Ultrasonic Fields as a Factor Affecting the Ion-exchange Rate in Molecular Sieves

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Summary The Na^+ to Ca^{2+} exchange rate in 13X zeolites is increased considerably on application of an 800 kHz ultrasonic field.

THE effect of an ultrasonic field on the ion-exchange rate in a 13X zeolite has been studied. In this zeolite, the only ion-exchangeable ions were Na^+ cations. The Na^+ to Ca^{2+} ion exchange was carried out in a 0·25 M standard solution of $CaCl_2$ with a solution to zeolite ratio of 20:2 ml g^{-1}. In order to avoid thermal effects caused by the heat of moistening the zeolite with $CaCl_2$ solution during the ion-exchange process, the zeolites were pretreated for 24 h with distilled water. Ion-exchange experiments were performed with an ultrasonic frequency of 800 kHz for 30, 60, 120, 240, 360, 480, and 600 s. Similar experiments were performed using mechanical mixing instead of the ultrasonic field.

After ion exchange, the Na^+ and Ca^{2+} ion content of the solutions was analysed (flame photometry for Na^+; titration with ethylenediaminetetra-acetic acid with murexide as indicator for Ca^{2+}). The exchange rate in the first 30 s was

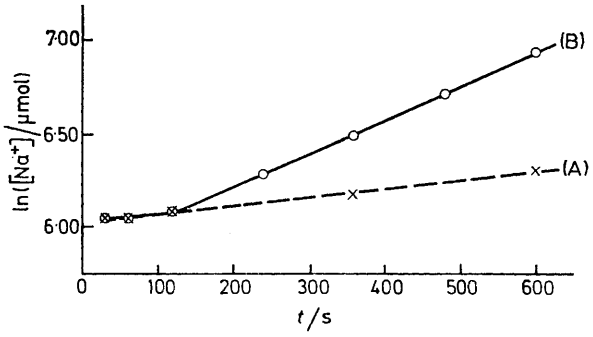

FIGURE. Plots of the ln of the concentration of Na^+ ions exchanged *vs.* time for: (A), mechanical mixing experiments; (B), experiments with an ultrasonic field.

high; *e.g.* 420 μmol of Na^+ ions appeared in the $CaCl_2$ solution after 30 s, and this had increased by only 20 μmol after 120 s. After the first 30 s, a plot of the ln of the concentration of Na^+ ions exchanged against time was linear for the mechanical mixing experiments over all the time range (30—600 s). For the ultrasonic experiments, the plot coincided with that for mechanical mixing from 30 to 120 s; from 120 to 600 s, a linear plot was still obtained, but of greater slope, indicating more exchange in this period in the ultrasonic experiments (Figure). The relationship between the concentration of Na^+ ions exchanged and time for the 30—120 s period of the ultrasonic experiments and for the whole period of the mechanical mixing experiments is given by equation (1), and that for the 120—600 s period of the ultrasonic experiments by equation (2).

$$c_m = \exp(4{\cdot}65 \times 10^{-4}t + 6{\cdot}0223) \quad (1)$$

$$c_u = \exp(1{\cdot}76 \times 10^{-3}t + 5{\cdot}8662) \quad (2)$$

Ion exchange in 13X zeolites involves the following processes: rapid diffusion of ions from solution, slow ion exchange, and slow diffusion of ions in the zeolite pores, the last of these being the slowest.[1] The higher exchange rate in the later parts of the ultrasonic experiments might be associated with the excitation of the so-called vibrational potentials in the zeolite by the ultrasonic field. Because of their lower mass, the Na^+ ions would be subject to greater periodic vibrations than the zeolite lattice under the influence of the ultrasonic field, thereby increasing their rate of diffusion through the zeolite. The high exchange rate in the first 30 s of both the mechanical mixing and the ultrasonic experiments could be attributed to washing out of non-stoicheiometrically connected sodium ions which were not removed during the pretreatment with distilled water.

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[1] F. Wolf, K. Pilchowski, F. Danes, and D. Cescareanu, *Math. Naturwiss. Reihe*, 1972, **21**, 87.