From an investigation into the sorption kinetics of Na\(^+\), K\(^+\), and Sr\(^{2+}\) ions from standard solutions on finely dispersed clinoptilolite incorporated in a highly permeable inert polyacrylamide gel we have determined the characteristic kinetic size of clinoptilolite and the diffusion coefficients for Na\(^+\), K\(^+\), and Sr\(^{2+}\) in the clinoptilolite microcrystallites and transport pores. Diagrams have been constructed to enable a valid selection of kinetic models for sorption of the ions from any solutions on clinoptilolite.

**Keywords:** clinoptilolite, sorption, diffusion, microcrystals, transport pores, kinetic moments.

In connection with the widespread use of the natural zeolite clinoptilolite (K1) in many technological ion-exchange processes and the need to optimize them a real problem arises in the correct choice of the corresponding kinetic sorption models [1]. We have presented here the results of an investigation into the sorption kinetics of metallic ions from standard solutions on synthetic bidispersed sorbents obtained by immobilizing fine fractions of K1 in a highly permeable polyacrylamide gel.

**EXPERIMENTAL**

Native K1 from Tedzami [2] was used. The procedures for obtaining narrow fractions of K1, the determination of the average particle radius, and synthesis of the bidispersed samples have been given elsewhere [3]. The average radii for the narrow fractions \(r\) were 0.0003, 0.00075, and 0.00125 cm. The K1 content of the gel samples with granule dimensions \(R = 0.013, 0.02, 0.038, 0.075, \) and 0.125 cm were found by calcining them at 350°C for 1 h.

The sorption kinetics of solutions containing 0.001 g-equiv/liter of Sr\(^{2+}\) or K\(^+\) in a supporting 0.01N NaCl solution were studied by the thin layer method [4] in cells with cross-sectional area 19.6 cm\(^2\) (\(v_{lin} = 0.2\) cm/sec). After specified time intervals the experiment was stopped, the sample was quickly washed with distilled water to remove the solution, transferred to a column with parameters \(S = 1\) cm\(^2\) and \(h = 30\) cm, and regenerated with 0.5 M NH\(_4\)NO\(_3\) solution at a specific rate of 1 h\(^{-1}\).

After this the sample was dried on filter paper in air for one day and the mass of the sample in the NH\(_4^+\)-form was determined. The solution that had been used for regeneration was analyzed for K\(^+\), Sr\(^{2+}\), and Na\(^+\) ions by atomic absorption.

**RESULTS AND DISCUSSION**

Analysis of the kinetic curves (Figs. 1-3) and comparison of the half-life times \(t_{1/2}\) show that for these bidispersed samples the sorption rate for Na\(^+\) is determined to a large extent by diffusion in the transport pores of the gel, while the sorption rate for Sr\(^{2+}\) is determined by diffusion in the K1, and for K\(^+\) both processes contribute to a similar degree. The time taken to reach equilibrium is significantly greater for Sr\(^{2+}\) than for K\(^+\) and Na\(^+\). In order to determine the kinetic parameters for the sorption process (characteristic sorption times in the transport pores \(t^T\) and microsections of K1 \(t^M\), the characteristic K1
size \( r_0 \), coefficients of diffusion in the transport pores \( D_T \) and the microsections \( D_M \) the kinetic results were treated by the moments method [5]. For sorption from an inorganic bulk phase the expression for the first moment \( M_1 \) of the kinetic curve is

\[
M_1 = \gamma T + \gamma M
\]

where \( \gamma \) is the coefficient of the sorbent particle shape equal to 1/15 for an approximately spherical shape. Finding the value of \( M_1 \) from Eq. (1) for granules of different dimensions \( R_1, R_2, \ldots, R_n \) but with the same value of \( T \) we can calculate the parameters \( t_T \) and \( t_M \) for the synthetic bidispersed samples. The diffusion coefficients for the microporous sections are determined from the equation

\[
t_M = r_0^2/D_M
\]

To do this we need to know the characteristic kinetic size of K1 \( r_0 \). From the relationships between \( t_M \) and \( r_0^2 \) shown in Fig. 4 it can be seen that on reaching a value \( \bar{r} > r_0 \) the value of \( t_M \) now becomes dependent on the K1 granule size in the \( \bar{r} \) value interval under investigation. This indicates that \( t_M = \text{const} \) is the characteristic time for the attainment of equilibrium in the K1 microcrystallites, the dimensions of which can easily be determined from Fig. 4 from the intersections of the extrapolations of the straight line sections of the curves. These constructions can be justified in physical terms for \( t_M = f(r_0)^2 \) since for \( \bar{r} < r_0 \, t_M \sim (r_0)^2 \). It can be seen from Fig. 4 that for any ion \( r_0^2 \sim 20 \times 10^{-8} \, \text{cm}^2 \) (\( d \sim 9 \, \mu\text{m} \)). Earlier a more approximate method gave a value of 10-15 \( \mu\text{m} \), close to the average dimensions of the microcrystallites determined from crystallographic measurements [6]).

Using \( t_M = \text{const} \) and taking \( \bar{r} > r_0 \) from Eq. 2 the internal diffusion coefficients for the K1 microcrystallites can be calculated, \( \text{cm}^2/\text{sec} \): \( D_{Sr}^M = 3.5 \times 10^{-13} \), \( D_K^M = 3.8 \times 10^{-11} \), and \( D_{Na}^M = 8.0 \times 10^{-11} \).

The values of \( r_0 \) and \( D_M \) determined for the synthetic bidispersed sorbents can be used to describe the sorption kinetics of metallic ions on regular K1 granules with any value of \( \bar{r} \) from solutions of other compositions. The necessary conditions are that the sorption isotherm should be approximately linear and sorption should occur via an internal diffusion mechanism. The diffusion coefficients for the K1 transport pores can be calculated from the equation

\[
t^2 = (r^2)(1+\Gamma)/D^T
\]

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