ZEOLITE CATION SELECTIVITY

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ABSTRACT

A proposal that cation selectivity of zeolites is mainly a function of anionic site separation distances was tested with high and low silica-to-alumina ratios of the same zeolite crystal structure (faujasite and Type A). Anionic site separation distances of the high silica zeolites were assumed to be relatively greater than the low silica zeolites. The high silica zeolites were considerably more cesium-selective from a sodium-cesium system than the lower silica zeolites, as expected. Strontium selectivity from a sodium-strontium system was generally greater with the low silica zeolites, but was complicated by anionic site separation distance heterogeneity.

INTRODUCTION

Previous study of the cation exchange characteristics of several natural and synthetic zeolites yielded an apparent relationship between silica to alumina ratio and cation selectivity, as seen in Table 1 (Ames, 1964a; Ames, 1964b). The work of Eisenman (1960) and Truesdell (1963) on the basis for ionic specificity was postulated as pertinent to an explanation of the relationship between cation selectivity and silica to alumina ratio of zeolites. According to Eisenman (1962, p. 283), the zeolite ion exchange reaction could be represented as:

TABLE 1. The relationship between the thermodynamic equilibrium constant, K, and silica to alumina ratio for several zeolites at 25° C. $Na_z \rightarrow Cs_z$ refers to the exchange of sodium on the zeolite to cesium on the zeolite, and $2Na_z \rightarrow Sr_z$ refers to the exchange of sodium on the zeolite to strontium on the zeolite

Zeolite	SiO_2/Al_2O_3	K $Na_z \rightarrow Cs_z$	K $2Na_s \rightarrow Sr_z$
Linde Type A	2.0	0.323	83.2
Linde Type X	2.4	0.355	19.9
Nevada Phillipsite	4	26.4	0.107
Linde AW-500	4–5	29.7	0.288
Nevada Erionite	6	32.9	0.794
Linde AW-400	6–7	39.0	0.363
Norton Zeolon	10	29.2	0.235
Hector Clinoptilolite	8–10	51.9	1.29

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$I^{+}_{(\text{zeolite})} + J^{+}_{(\text{aqueous})} \rightleftarrows J^{+}_{(\text{zeolite})} + I^{+}_{(\text{aqueous})} + \Delta F^{\circ}_{ij}$ where $I^{+}_{(\text{zeolite})}$ and $J^{+}_{(\text{zeolite})}$ are the cations I^{+} and J^{+} in the zeolite, and $I^{+}_{(\text{aqueous})}$ and $J^{+}_{(\text{aqueous})}$ are the cations in dilute solution. ΔF°_{ij} is the standard free-energy change for the above reaction, and equals $-RT\ln K$. R is the gas constant (1.9872 cal. deg.$^{-1}$mole^{-1}), T the absolute temperature (298° K in this case) and K is a thermodynamic equilibrium constant. Cation specificity, then, may be viewed as a result of interactions between cations and water, and cations and anionic sites, or $\Delta F^{\circ}_{ij} = \bar{F}_{I^{+}}{}^{\text{hyd}} - \bar{F}_{J^{+}}{}^{\text{hyd}} + \bar{F}_{J^{+}}{}^{\text{zeolite}} - \bar{F}_{I^{+}}{}^{\text{zeolite}}$, where $\bar{F}_{I^{+}}{}^{\text{hyd}}$ and $\bar{F}_{J^{+}}{}^{\text{hyd}}$ are the partial molal free-energies of hydration of cations I^{+} and J^{+}, and $\bar{F}_{J^{+}}{}^{\text{zeolite}}$ and $\bar{F}_{I^{+}}{}^{\text{zeolite}}$ are partial molal free-energies of reaction between cations I^{+} and J^{+} and the ionic sites of the zeolite. $\bar{F}_{I^{+}}{}^{\text{hyd}}$ and $\bar{F}_{J^{+}}{}^{\text{hyd}}$ are available from the literature, and are assumed to be similar for all the zeolites. However, the amount of water available to interact with the cations in the zeolite adsorption cavity is variable. In the special case where water is excluded, such as in a molten salt system, zeolite cation selectivity becomes a function of the relationship between the naked radii of I^{+} and J^{+} and the anionic sites (Ames, 1961, p. 1129).

Both the radii of the anionic sites and their distance apart on the zeolite structural framework influence $\bar{F}_{J^{+}}{}^{\text{zeolite}}$ and $\bar{F}_{I^{+}}{}^{\text{zeolite}}$. Since we are dealing exclusively with (AlO_4) groups as anionic sites, we may assume the anionic site radii are about the same. The separation distance between the anionic sites largely determines the contribution of $\bar{F}_{J^{+}}{}^{\text{zeolite}}$ and $\bar{F}_{I^{+}}{}^{\text{zeolite}}$ to zeolite cation selectivity. The anionic site separation distance should increase with increasing silica to alumina ratio. That the above statement is not rigorously true is evident from an examination of the data of Table 1. With the exception of Type A, there is very likely more than one distance of anionic site separation on a given zeolite structure. Heterogeneity in respect to anionic site separation distances may be the rule rather than the exception.

The object of the present study was to investigate further the relationship between zeolite cation selectivity and silica to alumina ratio, while maintaining the same zeolite crystal structure type.

METHODS OF INVESTIGATION

The cation selectivities of two high silica zeolites, ZK-4 (Kerr, 1961) and Type Y were compared to their lower silica structural counterparts, Type A and Type X (Breck *et al.*, 1956). The compositions and properties of the above zeolites are given in Table 2.

TABLE 2. COMPOSITIONS AND PROPERTIES OF THE SODIUM-BASED ZEOLITES USED IN THE STUDY

Zeolite	SiO_2/Al_2O_3	Structural Type	Anhydrous Unit Cell	Wt % Binder	Wt % Water	Measured Capacity, meq/g
Type X	2.4	Faujasite	$Na_{88}[(AlO_2)_{88}(SiO_2)_{104}]$	20	25	3.6
Type Y	4.6	Faujasite	$Na_{58}[(AlO_2)_{58}(SiO_2)_{134}]$	0	21	2.8
Type A	2.0	A	$Na_{12}[(AlO_2)_{12}(SiO_2)_{12}]$	10	30	3.9
ZK-4	3.3	A	$Na_{4.9}[(AlO_2)_{5.6}(SiO_2)_{18.4}]$	0	20	3.1

An equilibrium distribution of cations between solution and zeolite was determined, using methods described in detail in a previous paper (Ames, 1964b; Ames, in press). Reagent grade chemicals and distilled water were used along with high-purity cesium-134 and strontium-85 to trace the equilibrating solutions. Activity coefficient ratios for cations in solution were computed with Glueckauf's equation (1949). From these equilibrium data, a thermodynamic equilibrium constant was computed.

RESULTS AND DISCUSSION

A comparison of the 25° C. isotherms for cesium removal in sodium-cesium systems for Type Y and Type X and for ZK-4 and Type A are presented in Figs. 1 and 2, respectively. Strontium removal from a sodium-strontium system by Type Y and Type X is shown in Fig. 3, and Type A and ZK-4 in Fig. 4. The 25° C isotherms for cerium removal from a sodium-cerium system by Type X and Type Y are given in Fig. 5. The thermodynamic data derived from the equilibrium results are listed in Table 3.

TABLE 3. THERMODYNAMIC DATA. ΔF° IS THE STANDARD FREE-ENERGY CHANGE FOR THE EXCHANGE REACTION INDICATED

Zeolite	$\frac{SiO_2}{Al_2O_3}$	K, 25° C			ΔF°, 25° C		
		$Na_z \rightarrow Cs_z$	$2Na_z \rightarrow Sr_z$	$3Na_z \rightarrow Ce_z$	$Na_z \rightarrow Cs_z$	$2Na_z \rightarrow Sr_z$	$3Na_z \rightarrow Ce_z$
Type X	2.4	0.355	19.9	45.6	+ 600	−1800	−2300
Type Y	4.6	6.46	19.5	91.2	−1100	−1800	−2700
Type A	2.0	0.323	83.2	——	+ 700	−2600	——
ZK-4	3.3	4.57	4.22	——	− 900	− 900	——

According to Freeman & Stamires (1961), Stamires (1962) and Kerr (1962), depletion of the highest energy type anionic sites, to which the

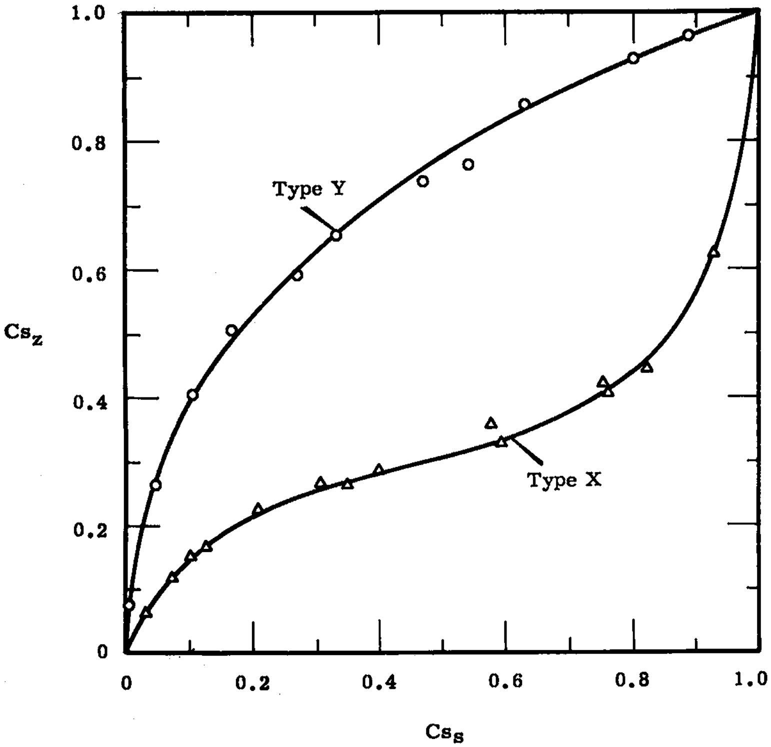

FIG. 1. The 25° C. isotherm for the reaction $Na_z + Cs_s \leftrightarrows Cs_z + Na_s$ with Type X and Type Y. Total equilibrium solution normality was constant at 1.0.
Cs_z = equivalent fraction of cesium on the zeolite.
Cs_s = equivalent fraction of cesium in the equilibrium solution.

cations are relatively loosely bound, are the first to be depleted. The structural positions from which the anionic sites were depleted of course, cannot be deduced from a consideration of the various isotherms. That sodium-selective anionic sites were depleted in favour of the cesium-selective sites, for example, can be determined from an examination of isotherms of the same structure with different silica to alumina ratios.

The higher silica faujasite structure, Type Y, is cesium-selective in a sodium-cesium system while the lower silica faujasite structure, Type X, as seen in Fig. 1, is sodium-selective in the same system. The cesium selectivity of Type Y was predictable in light of the previously-noted general trend of increasing cesium selectivity from a sodium-cesium system with increasing silica to alumina ratio. The strontium selectivity, however, from a sodium-strontium system of both Type X and Type Y is, for all practical purposes, identical. The sodium-selective sites have been seriously depleted, as shown in Fig. 1 and Fig. 5, while the isotherms of Fig. 3 apparently indicate no depletion of sodium-selective sites. Depletion of strontium-selective sites must occur to maintain the same relative strontium selectivity while sodium-selective sites are depleted. Perhaps a silica to alumina ratio between that of Type X and Type Y would have yielded an isotherm showing enhanced strontium selectivity, assuming that the depletion of sodium-selective sites began before the depletion of strontium-selective sites. The higher silica

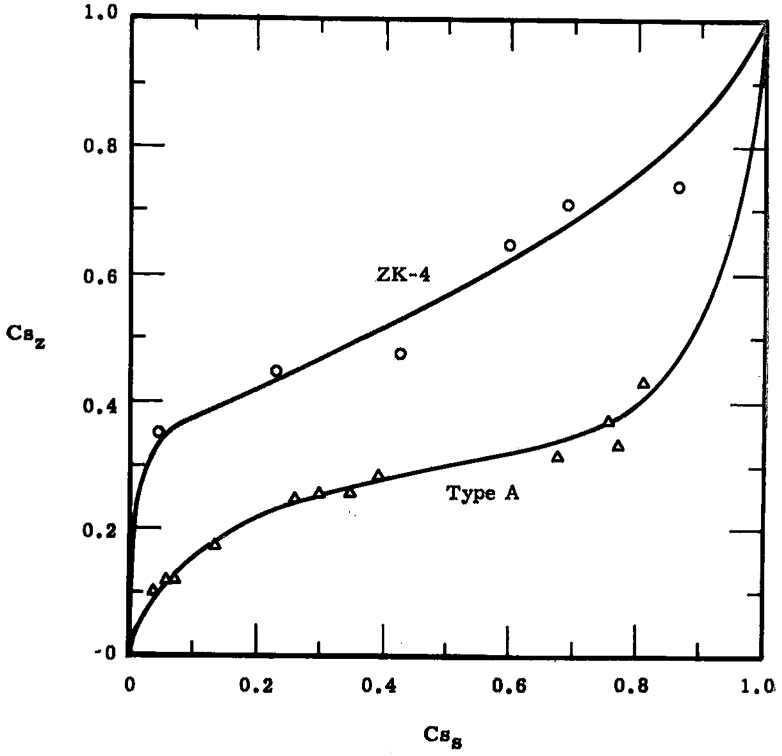

FIG. 2. The 25° C. isotherm for the reaction $Na_z + Cs_s \leftrightarrows Cs_z + Na_s$ with Type A and ZK-4. Total equilibrium solution normality was constant at 1.0.

Cs_z = equivalent fraction of cesium on the zeolite.
Cs_s = equivalent fraction of cesium in the equilibrium solution.

to alumina ratio Type X showed an enhanced cerium selectivity in relation to sodium as seen in Fig. 5, but the mass action expression for a sodium-cerium system contains cubic terms. A small change in the equilibrium therefore yields a large change in the distribution coefficient.

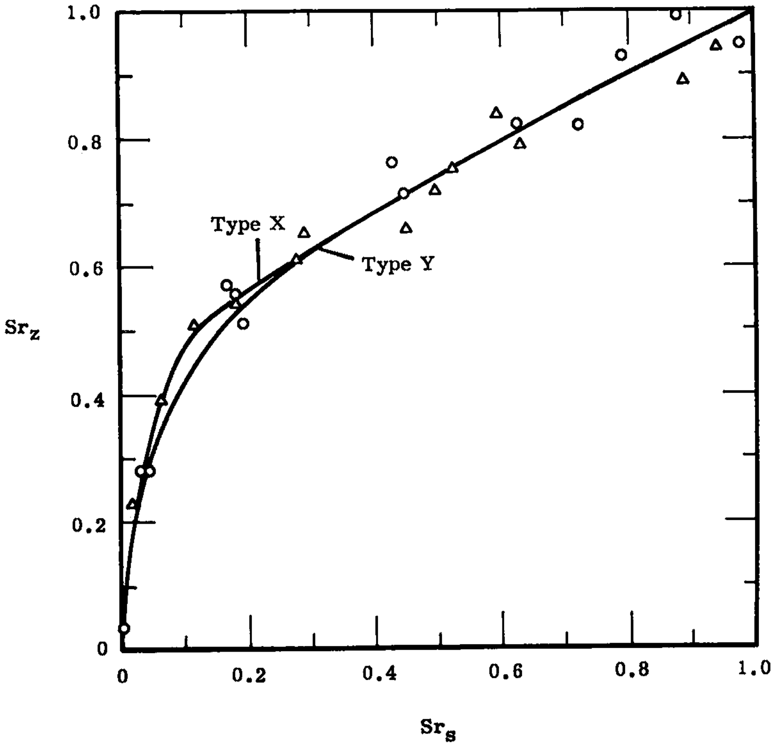

FIG. 3. The 25° C. isotherm for the reaction $2Na_z + Sr_s \leftrightarrows Sr_z + 2Na_s$ with Type X and Type Y. Total equilibrium solution normality was constant at 1.0.
Sr_z = equivalent fraction of strontium on the zeolite.
Sr_s = equivalent fraction of strontium in the equilibrium solution.

The anionic sites on Type A show a somewhat less complex depletion pattern, as seen in Fig. 2 and Fig. 4. The high silica to alumina ratio ZK-4 yields a higher cesium selectivity from a sodium-cesium system and lower strontium selectivity from a sodium-strontium system than does the lower silica to alumina ratio Type A. Since all the anionic sites of Type A are equidistant (Reed & Breck, 1956), or nearly so, one would expect a relatively simple site depletion sequence.

It appears that the theoretical treatment of Eisenman and Truesdell is useful for qualitative prediction of zeolite cation exchange behaviour. There are several unknowns that prevent quantitative computations,

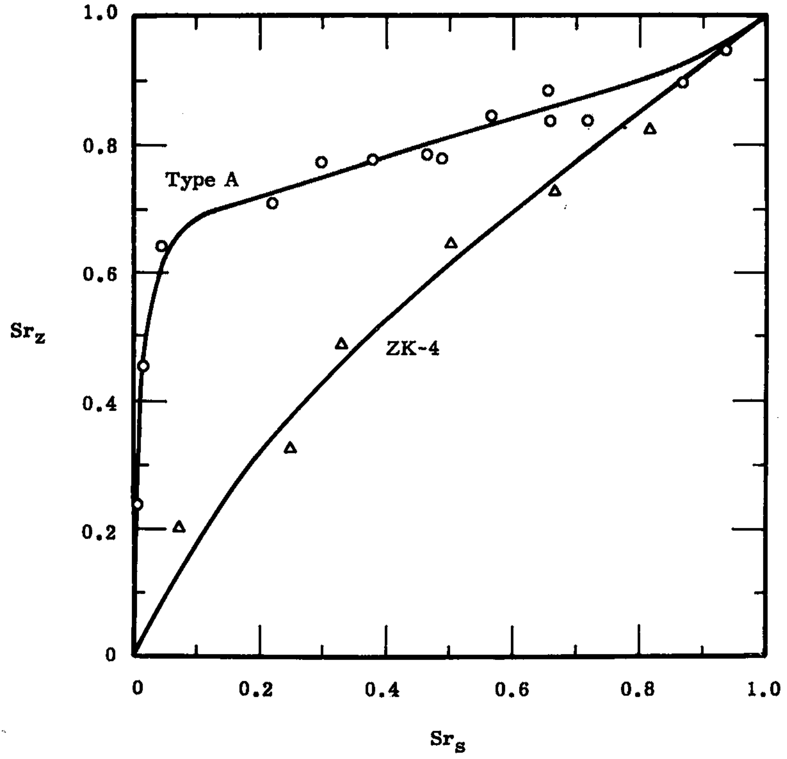

FIG. 4. The 25° C. isotherm for the reaction $2Na_z + Sr_s \leftrightarrows Sr_z + 2Na_s$ with Type A and ZK–4. Total equilibrium solution normality was constant at 1.0.
Sr_z = equivalent fraction of strontium on the zeolite.
Sr_s = equivalent fraction of strontium in the equilibrium solution.

including the distances between anionic sites on the zeolite crystal structure. It is possible to infer an average anionic site separation distance, given the experimentally-determined cation exchange sequence and anionic site radius. Such a treatment of zeolitic cation exchange does give a basic understanding of cation selectivity.

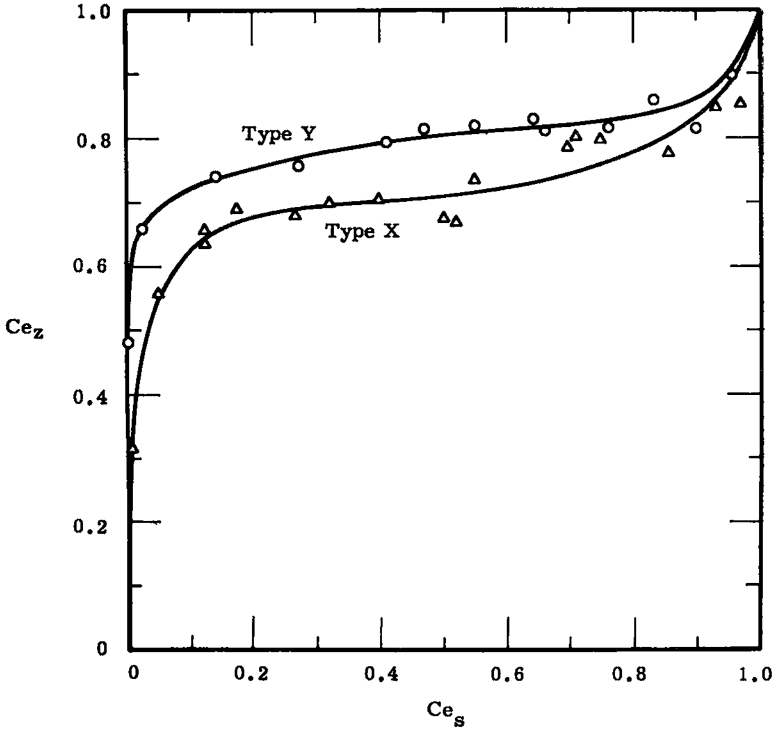

FIG. 5. The 25° C. isotherm for the reaction $3Na_z + Ce_s \leftrightarrows Ce_z + 3Na_s$ with Type X and Type Y. Total equilibrium solution was constant at 0.5.
Ce_z = equivalent fraction of cerium on the zeolite.
Ce_s = equivalent fraction of cerium in the equilibrium solution.

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