Three Binary Ion–Exchange Isotherms in Zeolite A: Cs^+-Ag^+, Ag^+-Na^+, and $NH_4^+-Na^+$

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Three binary ion–exchange isotherms of zeolite A have been determined using 0.1M solutions of the aqueous nitrates for the one-step preparation of particular mixed-cation zeolite A compositions. Analyses were done primarily by flame emission spectrometry (FES), together with crystallographic determinations of Cs^+ and colorimetric determinations of NH_4^+. Corrections for a presumed impurity of extra-lattice species in powder sample were made for the determination of Na^+. The Cs^+–Ag^+ isotherm indicates a strong selectivity for Ag^+ through the entire range of zeolite composition. The Ag^+-Na^+ isotherm agrees very closely with that reported by Sherry and Walton, and that of $NH_4^+-Na^+$ resembles those obtained using zeolite pellets.

Introduction

According to Breck's univalent selectivity series for zeolite A,[1] Ag^+ is the most favored cation of those studied, and Cs^+ the least. This is partly because of the compact size of Ag^+ ions, which allows them to fit 6-rings well, and the strong covalent interaction they have with zeolitic oxygens, as found in many Ag^+-exchanged zeolites A.[2-6] It is also because of an unusual "ion–sieve effect" which zeolite A shows for large cations like Cs^+.[7,8] When ion–exchange is carried out with solutions of such competing cations, unusual cation selectivities can be expected. Ion–exchange isotherms of such ions are useful for the one–step preparation of particular mixed–cation zeolite compositions.

It will be interesting to investigate certain mixed–ion compositions of zeolite A for a variety of reasons. For example, $Cs_6(NH_4)_6$–A might be decomposed thermally to yield a material with just three framework oxygens missing per 12 Å unit cell; the crystal structure is likely to survive this treatment, and the Lewis acid sites generated could be observed, perhaps in a complexed form as well. Cs_3Ag_9–A might react with hydrogen to give a high concentration of reduced silver atoms within the zeolite, without loss of crystallinity as occurs with Ag_{12}–A;[9] at a given temperature H_2 molecules might enter the zeolite through 8-rings blocked by Cs^+ while Ag atoms might remain trapped within. The work described here was directed at determining accurately three ion–exchange isotherms in zeolite A so that integral mixed–ion compositions of single crystals could readily be prepared for crystallographic experiments by a one–step ion–exchange procedure.

Experimental

Crystalline zeolite Na-A powder (courtesy of the PQ Corp.) with particle size of about 1 μm was used throughout.

Ion exchanges were carried out at 21 °C using solutions whose total cation concentration was 0.1M.

$NH_4^+-Na^+$ Exchange. A series of $Na^+-NH_4^+$ exchange solutions (mole fraction $NH_4^+ = 0.1$, 0.2, 0.4, 0.6, 0.8, 0.9 and 1.0) was made using $NaNO_3$ (99.9% reagent, Mallinckrodt), NH_4NO_3 (reagent grade, J. T. Baker), and deionized water. For each of these seven compositions, 300 ml of exchange solution was placed in a beaker with 2 gm of Na–A. This corresponded to a 2.7-fold excess of the entering cation with respect to the leaving ion. In order to discourage the exchange of hydronium ions into the zeolite, a few drops of NH_4OH were added to each exchange solution, making each pH approximately 8. Each exchange system was stirred occasionally and left overnight for the zeolite to settle fully. On the following day, each solution was replaced by a fresh ion–exchange solution of the same composition; this refreshment was done daily a total of six times. At the end of the last exchange, the crystals were collected on filter paper and washed with approximately 600 ml of water (with pH adjusted as above to about 8), and were allowed to dry.

It was noted that a considerable amount of zeolite was lost by this procedure as the solution were refreshed. The procedure was therefore modified (*vide infra*) for the determination of the two remaining isotherms.

Ag^+-Na^+ Exchange. A series of Na^+-Ag^+ exchange solutions (mole fractions $Ag^+ = 0.1$, 0.3, 0.5, 0.7, and 0.9) was prepared using $NaNO_3$ as before, $AgNO_3$ (99.9% pure reagent crystals, Chemical MFG Corp.), and deionized water. For each of these five compositions, 30 ml of exchange solution was placed in a beaker with 100 mg of Na–A (This corresponded to a 5.5-fold excess of the entering ion with respect to the leaving ion.). After ten minutes with occasional stirring, the crystals were filtered using a 0.45 μm membrane filter (HWAP, Millipore) (This time the filtrate was entirely clear.), and were transferred to a beaker containing fresh exchange solution. For each solution composi-

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Table 1. Determination of $(NH_4)^+$ in $(NH_4)_xNa_y$-A Based on FES (Na) and Colorimetry (NH_4^+)

$(NH_4)_s^{+a}$	FES (Na)		Colorimetry (NH_4^+)		$(NH_4^+)_z^a$ (av.)
	%Na^{+b}	No. of NH$_4^+$/u.c.^{c}	% NH$_4^{+b}$	No. of NH$_4^+$/u.c.^{c}	
0.0	12.60	0.00	0.00	0.00	0.00
0.1	9.64	2.88^d	1.51	1.83	0.15
0.2	7.54	2.97	2.14	2.58	0.24
0.4	7.82	4.62	3.62	4.36	0.38
0.6	6.78	5.62	4.52	5.42	0.46
0.8	4.40	7.88	6.29	7.52	0.65
0.9	3.15	9.05	7.79	9.27	0.76
1.0	0.00	12.00	10.15	12.00	1.00

^{a}Subscript "s" represents the molar ratio of that ion to the competing cation in the ion-exchange solution, while "z" means the cationic fraction of that ion in the unit cell of ion-exchanged zeolite A. ^{b}These values were corrected by a scale factor (1.1 = 13.9/12.6 and 10.15/9.3) to account for contamination and the presence of other phases (see data treatment). ^{c}The number of NH$_4^+$ per unit cell are calculated using the ideal stoichiometry, Na$_{12}$-A. ^{d}This value was assumed to be in error and was not used in the calculation of the last entry on this line (see discussion).

Table 2. Determination of $(Ag^+)_z$ and $(Cs^+)_z$ in Ag$_x$Na$_y$-A and Cs$_x$Ag$_y$-A by FES (Na and Cs)

	Ag$_x$Na$_y$-A				Cs$_x$Ag$_y$-A		
$(Ag^+)_s^a$	%Na^{+b}	No. of Na$^+$/u.c.^{c}	$(Ag^+)_z^a$	$(Cs^+)_s^a$	%Cs$^+$	No. of Cs$^+$/u.c.^{c}	$(Cs^+)_z^a$
0.0	12.60	12.00	0.00	0.00	0.00	0.00	0.00
0.1	0.37	0.52	0.96	0.10	1.29	0.31	0.03
0.3	0.08	0.11	0.99	0.50	5.51	1.34	0.11
0.5	0.03	0.05	1.00	0.80	9.05	2.22	0.19
0.7	0.00	0.00	1.00	0.90	11.61	2.87	0.24
0.9	0.00	0.00	1.00	0.95	12.27	3.03	0.25
1.0	0.00	0.00	1.00	0.98	14.54	3.61	0.30
				0.99	15.02	3.73	0.31

^{a}See footnote a in Table 1 for the notation. ^{b}Background calibration of Na$^+$ was carried out in addition to the correction by scale factor given in Table 1. ^{c}See footnote b in Table 1.

tion, this refreshment was performed six times. At the end of last exchange, the crystals were collected on membrane filter and washed with 30 ml of 0.001M solution with the same ratio of cations. The crystals were then allowed to dry in the atmosphere.

Cs$^+$-Ag$^+$ Exchange. Ag-A was first prepared by placing 3.83 gm of Na-A in 210 ml of 0.1M AgNO$_3$ exchange solution. The exchange and washing procedure was essentially the same as for the Ag$^+$-Na$^+$ exchange, except that the total number of refreshments of the exchange solution was four and the final wash was done with water. Since the exchange of Ag$^+$ for Na$^+$ occurs readily,[10] the total replacement of Na$^+$ by Ag$^+$ was assured in this case.

A series of Ag$^+$-Cs$^+$ exchange solutions (mole fraction Cs$^+$ = 0.10, 0.50, 0.80, 0.90, 0.95, 0.98, and 0.99) was made using AgNO$_3$ as before, CsNO$_3$ (99.99% pure, gold label, Aldrich Chemical Co.), and deionized water. For each of these seven compositions, 75 ml of each exchange solution was placed in a beaker with 0.4g of Ag-A. This corresponded to a 5.0-fold excess of the entering ion with respect to the leaving ion. Each exchange system was allowed to equilibrate for two hours with occasional stirring.

Analysis of Cation Content. Samples for analysis by flame emission spectrometry (FES) (Perkin-Elmer Model 3030B atomic absorption spectrophotometer) were dissolved in 0.01M HNO$_3$ (70.4%, analytical reagent, J. T. Baker

Chemical Co.). FES analysis for Na was performed on the NH$_4$,Na-A and Ag,Na-A samples; as a check it was also done on the Cs,Ag-A samples. Standard solutions with pH approximately 2 were prepared using the corresponding Na$^+$ and Cs$^+$ nitrates dissolved in 0.01M HNO$_3$. All solutions were kept in plastic (Nalgene) bottles.

Each NH$_4$,Na-A sample was also analyzed for NH$_4^+$ by a colorimetric method which employed the Berthelot reaction[11] and used a block digester and an AAII Technicon Auto Analyzer.[12]

Data Treatment

The analyses for Na$^+$ in Na-A by FES show relatively higher values (averaging 13.9%) than the 12.6% expected for hydrated Na$_{12}$-A, Na$_{12}$(AlO$_2$SiO$_2$)$_{12}$·27H$_2$O. This can be attributed to experimental error, to the occlusion of NaAlO$_2$ in the Na-A sample used, or to the presence of a second Na$^+$-containing phase such as NaAlO$_2$. For example, the existence of two extra units of Na$^+$ as occluded or external NaAlO$_2$ per unit cell of Na-A would cause the Na$^+$ content to be 13.7%. Since the known location of the presumed impurity, occluded NaAlO$_2$, is the center of sodalite unit[13,14] which is normally inaccessible to large cations like NH$_4^+$ and Cs$^+$ due to "double ion-sieving" effect of zeolite A[1] especially with the extra-lattice species in it, the effect of these ex-
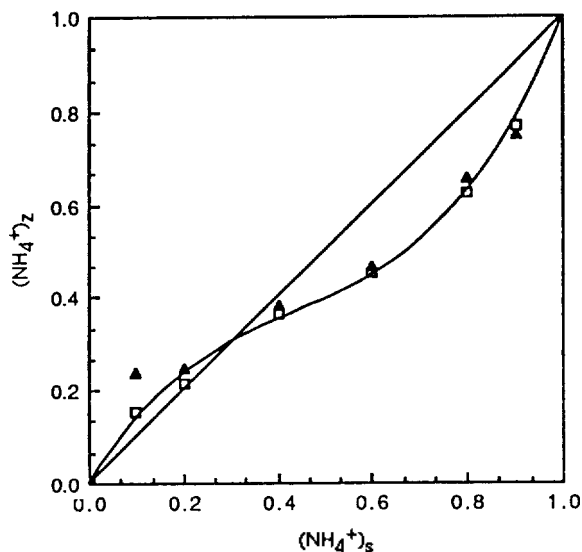
Figure 1. NH_4^+-Na^+ ion-exchange isotherm. Results based on flame emission spectrometry for sodium (▲) and on colorimetric determination of nitrogen (□) are shown. Subscript "s" represents the molar ratio of that cation to the competing cation in the ion-exchange solution, while "z" means the cationic-fraction of that ion in the unit cell of the ion-exchanged zeolite A.
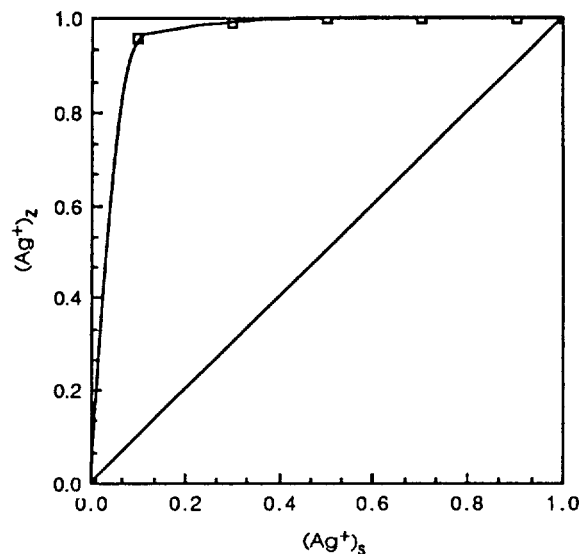
Figure 2. Ag^+-Na^+ ion-exchange isotherm. Results based on flame emission spectrometry for sodium (□). See the caption to Figure 1 for details.

tra-lattice species on the ion-exchange of Cs^+ and NH_4^+ in this study was assumed to be negligible. Therefore, corrections were made by a scale factor of (13.9%/12.6%) to account for this, showing a reasonable agreement with the results derived from the content of newly arrived cations as seen in Tables 1 and 2. Back ground calibration of Na^+ in the Cs_xAg_y-A system showed about 0.04% Na^+ (contamination from other sources), and was judged to be insignificant in the $(NH_4)_xNa_y$-A system.

The colorimetric determinations of NH_4^+ yielded results somewhat less than expected, even with $(NH_4^+)_{12}$-A (9.3% compared to 10.2%) which is assured to be completely NH_4^+-exchanged.[15] This can be understood by the same reasons given above, and by the additional possibility of losing NH_4^+ as $NH_3(g)$ in the sample drying process.

The extent of NH_4^+-exchange determined by the two methods is compared in Table 1, with numbers of NH_4^+ per unit cell and % content of each analysis corrected by scale factors to the theoretically calculated limiting values. Figure 1 shows the resulting NH_4^+-Na^+ ion-exchange isotherm.

The data for Ag_xNa_y-A were treated similarly except for an additional correction for Na^+ contamination as background. Therefore, for the samples equilibrated with solutions with mole fraction Ag^+ equal to 0.7, 0.9, and 1.0, the values of %Na^+ are taken to be zero based on crystallographic results.[16] The Ag^+-Na^+ ion-exchange isotherm based on the results of Table 2 is shown in Figure 2. It is identical to that obtained by Sherry and Walton[10] for the same system at 0.1 total concentration and 25 °C.

The values of %Cs^+ presented in the rest of Table 2 are obtained by FES analysis for Cs^+. Table 3 contains the X-ray crystallographic analyses of three Cs,Ag-A single crystals prepared by flow exchange methods at 25 °C[17] and show that the difference between the two methods is linear. Figure 3 shows the isotherms of Cs^+-Ag^+ ion-exchange based on

these results.

Discussion

According to Figure 1, the NH_4^+-Na^+ ion-exchange isotherm obtained by FES analysis for Na^+ agrees well with that acquired by colorimetric determination of NH_4^+, with the exception of the one data point at $(NH_4^+)_s = 0.1$. This remained discrepant when this FES analysis was repeated. Thus this discrepancy can only be attributed to experimental error involved in the preparation of that particular sample. The characteristic s-shaped isotherm implies that the selectivity for the entering ion NH_4^+ is reversed when the equivalent fraction of NH_4^+ in solution is greater than a certain amount. This observation is consistent with the expectation that the NH_4^+ ion, which is considerably larger than Na^+ (1.40 and 0.95 Å, respectively)[18], will be selected for exchange only as long as 8-ring sites are available, that is, only for the first three NH_4^+ ions to enter per unit cell. Although several reports of ion exchange on zeolite A involving the pair NH_4^+-Na^+ have been reported,[19-21] a direct comparison with the result obtained in this research cannot be made. For instance, the NH_4^+-Na^+ ion-exchange isotherm found in Breck's work[22] was acquired using exchange solutions whose total concentration is twice that used here, and at a temperature 4 °C higher. Therefore, ion-exchange isotherms may be dependent on the total concentration of the exchange solution and, of course, temperature (but not much with 4 °C difference) in the case of NH_4^+-Na^+. In other reports,[20,21] no specification of total concentration of the exchange solution is given, or pellets of zeolite made impure with clay binder were used, although their patterns of NH_4^+-Na^+ ion-exchange isotherms are similar with the one obtained in this work.

The Ag^+-Na^+ ion-exchange isotherm shown in Figure 2 is in excellent agreement with that obtained by Sherry and Walton,[10] despite the fact that the latter was obtained at a somewhat higher temperature. It clearly demonstrates the

Table 3. Comparison of No. of Cs^+ per Unit Cell Based on This Work and Crystallographic Determinations[a]

| $(Cs^+)_s$[b] | No. Cs+ per U.C. | | Ratio |
	FES (Cs)	Crystallogr.	
0.50	1.35	2.00	1.48
0.75	—	3.00	—
0.83	2.32[c]	3.33	1.44
1.00	5.00[c]	7.30	1.46
		Average Ratio	1.46

[a]Reference 17. [b]See footnote a in Table 1 for the notation. [c]Value read from Figure 3.
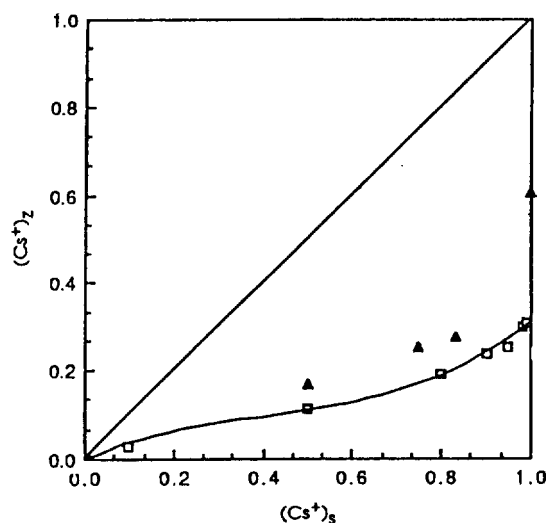
Figure 3. Cs^+-Ag^+ ion-exchange isotherm. Results based on flame emission spectrometry for cesium (□) and on X-ray crystallography (▲) as shown. See the caption to Figure 1 for details.

over-whelmingly greater preference of zeolite A for Ag^+ over Na^+. This is despite the fact that the ionic radius of Ag^+ is considerably large than that of Na^+ (1.26 vs. 0.95 Å)[17]. It is clear that Ag^+ forms an unusually strong bond (particularly short and covalent) to oxide ions of the zeolite framework, so the resulting complex has high stability. Thus conventional ionic radii are not always good indicators for the prediction of ion selectiviy. Indeed, Ag-O bond lengths measured crystallographically in zeolite A are among the shortest found.[2-7,17]

Table 3 strongly suggests that the discrepancy shown in Figure 3 is predominantly one of scale, which might be attributed to a systematic error in the preparation of the Cs standard solution, or to instrumental error in the FES analysis. Perhaps also ion-exchange equilibrium was not achieved, and perhaps some displacement of Cs^+ by H_2O^+ occurred when the Cs^+-exchanged samples were rinsed with deionized water in the final step. In any case, the Cs^+-Ag^+ ion-exchange isotherm obviously indicates a strong selectivity for the leaving ion Ag^+ through the entire range of zeolite composition, and shows that the entering Cs^+ ions cannot fully displace all of the Ag^+ ions in the structure. This observation is consistent with the fact that Cs^+ is much larger than Ag^+ (1.69 and 1.26 Å)[18]: consequently twelve of them cannot readily be accommodated by the cation sites available in the crystal framework.[6,7,23,24] Hence, in this case, ion size has a

role in defining the ion-exchange isotherm. The Cs^+-Ag^+ isotherm is very similar to that of Cs^+-Na^+,[25-27] except that a greater degree of Cs^+ exchange can be achieved in the latter. This observation is consistent with the Ag^+-Na^+ ion-exchange isotherm, which shows the preference of zeolite A for Ag^+.

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