution. The latter scale also represents strontium or cesium normality in the equilibrium solution because total solution normality was held constant at 1.0. This type of plot allows the reader to determine zeolite column loading directly in univalent-univalent or divalent-divalent systems if the cesium or strontium normality ratio in the influent solution is known. Zeolite loading from an influent solution in a column system is synonymous with zeolite loading from

the same composition of equilibrium solution in an equilibrium system. Zeolite loads in univalent-divalent systems cannot be directly determined from the equilibrium data. The use of a k value, or mass action quotient is required (Walton, *et al.*, 1961). A definition of k in the 1.0 normal strontium-sodium system is,

$$k = \frac{\left(\frac{z_{\text{meq Sr}}}{\text{meq (Sr + Na)}} \right)^s (\text{normality Na})^2}{\left(\frac{z_{\text{meq Na}}}{\text{meq (Na + Sr)}} \right)^2 (\text{normality Sr})}$$

where z is the zeolite and s is the equilibrium solution. The assumption is made in using concentration terms for the solution, uncorrected for activity, that the activity terms cancel, as do activity coefficients of the cations on the zeolite. This is a first approximation (Kitchener, 1955; Amphlett and McDonald, 1956), but k obviously is not a true thermodynamic equilibrium constant. The thermodynamics of zeolite cation exchange equilibria will be the subject of a forthcoming paper.

An example of the computation required to determine zeolite loading in the strontium-sodium system will illustrate the use of k values. Given that the zeolite is 13X and the influent solution composition is 0.01N Na^+ plus 0.002N Sr^{2+} ;

$$\frac{\text{normality of Sr}}{\text{normality of Sr plus Na}} = \frac{0.002}{0.012} = 0.167.$$

From Fig. 7, k for 13X at 0.167 = 8.5.

Now

$$k = \frac{(\text{Sr}_z)(\text{Na}_s)^2}{(\text{Na}_z)^2(\text{Sr}_s)}$$

where fractions of strontium and sodium on the zeolite are Sr_z and Na_z , respectively, and Na_s and Sr_s are sodium and strontium equilibrium solution normalities. Thus,

$$8.5 = (X) \frac{(0.01)^2}{(0.002)}, \text{ and } X = 170 = \frac{(\text{Sr}_z)}{(\text{Na}_z)^2}, \text{ or } (\text{Sr}_z) = (\text{Na}_z)^2(170).$$

By definition,

$$(\text{Na}_z) + 170(\text{Na}_z)^2 = 1.$$

Rearranging,

$$(\text{Na}_z)^2 + \frac{1}{170} (\text{Na}_z) - \frac{1}{170} = 0.$$

Solving with the quadratic equation,

$$\frac{-\frac{1}{170} \pm \sqrt{\left(\frac{1}{170}\right)^2 + \frac{4}{170}}}{2} = (\text{Na}_z)$$

Only the positive root is real, so $(Na_z)=0.0738$ and $(Sr_z)=0.9262$. The total capacity of 13X is 3.6 meq Sr/g. Thus $(0.9262)(3.6)=3.33$ meq Sr/g 13X. If the column weight was one kg, column capacity would be 3333 meq Sr or 1667 liters of the above 0.002*N* Sr influent.

The reader should take care when using the curves to determine zeolite loading with solutions of greater than 1.0 total system normality. Activity coefficients of the various cations tend to diverge above 1.0 normal (Harned and Owen, 1950). Due to the tendency of the binary curves to flatten as the load on the zeolite increases, errors on the upper region of the curves can amount to plus or minus five per cent of the indicated values.

Several sections in the ternary system hydrogen-sodium-cesium were determined for clinoptilolite by another technique. Small, two ml (1.5 g) columns of clinoptilolite were placed in 15 ml lusteroid tubes. Two or three pin holes were made in the bottom of the lusteroid tubes and 250 ml of contacting solution was added, requiring eight to ten hours to pass through the two ml column. The loaded clinoptilolite column was washed with distilled water, the holes in the tube base sealed, and the whole column counted in a NaI well crystal. A comparison of the activity on the two ml column with the activity in two ml of influent solution containing a known amount of non-radioactive cesium, hydrogen and sodium yielded the load of the traced constituent on the column. The capacity of the clinoptilolite was known, requiring that only the cesium and sodium loading be determined. The sum of cesium plus sodium subtracted from the total exchange capacity of the clinoptilolite was assumed to represent hydrogen loading. Results in the hydrogen-sodium-cesium system were plotted on a standard ternary diagram. Composition of the equilibrium solution (the influent solution in this instance) and composition of the equilibrium loading on the zeolite are related in a manner similar to a ternary salt-solution diagram.

RESULTS AND DISCUSSION

Table 2 gives the total exchange capacities of each zeolite used in the study. It is necessary to know the total zeolite capacity to be able to compute the fraction of zeolite loading, which is the ordinate in the following figures.

Table 2 shows a general trend of decreasing cation exchange capacity with increasing silica to alumina ratio. The greater the number of $(AlO_4)^{5-}$ substitutions for $(SiO_4)^{4-}$, the greater the number of anionic sites per unit weight. The net result, everything else being equal, is a larger exchange capacity/unit weight of zeolite.

Figures 1 through 4 show binary equilibrium in the systems cesium-

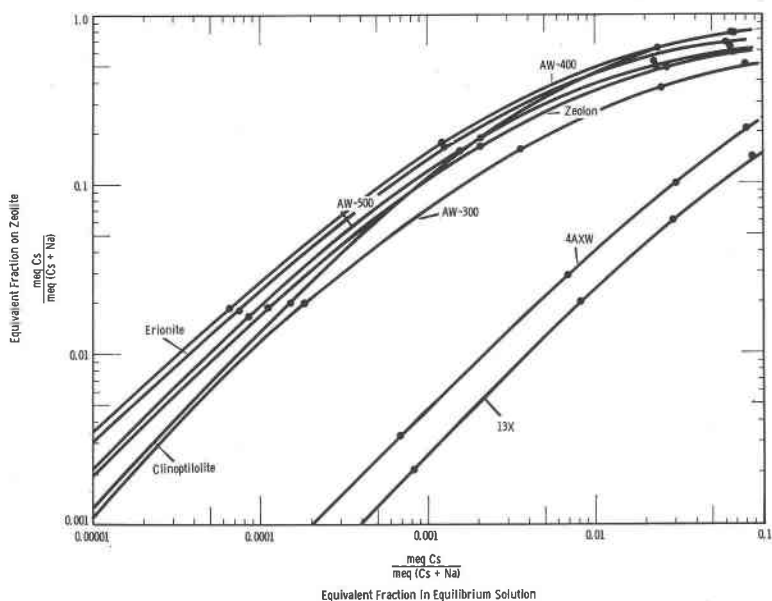


FIG. 1. The effect of sodium on the equilibrium cesium loading of 4AXW, 13X, AW-300, AW-400, AW-500, Zeolon, erionite and clinoptilolite.

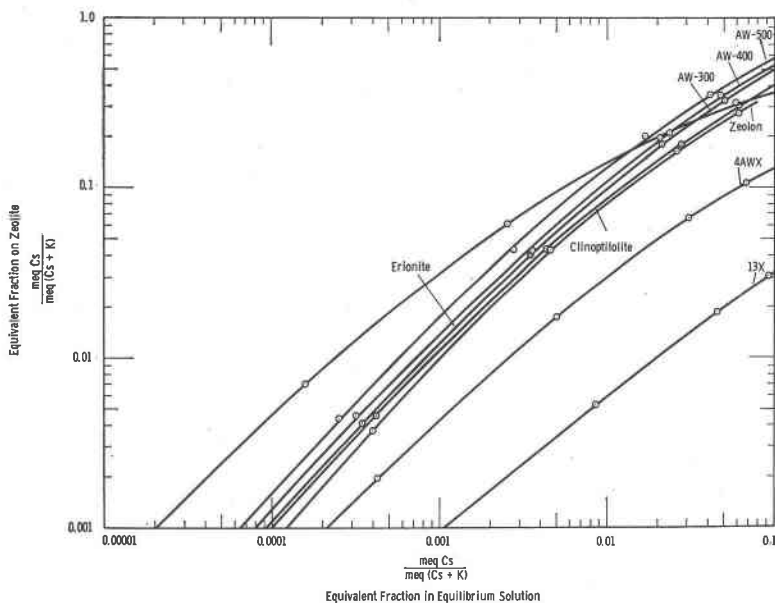


FIG. 2. The effect of potassium on the equilibrium cesium loading of 4AXW, 13X, AW-300, AW-400, AW-500, Zeolon, erionite and clinoptilolite.

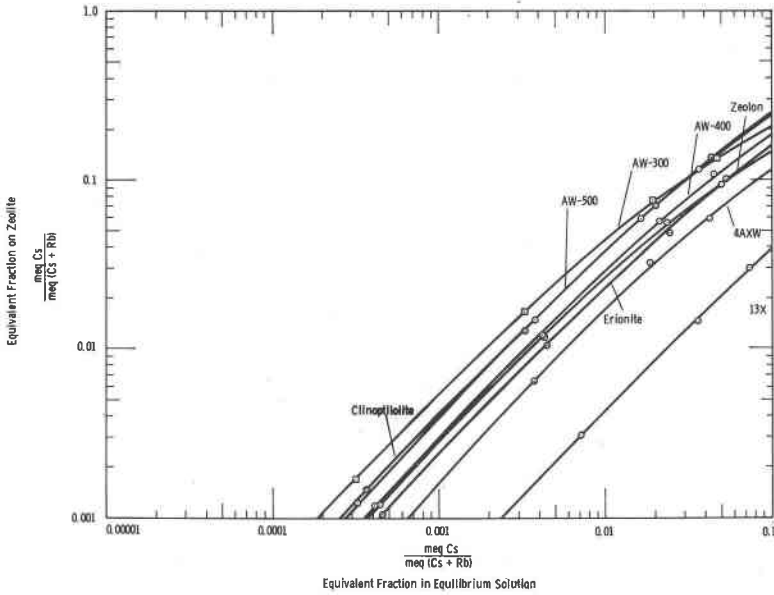


FIG. 3. The effect of rubidium on the equilibrium cesium loading of 4AXW, 13X, AW-300, AW-400, AW-500, Zeolon, erionite and clinoptilolite.

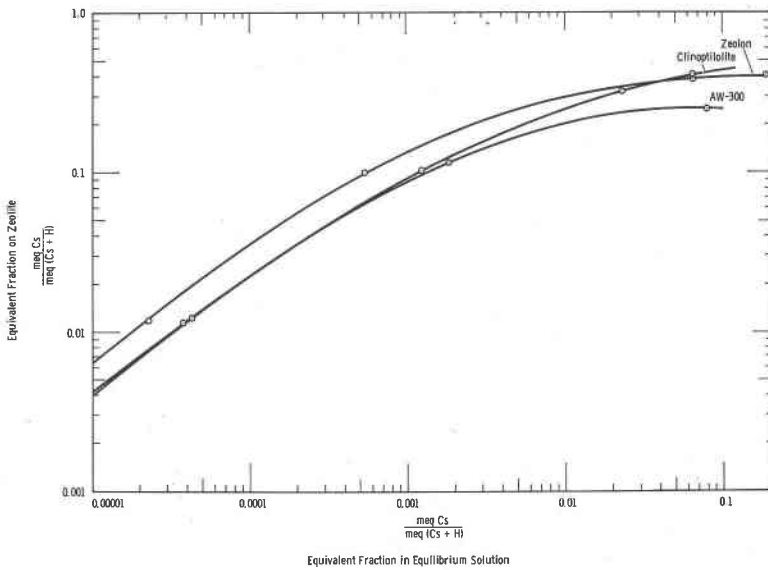


FIG. 4. The effect of hydrogen on the equilibrium cesium loading of AW-300 Zeolon and clinoptilolite.

sodium, cesium-potassium, cesium-rubidium and cesium-hydrogen, respectively. Only the zeolites AW-300, Zeolon and clinoptilolite were sufficiently acid-resistant, as indicated by acid-base titrations, to insure that the necessary hydrogen-basing was feasible. Figure 5 shows the strontium-calcium system. All of the above are univalent-univalent or divalent-divalent systems and system equilibrium distributions can be read directly from these figures. If the solution composition is known, the zeolite cation composition may be read directly, or vice versa. However, solution-zeolite equilibrium relationships cannot be taken directly from Fig. 6, the strontium-sodium system. A computation such as that

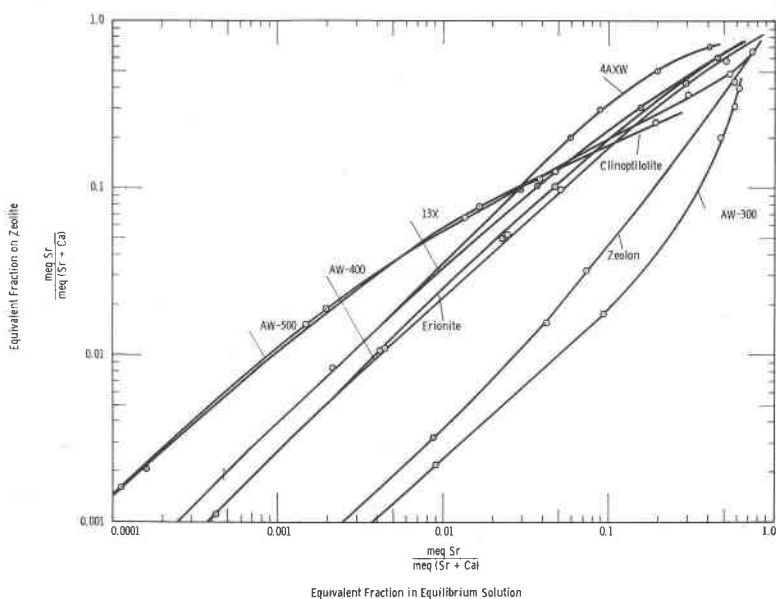


FIG. 5. The effect of calcium on the equilibrium strontium loading of 4AXW, 13X, AW-300, AW-400, AW-500, Zeolon, erionite and clinoptilolite.

given in a previous example is necessary, using the strontium-sodium k values of Fig. 7. Figure 8 presents k values for the system strontium-hydrogen.

As shown in Figs. 5 and 6, all of the binary systems should terminate at full loading with the 1.0*N* cesium or strontium equilibrium solution. Since traced cation to competing cation ratios of less than 0.1 were of primary interest, no points above that ratio were determined except in the case of Figs. 5 and 6.

Data from the ternary system hydrogen-sodium-cesium are given in Fig. 9. The same cesium content of the equilibrium solutions are con-

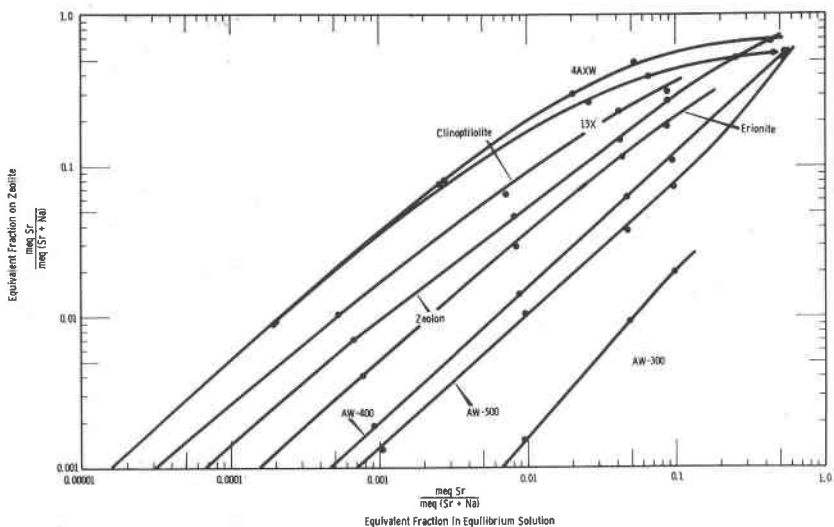


FIG. 6. The effect of sodium on the equilibrium strontium loading of 4AXW, 13X, AW-300, AW-400, AW-500, Zeolon, erionite and clinoptilolite.

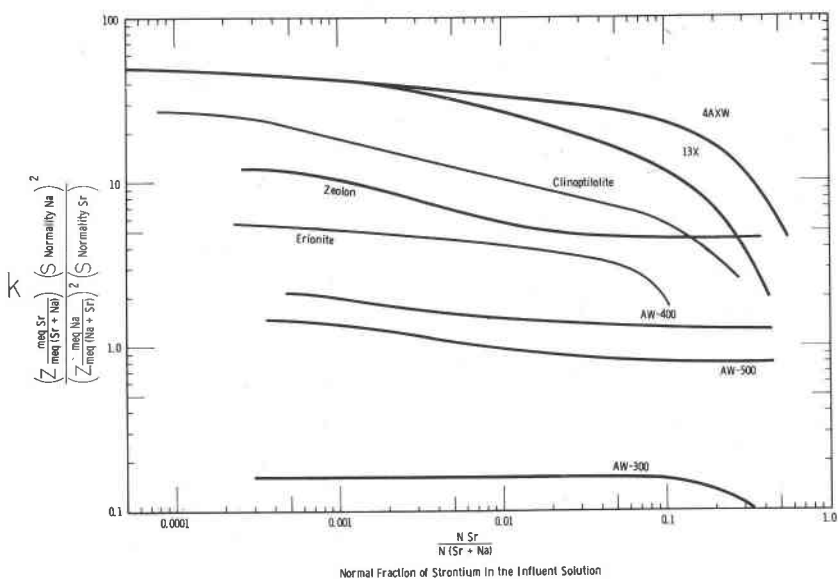


FIG. 7. The effect of sodium on the strontium mass action quotient k , of 4AXW, 13X, AW-300, AW-400, AW-500, Zeolon, erionite and clinoptilolite.

connected with a solid line. Related equilibrium zeolite loadings are connected with dotted lines. Some of the equilibrium solution compositions were deleted from the cesium-sodium and cesium-hydrogen binary joins to avoid further cluttering of the diagram. The complex nature of the ternary equilibria is apparent from Fig. 9. It is evident also that the number of experiments required to understand thoroughly ternary equilibria can be quite large.

In general, the mass action quotient is not a constant for a given cation as the zeolite approaches full loading with that cation (Samuelson, 1953). Rather, k for a given cation is a function of the activity of that cation on the zeolite and in the equilibrium solution. Consequently, only very general conclusions may be drawn from the mass action quotients per se. Table 3, as an example, gives the cesium mass action quotients, defined as

$$\frac{[Cs_z][Na_s]}{[Na_z][Cs_s]}$$

for several zeolites. The z and s refer to zeolite and equilibrium solution cation concentrations. The 13X and 4AXW are cesium-selective at one per cent loading, but rapidly become sodium-selective as cesium loading progresses. Note that clinoptilolite tends to maintain a relatively high cesium selectivity at 50 per cent cesium loading. The fact that the 13X

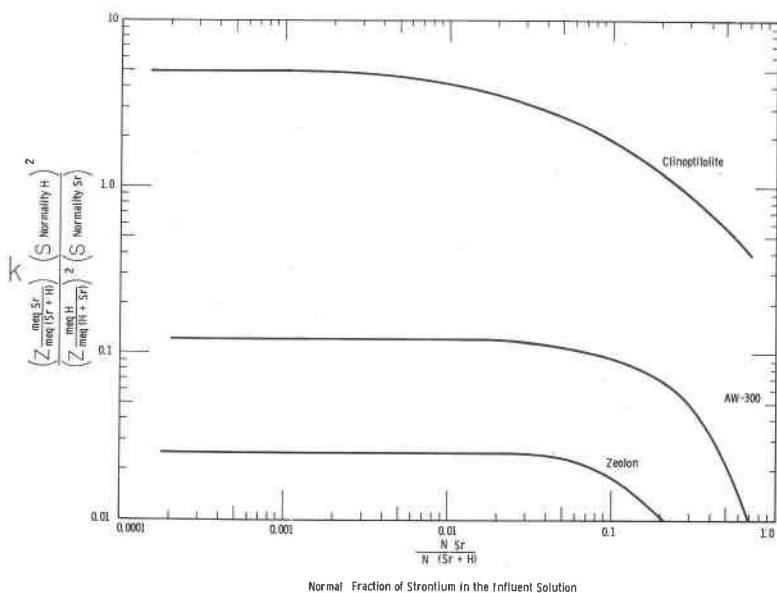


FIG. 8. The effect of hydrogen on the strontium mass action quotient k , of AW-300, Zeolon and clinoptilolite.

TABLE 3. ZEOLITE CESIUM MASS ACTION QUOTIENTS IN A CESIUM-SODIUM SYSTEM AT ONE AND FIFTY % OF ZEOLITE CESIUM LOADING

Zeolite	1% cesium loading	50% cesium loading
4AXW	5.04	0.134
13X	2.52	0.176
AW-300	126.3	0.34
AW-400	288.6	50.6
AW-500	202.1	39.0
Zeolon	170.5	19.0
Clinoptilolite	149.0	68.3
Erionite	246.6	44.7

and 4AXW curves cross between 10 and 50 per cent cesium loading is not readily apparent from Fig. 1.

The comparison of natural and synthetic zeolite species is of interest in the cesium-sodium system. Zeolon and AW-300 are both mordenites. Structural differences between the two mordenites include the absence of "stacking faults" in the Zeolon, resulting in an effective pore diameter

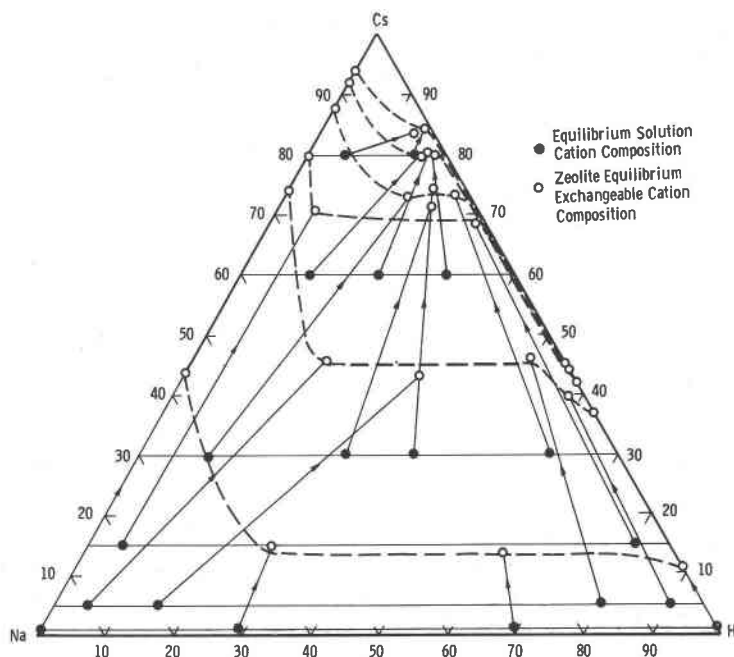


FIG. 9. A portion of the ternary equilibrium system hydrogen-sodium-cesium on clinoptilolite.

of about 10 Å (Anon., 1962). The AW-300, on the other hand has an effective pore diameter of about 4 Å. The effect of the structural differences on the cesium mass action coefficient can be seen in Table 3. Not only are the AW-300 one and fifty per cent cesium loading values lower than those of Zeolon, but the relative distance between the two values is greater for AW-300. However, AW-300 with its stacking faults is the better media for the separation of cesium from potassium and rubidium.

Erionite and AW-400 also are the same zeolite species. Except for the

TABLE 4. PREDICTED AND ACTUAL COLUMN CAPACITIES

Zeolite	Influent solution	Column wt., g.	Grain size range, mm.	Predicted load, meq/g.	Actual load, meq/g.
13X	0.002 <i>N</i> Sr ²⁺ +Sr ⁸⁸ +0.01 <i>N</i> Na ⁺	5.5	0.4-0.7	3.3 (Sr)	3.2 (Sr)
4A	0.002 <i>N</i> Sr ²⁺ +Sr ⁸⁸ +0.01 <i>N</i> Na ⁺	5.5	0.4-0.7	3.5 (Sr)	3.4 (Sr)
4A	0.07 Sr ²⁺ +Sr ⁸⁸ +0.1 <i>N</i> Na ⁺	5.5	0.4-0.7	3.5 (Sr)	3.5 (Sr)
4A	0.07 <i>N</i> Sr ²⁺ +Sr ⁸⁸ +0.1 <i>N</i> Na ⁺	50	1.6	3.5 (Sr)	0.9 (Sr)
Clinoptilolite	0.01 <i>N</i> Na ⁺ +Cs ¹³⁴ +1.0 <i>N</i> Na ⁺	50	0.25-1.00	0.75 (Cs)	0.73 (Cs)
Clinoptilolite	0.01 <i>N</i> Cs ⁺ +Cs ¹³⁴ +0.5 <i>N</i> Na ⁺	50	0.25-1.00	1.02 (Cs)	1.01 (Cs)
AW-500	0.001 <i>N</i> Cs ⁺ +Cs ¹³⁴ +1.0 <i>N</i> NH ₄	50	1.6	0.037 (Cs)	0.039 (Cs)
4AXW	0.001 <i>N</i> Cs ⁺ +Cs ¹³⁴ +1.0 <i>N</i> NH ₄	50	1.6	0.011 (Cs)	0.011 (Cs)
AW-500	0.001 <i>N</i> Cs ⁺ +Cs ¹³⁴ +1.0 <i>N</i> K ⁺	50	1.6	0.040 (Cs)	0.050 (Cs)
Clinoptilolite	0.01 <i>N</i> Cs ⁺ +Cs ¹³⁴ +1.0 <i>N</i> K ⁺	50	0.25-1.00	0.143 (Cs)	0.145 (Cs)
AW-400	0.001 <i>N</i> Cs ⁺ +Cs ¹³⁴ +1.1 <i>N</i> Na ⁺	50	1.6	0.240 (Cs)	0.241 (Cs)

slightly lower cesium mass action quotients of natural erionite, AW-400 and erionite values are comparable.

Mass action quotients for cesium generally decline as the size of the competing cation approaches that of cesium. Sodium, for example, furnishes less competition for cesium than does rubidium when present in equal concentrations.

The large selectivity differences between strontium-hydrogen and cesium-hydrogen (see Figs. 4 and 8) suggest that a chromatographic separation of alkali and alkaline earth metal cations could be easily accomplished in an acidic system. Note also from Fig. 5 that AW-500, a chabazite, is effective for the separation of strontium and calcium, as reported previously by Noll (1933).

Several column experiments were used to verify that the binary data could be used to determine zeolite loads or partial capacities in those systems. Table 4 compares predicted zeolite loading with actual zeolite loading values obtained in column experiments with comparable flow rates at 25° C. Column capacities were computed at 50 per cent loading by the method of Samuelson (1953). Note that the predicted load of 4A in 1.6 mm (one-sixteenth inch) pellets does not agree with the actual

loading capacity. Equilibrium was not attained between contacting solution and zeolite because the column flow rate was too fast for the zeolite particle size. Only under the condition of zeolite-solution equilibrium can the equilibrium data be used to predict column loads.

CONCLUSIONS

Mass action quotients per se are of limited value for the basic study of cation exchange equilibria on zeolites; *i.e.*, the determination of mass action quotients constitutes only a first step in such a study. The quotients are useful by themselves, however, for prediction of zeolite column loading. Cation loading on the zeolite from multicomponent systems also can be estimated if the approximation that the competing cation effects are additive is assumed.

The cation exchange equilibria of only a small number of the many zeolites reported in the literature are known. It is evident from the few data available that the zeolites constitute a potentially highly-useful family of cation exchange media, especially when high selectivity is imperative.

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