ISOTHERMS OF THE EQUILIBRIUM EXCHANGE OF Mg$^{2+}$, Ca$^{2+}$, Zn$^{2+}$, AND Cd$^{2+}$ IONS ON NaA ZEOLITE

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It is known that zeolites are effective inorganic cation exchangers. However, there have been unjustifiably few studies devoted specially to processes of the equilibrium exchange of ions on zeolites. Moreover, the available data for the exchange of ions of different valence are frequently contradictory. This pertains especially to type A zeolites, which are stable in a limited range of pH of solutions. We did not undertake a study of the processes of ion exchange on zeolites by classical methods, but only attempted to create a method suitable for calorimetric measurements of the differential heats of ion exchange, and to prepare a number of cationic forms of type A zeolites for subsequent study of their adsorption-energy characteristics. Careful monitoring of the degree of equilibrium exchange in the process of multiple treatment of the zeolite with solutions of salts of certain divalent metals, essential for the method being developed, yielded the corresponding ion exchange isotherms. An analysis of these data and the data of the thermogravimetric studies of the prepared forms of zeolites led to results of independent scientific significance, which constituted the subject of this publication.

EXPERIMENTAL METHOD

Ion exchange was conducted on two samples of molded NaA zeolite; produced by the Gor'kii experimental base (lot Ts-202-689-690, produced under the observation of B. A. Lipkind) and by the Linde Company, which will henceforth be denoted as NaA (G) and NaA (L), respectively. The granules were cylindrical with dimensions for NaA (G) $0.2 \times 3$ mm$^2$ and for NaA (L) $0.4 \times 7$ mm$^2$. The content of the binder clay in the samples was determined from adsorption measurements by a gravimetric method. Samples weighing 20 g were first evacuated at 470°, weighed under vacuum, covered with distilled water, and dried in air at 70°. Then these zeolite samples were saturated with H$_2$O vapors in a desiccator, first over a saturated solution of NH$_4$Cl (relative vapor pressure $p/p_s 0.8$), and weighed. Then the same samples were exposed for long periods at room temperature and humidity and again weighed. The adsorption isotherms obtained in this way are cited in Fig. 1. The various notations of the points on the same isotherm correspond to various weights of one sample of zeolite and show satisfactory reproducibility of the measurements.

The fraction of clay in the granules was determined according to the isotherms obtained at the same $p/p_s$ in the region from 0.3 to 0.5 from the ratio $(a_0-a)/a_0$, where $a_0$ is the value of the adsorption of H$_2$O on powdered NaA [1] and $a$ is the value of the adsorption on a molded sample of NaA. The values that we obtained earlier [2] for the adsorption of H$_2$O on NaA (G) proved to be 5% higher than the values obtained in this work, which is evidently explained by a difference in the methods of measurement and specific constant errors. Since the authors of [1] also used a desiccator method, the content of clay, equal to 18.5% for NaA (G) and 21% for NaA (L) is evidently closer to the truth than the content of clay in NaA (G) equal to 12% that we obtained in [2].

Salts of divalent metals, cp or analytical grade, were used for ion exchange.
Isotherms of ion exchange at 25° on molded NaA zeolites from 1.4 N solutions of salts. a) MgSO₄ - NaA (G). b: 1, 2) ZnSO₄ - NaA (G). c: 1, 2) Ca(NO₃)₂ - NaA (G); 3) CaCl₂ - NaA (G); 4) CaCl₂ - NaA (L). d: 1, 2) Cd(NO₃)₂ - NaA (G); 3) CdCl₂ - NaA (G); 4, 5) CdCl₂ - NaA (L). Along x-axes: \( n_2^M \), the equivalent fractions of ions of divalent metals in zeolites (degree of exchange). Along y-axes: \( n_2^M \), the equivalent fractions of the same ions in equilibrium isonormal (~1.4 N) solutions.

Thermal analysis was conducted on a derivatograph produced by F. Paulik–J. Paulik–L. Erdey. The weight of the samples was 0.3-0.4 g. The rate of heating was 10 deg/min. Before the experiment the granules were crushed and exposed in an open petri dish at room temperature and humidity.

Ion exchange was conducted under static conditions in polyethylene tanks with sample weights ~20 g. The samples were preliminarily evacuated, the weight determined under vacuum, and distilled water poured in. Then the excess H₂O was entirely decanted, and 10-20 ml of 2 N salt solution was poured in so that the liquid covered the zeolite with a thin layer. Considering the residual water in the zeolite, the salt concentration in solution was ~1.4 N; after equilibrium was reached (usually after three to seven days), the solution was decanted, and the zeolite transferred to a funnel and washed with distilled H₂O (1-2 liter) until appreciable leaching out of M²⁺ stopped. The decanted solution and wash waters were analyzed in a buffer medium (NH₃ + NH₄Cl) for its content of M²⁺ with EDTA and eriochrome black. The washed zeolite was again covered with the initial salt solution and the procedure repeated. Such a method of ion exchange (repeated treatment of one portion of zeolite with salt solution and distilled H₂O) might lead to an appreciable breakdown of the crystal lattice of type A zeolite. However, in the case of small quantities of the solution in one experiment (~1 ml/g) and the minimum amount of wash H₂O (no more than 1-1.5 liter/g), evidently there was no significant breakdown of the zeolite.

The limiting degree of ion exchange was usually reached after 10-20 successive treatments of the zeolite sample. The error of one measurement of the degree of ion exchange was 0.5%, i.e., the maximum error of the determination of the final degree of ion exchange might be 5-10%; however, in practice it was less than the maximum value.

Isotherms of Ion Exchange. For the exchange of Na ions in type A zeolite, we selected divalent metal ions with electronic structures similar in pairs: Mg²⁺ and Ca²⁺, Zn²⁺ and Cd²⁺, for which the 2p and 3p, 3d and 4d electron shells are entirely occupied. As the anions we used SO₄²⁻, NO₃⁻, or Cl⁻; moreover, in exchange for Ca²⁺ and Cd²⁺, to determine the influence of the anion on the isotherm and kinetics of ion exchange, we proceeded both from the nitrates and from the chlorides.