Reports

Tactoid Formation in Montmorillonite: Effect on Ion Exchange Kinetics

Abstract. *Exchange between calcium from montmorillonite and hydrogen from resin is much slower than exchange between sodium from montmorillonite and hydrogen from resin. Film kinetics are prevailing in both cases, but the location of the rate-determining step is shifted from the Nernst films of the resin particles in the sodium-hydrogen exchange to the Nernst films of the clay particles in the calcium-hydrogen exchange. The increased particle size of the montmorillonite in the calcium state, caused by tactoid formation, appears to be the main reason for the shift.*

The clay mineral montmorillonite has a mica-type plate structure. Evidence has accumulated showing that when montmorillonite is adsorbed with Ca, stable tactoids, containing 5 to 20 parallel plates, are formed (*1*). When the mineral is adsorbed with Na, the tactoids are not stable, and the single plates are separated from each other. The effect of this difference in structure on the ion-exchange properties of montmorillonite has not been studied. Here I report the study of the kinetics of ion exchange between either Ca or Na adsorbed on montmorillonite in suspension and H added to it on ion-exchange resin; the Ca-H exchange was considerably slower than the Na-H exchange and had a different rate-determining step. The differences in the kinetics between the two exchange reactions are attributed to the aforementioned difference in the clay structure.

Portions (50 ml) of either Na or Ca montmorillonite suspension (2.83 g of clay per liter) were vigorously stirred in a reaction vessel kept at a temperature of 25° ± 0.03°C, and 0.500 g of H-resin was added (*2*). After various periods of contact the resin was separated from the suspension, and the quantity of H adsorbed in the clay and the concentration of H in the supernatant solution were determined as described (*3*). This procedure was repeated with suspensions adjusted to different initial electrolyte concentrations by the addition of NaCl or $CaCl_2$. From the data the fractional attainment of equilibrium (U),

$$U = H/H_{\max} \qquad (1)$$

where H is the hydrogen content after a given time and $H_{\max}$ is the maximal possible hydrogen content, was calculated and plotted against time (Fig. 1). The Na-H exchange in the clay proceeded at the same rate as in the supernatant. The Ca-H exchange in the clay was much slower and lagged considerably behind that in the supernatant. Similar behavior was observed at the other electrolyte concentrations.

The time ($t_{1/2}$) at which $U = 0.5$ is plotted in Fig. 2 as a function of the electrolyte concentration. The rate of exchange, as measured by $t_{1/2}$, depends on electrolyte concentration. This indicates that film kinetics are prevailing, and the rate-determining step is the flux of ions through unstirred films (Nernst films) surrounding the exchanger particles. However, as two kinds of exchangers, such as clay and resin, are present, the rate-determining step may be in the Nernst films of the particles of either one. In order to locate it further, the rate of exchange of Na and Ca in aqueous solution with H in the resin was measured. The $t_{1/2}$ values, at solution concentration of 1 meq/liter, were 0.75 and 0.95 minutes for the Na-H and Ca-H exchange reactions, respectively.

By Helfferich's criterion (*4*) it was calculated that film diffusion, occurring obviously in the Nernst films of the resin particles, is rate controlling in the exchange between the ions in aqueous solution and the H in the resin. In the clay-resin systems having the same electrolyte concentration, the half times of exchange were increased, as compared with the relevant solution-resin systems, by factors of 3.1, 3.1, 5.9, and 90, for the exchange reactions: (Na-H) in the supernatant; (Na-H) in the clay; (Ca-H) in the supernatant; and (Ca-H) in the clay, respectively. Clearly, the exchange of H from the solution to the clay is considerably retarded, once the clay is in the Ca state. However, there is only a slight slowing down in the Na-H exchange both in the supernatant and in the clay, and, as already mentioned, the two reactions proceed at exactly the same rate. Thus it appears that in the overall exchange between Na in montmorillonite and H in resin the rate-controlling step remained in the Nernst films surrounding the resin particles, whereas in the overall Ca-H exchange it was shifted to the Nernst films surrounding the clay particles.

For the boundary conditions of the

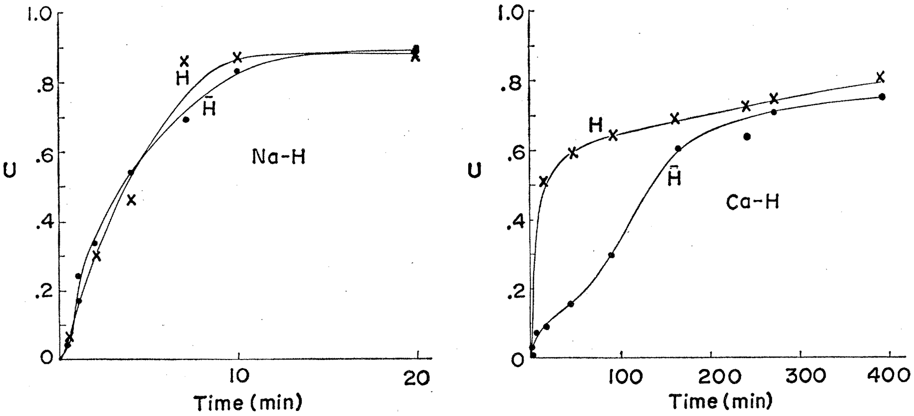

Fig. 1. Fractional attainment of equilibrium (U) as a function of time in the exchange between Na or Ca from montmorillonite suspension and H from Amberlite IR-120. $\bar{H}$, in clay; H, in supernatant solution. Concentration of added electrolyte: Na-montmorillonite, 0.4 meq/liter NaCl; Ca-montmorillonite, 0.5 meq/liter $CaCl_2$.

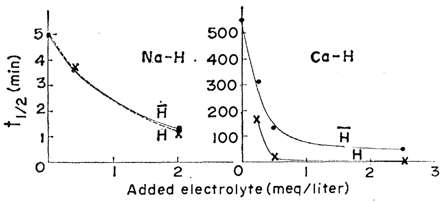

Fig. 2. Half time of exchange between Na or Ca from montmorillonite suspension and H from Amberlite IR-$12\underline{0}$ at different electrolyte concentrations. $\overline{H}$, in clay; H, in supernatant solution.

exchange between Na or Ca on the montmorillonite and H in the supernatant, $t_{1/2}$ may be given (*4*) by

$$t_{1/2} = (0.167 + 0.064\ \alpha_{\mathrm{H}}{}^{\mathrm{M}}) \frac{r\delta\bar{c}}{Dc} \qquad (2)$$

where $\alpha_{\mathrm{H}}{}^{\mathrm{M}}$ is the separation factor for exchange of the metallic ion for hydrogen, r is the particle radius, δ is the thickness of the Nernst layer, $\bar{c}$ the exchange capacity of the exchanger, D the interdiffusion coefficient in the film, and c the electrolyte concentration in solution. As r and δ for montmorillonite are not known and are difficult to evaluate, no absolute value for $t_{1/2}$ can be calculated. However, it is possible to calculate the ratio $t_{1/2}$(Ca-H)/$t_{1/2}$(Na-H) with δ (which mainly depends on the stirring conditions), $\bar{c}$, and c equal for the two ionic states, with known values for $\alpha_{\mathrm{H}}{}^{\mathrm{M}}$ and D ratios (*5*) and estimated ratios of $r_{\mathrm{Ca}}/r_{\mathrm{Na}}$. The calculated and observed ratios are given in Table 1. A slight slowing is predicted in the Ca-H exchange relative to the Na-H exchange even if the montmorillonite particle size is the same in the two ionic states. This is due to the smaller diffusion coefficient of the Ca ion and the higher preference of the clay for it. However, most of the observed reduction in rate may be explained if the Ca-montmorillonite particle is about ten times larger than the Na-montmorillonite particle. This can be brought by the adhering of the clay plates, totally separated when in the Na state, to form tactoids, containing about ten plates each, when in the Ca state (*6*).

Table 1. Observed and calculated ratios of half time of exchange between Na or Ca on montmorillonite and H on Amberlite IR-120.

Electrolyte conc. (meq/liter)	Observed $t_{1/2}$(min) (Ca-H)	Observed $t_{1/2}$(min) (Na-H)	$t_{1/2}$(Ca-H) / $t_{1/2}$(Na-H)
0.5	135	3.4	40
1.0	85	2.3	37
2.0	50	1.3	38
	Calculated		
$r_{\mathrm{Ca}}/r_{\mathrm{Na}}$*			$t_{1/2}$(Ca-H)/$t_{1/2}$(Na-H)
1			3.7
5			19
10			37
20			74

* Estimated ratios of particle size of montmorillonite in the Ca and Na states, respectively.

The clay-resin system described above can be used as a model for the soil-plant root system. Ion exchange between H from the root and metallic cations adsorbed on clay particles in the soil is taking place as part of the nutrient uptake process by the plant. Since the soil solution is not stirred, and usually has low electrolyte concentration, film kinetics probably prevails in this exchange reaction. In this case, as the results for the clay-resin systems show, a considerable difference between the rates of the H-divalent and the H-monovalent exchange reactions exists when montmorillonite is present as the main clay mineral. The difference in rate will affect the composition of the ionic flux reaching the root in exchange for its secreted hydrogen and cause what might be called a "kinetic selection," which tends to increase the fraction of monovalent ions adsorbed by the plant (*7*).

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References and Notes

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2. The clay used in this study was the fraction of Wyoming Bentonite (Cenco c-1051) less than 2 μ. The exchange capacity of the clay was 82 meq per 100 g. The resin used was Amberlite IR-120. It had a particle radius range of 0.015 to 0.060 cm and exchange capacity of 4.70 meq per gram.
3. A. Banin and S. Ravikovitch, in *Clays and Clay Minerals, 14th Conference* (Pergamon, New York, 1966), p. 193.
4. F. Helfferich, *Ion Exchange* (McGraw-Hill, New York, 1962), pp. 255, 275.
5. Separation factors were taken at the half-conversion point on the exchange isotherms (A. Banin, in preparation) and were 0.04 and 5.32 for the Na-H and Ca-H exchange reactions, respectively. The ratio of the interdiffusion coefficients in the film was assumed not to differ from the ratio of the diffusion coefficients in solution. Values for the diffusion coefficients of Na and Ca in solution were taken from H. S. Harned and B. B. Owen, *The Physical Chemistry of Electrolytic Solutions* (Reinhold, New York, ed 3, 1958).
6. A. V. Blackmore and R. D. Miller, *Soil Sci. Soc. Am. Proc.* **25**, 169 (1961).
7. Evidence for such a selection can be found in S. Mattson, *Ann. Agr. College Sweden* **12**, 221 (1948); M. M. Elgabaly and L. Wiklander, *Soil Sci.* **67**, 419 (1949); L. Wiklander and M. M. Elgabaly, *ibid.* **80**, 91 (1955).

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Extension of Northeastern-Pacific Fracture Zones

Abstract. *The great fracture zones of the northeastern Pacific extend into the central Pacific. At a relatively constant distance of 4500 to 4900 kilometers west of the crest of the East Pacific Rise and of its projection through North America, the typically straight and simple fracture zones branch and become more complex. However, the Clipperton fracture zone, including one branch, follows a great circle for almost 10,000 kilometers, a quarter of Earth's circumference.*

Recent work has shown that some of the great fracture zones of the northeastern Pacific (*1*) extend beyond the margins of the East Pacific Rise (*2*). The whole pattern of great fractures can be traced far into the central Pacific on recently acquired echograms (*3*) and soundings (*4*).

The Clipperton fracture zone is an outstanding example (Fig. 1), readily traceable as an essentially continuous topographic feature from the crest of the East Pacific Rise to just east of the Line Islands; there it is lost, being apparently buried under the archipelagic apron and volcanoes of the islands as well as the pelagic sediments of the equatorial belt (*5*). It reappears along the same trend south of the equatorial sedimentation belt as a line of troughs, ridges, and changes in regional depth. The relief is generally subdued, but, just east of Enderbury Island in the Phoenix group, an echogram by C.S. *Recorder* shows a trough with a depth of 7300 m, while older spot soundings indicate a maximum depth of 8030 m—by far the greatest known depths in the central Pacific. Bordering the deep trough on the south is a ridge rising to 2330 m and giving a local relief on a steep scarp of 5700 m. The fracture zone continues west along the northern edge of the Phoenix Islands and toward the Gilbert Islands as a band of narrow troughs and ridges with moderate relief. It cannot be found in the vicinity of the Gilberts, although it is quite possibly buried by the archipelagic apron. East of the Line Islands a branch extends westward from the main trend of the fracture zone but cannot be traced beyond the edge of the archipelagic apron; another branch, toward the southwest, exists east of the Phoenix Islands and appears to extend through them. The total known length of the fracture zone