NOTES

THE EFFECT OF CLAY DISPERSION ON THE SORPTION OF ACETONITRILE

Key Words—Clay dispersion, Organic sorption, Partition, Sorption mechanism.

The partition or distribution of a solute between two immiscible solvents was first treated by Nernst (Bromberg, 1980). Generally the partition coefficient, which is the ratio of the concentrations of the solute in the two solvents, is a constant. The partition mechanism has been extended to describe the sorption of solutes on clay minerals and soil materials for systems in which no specific bonding was involved. It should be noted that two types of partition mechanisms have been proposed. Earlier, Greenland *et al.* (1962, 1965), Theng (1972), and Theng and Scharpenseel (1976) proposed that the linear sorption isotherm observed with clay minerals can be characterized by a partition of a solute between the bulk and intercrystalline water. Later, Chiou *et al.* (1979, 1983) proposed that the sorption of neutral organic chemicals is essentially a partition process between the soil organic matter and soil water. More recently, Lee *et al.* (1989), Smith *et al.* (1990), and Jaynes and Boyd (1991) attributed this mechanism to the enhanced sorption of neutral organic molecules on soils and clays exchanged with organic cations with one or more long alkyl groups. Because clay minerals saturated with metal cations contain negligible amounts of organic matter, the sorption of neutral organic molecules on these clays only involves the partition mechanism proposed by the earlier investigators (Greenland *et al.*, 1962, 1965; Theng, 1972; Theng and Scharpenseel, 1976).

Recently, Zhang *et al.* (1990a, 1990b, 1990c) have studied the sorption of several neutral organic molecules on montmorillonites saturated with different metal cations. Based on the partition mechanism, they have derived the following equation (Zhang *et al.*, 1990b),

$$C_2^s \alpha V = KC_2^b \alpha V, \tag{1}$$

in which C_2^s is the equilibrium concentration of the organic solute in the interfacial phase, C_2^b is the concentration in the bulk solution phase, K is the partition coefficient, α is the fraction of the volume that is occupied by the interfacial phase, and V is the volume of solution per unit mass of solid adsorbent. It should be noted that the left-hand side of Eq. (1), to a first approximation, is the amount of solute adsorbed in the interfacial phase. Therefore, one can write

$$\Gamma_2^{(1)}S = KC_2^b \alpha V, \tag{2}$$

where $\Gamma_2^{(1)}$ is the relative surface excess of the solute per unit surface area of solid adsorbent and S is the specific surface area of the solid adsorbent, and consequently, $\Gamma_2^{(1)}S$ is the relative surface excess of the solute per unit mass of solid adsorbent. It is clear from Eq. (2) that the amount of adsorption is not only related to K and C_2^b, but is also related to α. A linear isotherm would result only if both K and α remain constant over the entire concentration range of the isotherm.

It was shown earlier that for sorption of neutral organic molecules on clays, K increases as the organic concentration increases (Zhang *et al.*, 1990b). This is due to the increase in the organophilic nature of the interfacial phase as more organic molecules accumulate on the clay surfaces. The effect of α on the sorption has not been addressed, except by Zhang *et al.* (1990b, 1990c), who noticed that downward curvature of the sorption isotherms of acetonitrile and acrylonitrile on K-montmorillonite could be attributed to a decrease in α.

Although the values of α are not precisely defined for expanded clay layers, it can be generally accepted that α is directly related to the dispersion status of the clays. Therefore, we shall examine the effect of clay dispersion on the sorption of neutral organic molecules. This research is based on the premise that if the measured sorption of neutral organic molecules is related to the dispersion status of the clay as predicted by Eq. (2), the general validity of the partition mechanism, on which Eq. (2) was based, can also be further demonstrated.

EXPERIMENTAL

Homoionic Na- and K-montmorillonite were prepared using Wyoming montmorillonite (SWy-1) and Cl salts (Zhang *et al.*, 1990b). The acetonitrile was obtained from Aldrich Chemical Company and the ^{14}C labeled acetonitrile was from Sigma Chemical Company. They were used without further purification.

Batch experiments were conducted to determine the sorption isotherms of acetonitrile on Na- and K-mont-
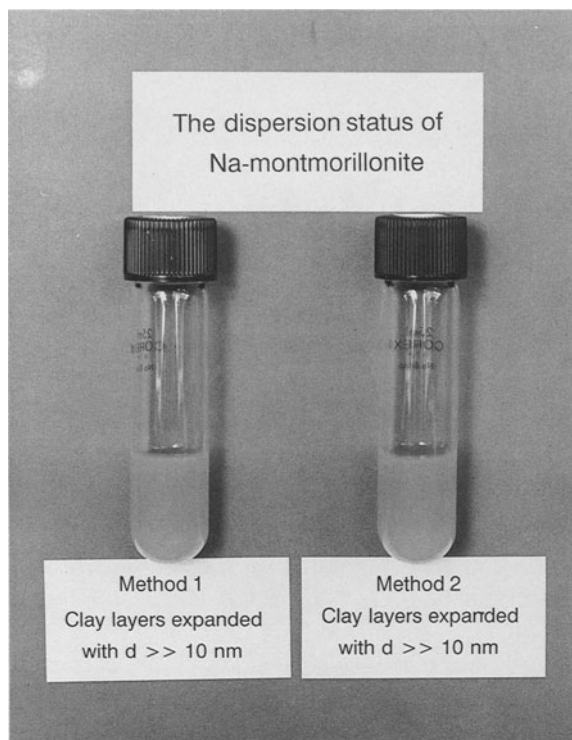
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Figure 1. The dispersion status of Na-montmorillonite prepared using two methods when the initial concentration of acetonitrile is 1.0 M.
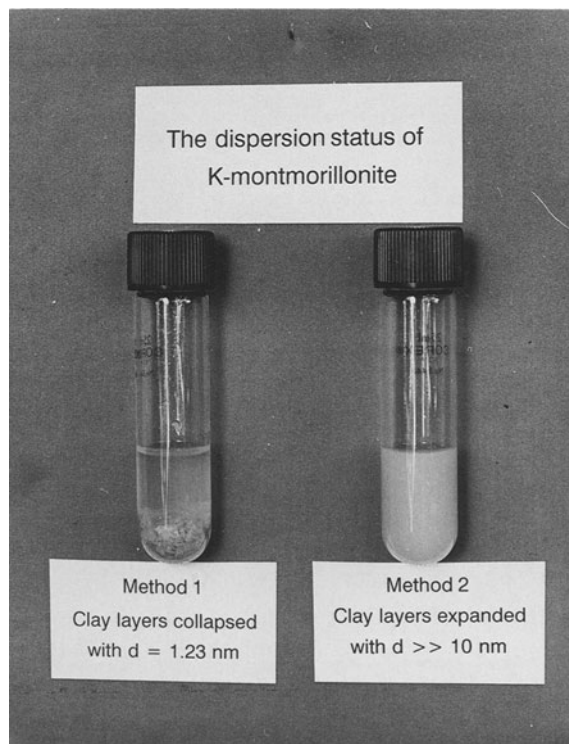

Figure 2. The dispersion status of K-montmorillonite prepared using two methods when the initial concentration of acetonitrile is 1.0 M.

morillonite at 25°C. Two methods were used to control the dispersion status of the clays.

Method 1

A series of acetonitrile solutions ranging from 0.05 to 2.0 M (mol L^{-1}) was prepared. The ^{14}C labeled acetonitrile solutions were prepared by adding ^{14}C labeled acetonitrile to each of the solutions in the above series to yield a specific activity of ~400 Bq mL^{-1} (~23,000 cpm mL^{-1}, assuming a counting efficiency of 95%). Approximately 0.5 g K-montmorillonite (or 0.3 g Na-montmorillonite) was weighed in a series of centrifuge tubes and 10 mL of each of the ^{14}C labeled solutions were added to the tubes. The resulting clay suspensions were shaken on a reciprocating shaker for 24 h, centrifuged, and two, 1 mL aliquots of the supernatant solution from each tube were removed and added to separate vials containing 12 mL of aqueous counting scintillant. The radioactivities of these supernatant solutions were measured in a Beckman LS 5000 TA scintillation counter (Beckman Instruments, Fullerton, CA) with a counting error setting at $2\sigma = 0.5\%$. The radioactivities of reference solutions (no clay added) were also determined. The values of $\Gamma_2^{(1)}$S were determined using the procedure outlined by Zhang *et al.* (1990b).

Method 2

A second series of acetonitrile solutions ranging from 0.1 to 4.0 M was prepared. The ^{14}C labeled acetonitrile solutions were prepared by adding ^{14}C labeled acetonitrile to each of the solutions in the above series to yield a specific activity of ~800 Bq mL^{-1}. Approximately 0.5 g K-montmorillonite (or 0.3 g Na-montmorillonite) was weighed in a series of centrifuge tubes and 5 mL deionized water was added to pre-wet the clays overnight. Then 5 mL of each of the ^{14}C labeled solutions were added to these tubes. The resulting clay suspensions were equilibrated on a reciprocating shaker for 24 h. Then the clay suspensions were centrifuged, the radioactivities of the supernatant solutions and reference solutions were measured, and the values of $\Gamma_2^{(1)}$S were determined.

RESULTS AND DISCUSSION

The dispersion status of Na- and K-montmorillonite samples for the two methods is shown in Figures 1 and 2, respectively. One can see that the dispersion status of Na-montmorillonite was not affected by acetonitrile solution. Both methods yielded fully expanded clay layers with c-axis spacings greater than 10 nm. In contrast to Na-montmorillonite, the dispersion status of K-montmorillonite was affected by acetonitrile solution. The layers of K-montmorillonite remained collapsed when acetonitrile solutions with concentrations above 0.6 M were added to dry clay (Method 1). On the other hand, the layers of K-montmorillonite were
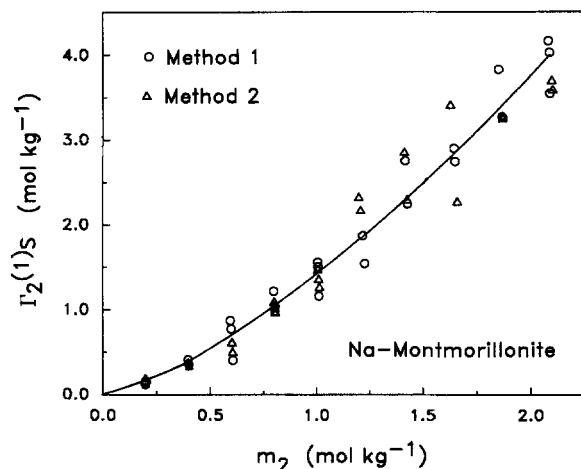
Figure 3.   The relative surface excess of acetonitrile per unit mass of clay, $\Gamma_2^{(1)}S$, measured by the two methods, as related to the equilibrium concentration of acetonitrile, m_2, for Na-montmorillonite.
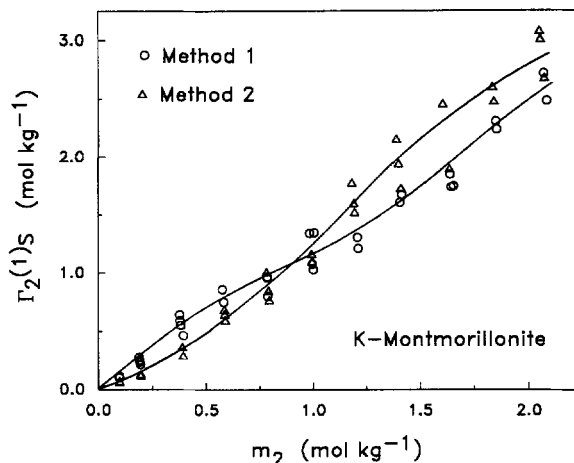

Figure 4.   The relative surface excess of acetonitrile per unit mass of clay, $\Gamma_2^{(1)}S$, measured by the two methods, as related to the equilibrium concentration of acetonitrile, m_2, for K-montmorillonite.

expanded when the clay was pre-wetted with water (Method 2). It can be seen from Figure 2 that when Method 1 was used, K-montmorillonite particles retained their shape and the supernatant solution remained clear at an initial acetonitrile concentration of 1.0 M. X-ray diffraction showed that the c-axis spacing of the collapsed K-montmorillonite layers was 1.23 nm (Zhang et al., 1990b).

Figures 3 and 4 show the sorption data for acetonitrile on Na- and K-montmorillonite that were obtained using the two methods described above. It appeared that values of $\Gamma_2^{(1)}S$ for Na-montmorillonite were not affected by the methods used (Figure 3), while values of $\Gamma_2^{(1)}S$ for K-montmorillonite were affected (Figure 4). To examine if indeed the values of $\Gamma_2^{(1)}S$ were affected by the methods used, we employed the following statistical test. We noticed that $\Gamma_2^{(1)}S$ was approximately proportional to m_2, the equilibrium concentration of acetonitrile, hence, it was reasonable to assume that the $\Gamma_2^{(1)}S/m_2$ ratio follows a normal distribution. Because the values of this ratio were still somewhat dependent on the concentration, we treated these values for the two methods as dependent samples. By dependent, we mean that the corresponding values of the $\Gamma_2^{(1)}S/m_2$ ratio for the two methods are paired. We averaged the replicate values of the $\Gamma_2^{(1)}S/m_2$ ratio for Na- and K-montmorillonite at each initial concentration of acetonitrile, C_2^i, for Methods 1 and 2, respectively, and determined the differences between them. The resulting data are presented in Table 1, and were examined by the following t test (Kvanli, 1988):

$$t_d = \frac{\bar{d}}{s_d/\sqrt{n}}, \qquad (3)$$

where n is the number of pairs of observations, $\bar{d}$ is the mean and s_d is the standard deviation of the n

differences, respectively. The degree of freedom, df for t_d is $n - 1$.

From the data presented in Table 1, we found that $t_d = 0.281$ for Na-montmorillonite. To conclude that the values of $\Gamma_2^{(1)}S/m_2$ determined by the two methods are different at the 95% confidence interval, the required value of t_d for $df = 9$ is 2.262. We were led to conclude that values of the $\Gamma_2^{(1)}S/m_2$ ratio, and thereby values of $\Gamma_2^{(1)}S$ for Na-montmorillonite, were independent of the methods used. This result is expected in accordance with Eq. (2). If the dispersion status and the α values of a clay were the same for the two methods, one would expect the amounts of sorption to be the same, provided the values of K were not affected by the methods. Conversely, if the dispersion status and the α values of a clay were not the same for the two methods, one would expect the amounts of sorption to be different. When the clay layers were col-

Table 1.   The average values of the $\Gamma_2^{(1)}S/m_2$ ratio obtained using Methods 1 and 2, and the difference between them, d, at different initial concentrations of acetonitrile, C_2^i (mol L^{-1}), for Na- and K-montmorillonite.

	Na-montmorillonite			K-montmorillonite		
	$\Gamma_2^{(1)}S/m_2$			$\Gamma_2^{(1)}S/m_2$		
C_2^i	Method 1	Method 2	d	Method 1	Method 2	d
0.1	—	—	—	1.111	0.716	−0.394
0.2	0.722	0.928	0.206	1.283	0.643	−0.640
0.4	0.933	0.905	−0.028	1.316	0.844	−0.472
0.6	1.143	0.967	−0.176	1.421	1.099	−0.322
0.8	1.264	1.317	0.053	1.153	1.018	−0.045
1.0	1.395	1.355	−0.040	1.201	1.127	−0.074
1.2	1.396	1.874	0.478	1.039	1.372	0.333
1.4	1.760	1.818	0.058	1.159	1.386	0.227
1.6	1.715	1.736	0.021	1.081	1.346	0.265
1.8	1.909	1.749	−0.160	1.226	1.383	0.158
2.0	1.877	1.740	−0.137	1.253	1.422	0.169

lapsed, the α value decreased, and the amount of sorption should be reduced.

We have observed that the layers of K-montmorillonite remained collapsed for Method 1 when $C_2^i >$ 0.6 M, whereas the layers were expanded for Method 2 (Figure 2). Based on the above analysis, we expected that the amount of sorption on K-montmorillonite should be dependent on the methods used when $C_2^i >$ 0.6 M. To validate our analysis, we performed the above t test for the differences in $\Gamma_2^{(1)}S/m_2$ for C_2^i above 0.6 M. To conclude that the values $\Gamma_2^{(1)}S/m_2$ measured by Method 2 are higher than those by Method 1 at the 95% confidence interval, the required value of t_d for $df = 6$ is 2.447. The resulting t_d value is 2.544. Hence, we concluded that the amount of sorption was indeed related to the dispersion status of the clay. Namely, the amounts of sorption were at least qualitatively in agreement with Eq. (2) at higher acetonitrile concentrations.

At lower concentrations, however, the amounts of sorption appeared to be reduced when the clay was pre-wetted with water (Method 2). When the differences in $\Gamma_2^{(1)}S/m_2$ at lower C_2^i (0.1 to 0.6 M) were analyzed by the same t test, it was found that $t_d = -6.712$, indicating a significant decrease in the amount of sorption for Method 2. In this regard, one should note that the sorption from solution is essentially a displacement process, i.e., the sorption of the solute molecules is coupled with the desorption of solvent molecules. The reduced amounts of sorption when the clay was prewetted with water suggest that at lower concentrations the acetonitrile molecules cannot effectively compete with water molecules adsorbed on the surfaces of K-montmorillonite. Thus, the measured effect of clay dispersion on sorption using sorption differences for the two methods could be lower than the true effect itself. The enhanced sorption, as a result of clay dispersion, was partially neutralized by the ineffective competition of acetonitrile molecules over water molecules on K-montmorillonite when Method 2 was used. Conceivably, the reduced sorption for Method 2 in the concentration range of 0.8 to 1.0 mol kg^{-1} was due to this ineffective competition. Hence, the real effect of clay dispersion on sorption would be even more profound than we stated earlier.

In summary, experiments were conducted to examine the effect of clay dispersion on the sorption of acetonitrile. The experimental data were used to test an equation, derived from the partition mechanism, which relates the amount of sorption of neutral organic molecules on clay surfaces to the partition coefficient, concentration of the organic solute in the bulk solution, and the fraction of the volume that is occupied by the interfacial phase. The results were at least qualitatively

in agreement with the equation, further demonstrating the general validity of the partition mechanism.

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