and Kennedy data (*4*). Consequently one must conclude that, using current technology, boiler feedwater of necessary purity cannot be achieved to avoid supersaturation of the steam with respect to sodium ion present with chloride.

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Ion Exchange in Mordenite. Verification of the Triangle Rule

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Ion-exchange isotherms obtained with synthetic mordenite have been measured at 25 °C involving the cation pairs $Na^+ \rightleftarrows Li^+$, $2Na^+ \rightleftarrows Co^{2+}$, and $H_3O^+ \rightleftarrows Li^+$. In all cases the exchange was reversible. Values for the thermodynamic equilibrium constant, K_a, and the standard free energy of exchange, ΔG°, were calculated for each exchange. The K_a values determined for the above exchange reactions are respectively 0.048, 0.63, and 0.0052, while the corresponding ΔG° values are 1.80, 0.14, and 3.11 kcal/equiv. These experimental K_a and ΔG° values were then compared with values derived by the triangle rule. It was determined that this rule is effective in deriving thermodynamic equilibrium constants for these reactions.

Introduction

There is interest in mordenite as a selective adsorbent in the production of oxygen-enriched air. This zeolite exhibits enhanced adsorption of nitrogen over oxygen due to a quadrupole interaction between the nitrogen molecule and the polar zeolite surface. Considerable attention has been paid to the possibilities of modifying the adsorption selectivity of zeolites. An effective method of modification is the ion exchange of the cations in the zeolite structure, which leads to changes in the adsorption energy of the adsorbate molecules.

The structure of mordenite has been elucidated by Meier (*1*) and further described by Barrer and Klinowski (*2*). Ion-exchange data have been published on the behavior of mordenite toward selected alkali and alkaline-earth metal cations and the NH_4^+ cation (*2*). Also, an investigation into transition-metal ion exchange in ammonium mordenite has been reported (*3*). The purpose of this letter is to present ion-exchange isotherms obtained with mordenite not previously published, to determine the standard free energy of these exchanges, and to compare the experimental values of ΔG° with values derived by the triangle rule (*2*, *3*).

Experimental Section

Synthetic sodium and hydrogen mordenites (sodium and hydrogen Zeolon) were supplied by the Norton Co. Analysis of the zeolites gave a Si/Al ratio for the sodium mordenite of 5.42, while that for the hydrogen mordenite was 6.65. These Si/Al ratios are indicative of alumina-deficient materials.

Either the sodium or hydrogen form, as indicated, was employed to determine the exchange isotherms of $Na^+ \rightleftarrows Li^+$, $2Na^+ \rightleftarrows Co^{2+}$, and $H_3O^+ \rightleftarrows Li^+$. The $Na^+ \rightleftarrows Li^+$ and $2Na^+ \rightleftarrows Co^{2+}$ exchanges were measured at 25 °C with total solution concentration of 0.1 N. Weighed amounts of the sodium mordenite were rotated in plastic bottles with solutions containing known quantities of the two exchanging ions. For each point on the isotherm, the bottles were rotated for 5 days. Preliminary kinetic experiments indicated that equilibrium was established in 48 h. Subsequently, the solid zeolite was separated from the solution by centrifugation. The extent of exchange was determined by monitoring the change in solution concentration before and after exchange. Isotherm points were also measured in the reverse direction so that ion-exchange reversibility could be demonstrated.

The $H_3O^+ \rightleftarrows Li^+$ exchange was measured in stepwise fashion using a procedure developed by Barrer and Klinowski (*4*). A weighed amount of hydrogen mordenite (pretreated with acetic acid to ensure the absence of sodium) was added to a solution of 0.05 N LiCl and rotated at 25 °C for 2 days. Kinetic experiments indicated that equilibrium was reached in less than 24 h. The zeolite was then separated from solution by centrifugation, and the extent of exchange was again determined by solution analysis. Additional isotherm points were obtained by adding fresh LiCl solutions to the partially exchanged zeolite. Lithium mordenite was back-exchanged into the hydrogen form, also in steps, by using 0.04 N acetic acid solutions.

Results and Discussion

The experimental isotherms are shown in Figures 1-3. The subscript c denotes the equivalent fraction of the given ion in the zeolite crystal, while the subscript s indicates the equivalent fraction of the given ion in solution.

The thermodynamic equilibrium constant, K_a, was evaluated graphically by calculating the area under the curve obtained by plotting the logarithm of the rational selectivity coefficient vs. the ionic composition in the zeolite (*5*). Plots for the cobalt exchange were calculated from normalized ion-exchange isotherms because the equivalent fraction of cobalt in the crystal never reached unity (*3*). Finally, the standard free energy of

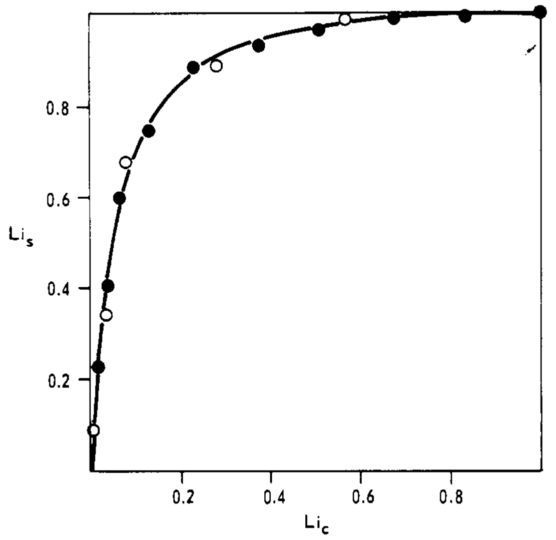

Figure 1. Ion-exchange isotherm in synthetic mordenite: $Na^+ \rightleftarrows Li^+$, maximum exchange = 100%. In all isotherms, filled circles indicate forward isotherm points and open circles indicate reverse isotherm points.

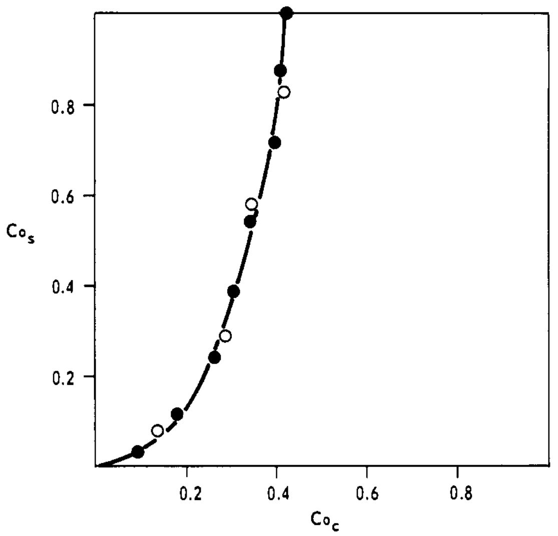

Figure 2. Ion-exchange isotherm in synthetic mordenite: $2Na^+ \rightleftarrows Co^{2+}$, maximum exchange = 41.8%.

exchange at 25 °C was calculated by using the following equation:

$$\Delta G° = -(RT/Z_1Z_2) \ln K_a \qquad (1)$$

where Z_1 and Z_2 are the valences of ions 1 and 2, respectively.

In Table I the experimental K_a and $\Delta G°$ values for each exchange are compared with values derived by the triangle rule (*2*, *3*). This rule enables theoretical K_a values to be determined from experimental K_a values. The most general form of the triangle rule is given by

$$K_a^{A,B} = K_a^{A,C} K_a^{C,B} \qquad (2)$$

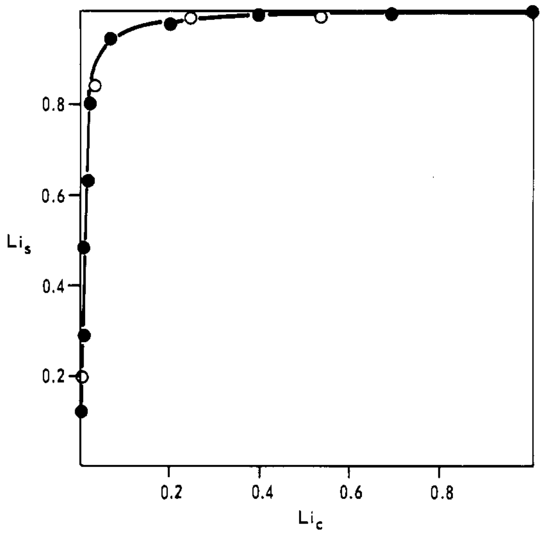

Figure 3. Ion-exchange isotherm in synthetic mordenite: $H_3O^+ \rightleftarrows Li^+$, maximum exchange = 100%. Not all experimental points are shown.

Table I. Experimental and Theoretical Values of $\Delta G°$ and K_a

	exptl		triangle rule	
exchange	K_a	$\Delta G°$, kcal/equiv	K_a	$\Delta G°$, kcal/equiv
$Na^+ \rightleftarrows Li^+$	0.048	1.80	0.053	1.72 (*2*)
$2Na \rightleftarrows Co^{2+}$	0.63	0.14	0.58	0.16 (*3*)
$H_3O^+ \rightleftarrows Li^+$	0.0052	3.11		

where $K_a^{A,B}$, $K_a^{A,C}$, and $K_a^{C,B}$ are the thermodynamic equilibrium constants for the exchange reactions A $\rightleftarrows$ B, A $\rightleftarrows$ C, and C $\rightleftarrows$ B, respectively.

Other workers (*2*, *3*) have applied this rule to ion exchange in mordenite, and it appears, at least in the two cases in which comparisons are possible, that this rule is effective in deriving thermodynamic equilibrium constants for these reactions.

Further, the observation that the exchange reaction $2Na^+ \rightleftarrows Co^{2+}$ does not go to completion brings forth an important point; i.e., the ion-exchange capacity of zeolites can vary significantly with the entering ion. Therefore, whenever ion-exchange isotherms are reported, it is important to include ion-exchange capacities for each ion.

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