

DIVISION S-2—SOIL CHEMISTRY

Acetonitrile and Acrylonitrile Sorption on Montmorillonite from Binary and Ternary Aqueous Solutions

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ABSTRACT

The main objective of this study was to gain mechanistic information on clay-organic interactions in aqueous environments containing multiple organics. Three different measurements were made to achieve this objective. The sorption of acetonitrile and acrylonitrile on K, Na, Ca, and Mg montmorillonite from binary and ternary aqueous solutions were determined using a ^{14}C isotope tracer method. The infrared spectra of acrylonitrile in solution and adsorbed on montmorillonite were recorded on a Fourier-transform infrared (FTIR) spectrometer and the *c*-axis spacings of montmorillonites in the acrylonitrile solutions were determined by x-ray diffraction. It was found that the sorption of acetonitrile and acrylonitrile from ternary solutions on K montmorillonite was competitive across the entire concentration range. The sorption was slightly competitive at lower concentrations on Na, Ca, and Mg montmorillonite, but enhanced at higher concentrations. The competitive sorption on K montmorillonite was probably associated with the decrease in the interfacial volume, since the layers of K montmorillonite were collapsed at higher concentrations, while the enhanced sorption on Na, Ca, and Mg montmorillonite appeared to be caused by an increase in the partition coefficient as more organic molecules entered the interfacial phase. These results led to the conclusion that the sorption of acetonitrile and acrylonitrile on montmorillonite was not due to specific bonding between the organic molecules and the clay surfaces, but rather to a partition between the interfacial phase and the bulk solution phase.

THE INTERACTION OF ORGANICS in aqueous solutions with soils and soil constituents has gained considerable attention in recent years because of concerns about environmental quality. For example, studies have been conducted on the effect of organics with different structures and functional groups on the physical behavior of clay minerals (Chen et al., 1987), and the sorption and desorption of organics on soils (Hassett et al., 1980, 1981; Chiou et al., 1983; Ainsworth et al., 1989), and clays (Boyd et al., 1988; Zhang et al., 1990a, 1990b). All of these investigations were conducted in binary aqueous solutions that contained a single organic component. These studies are important, since they aid in obtaining mechanistic information on the soil-organic interactions in an aqueous environment.

To understand pollution problems, however, soil-organic interactions in aqueous systems containing multiple organics should be investigated, since these

more closely resemble field settings. Recently, several studies on the sorption of naturally occurring organic substances on oxides (Davis and Glour, 1981; Davis, 1982) and soils (Jardine et al., 1989) have been reported in the literature. The present study investigated the sorption of acetonitrile and acrylonitrile on homoionic K, Na, Ca, and Mg montmorillonite from binary and ternary aqueous solutions. Acetonitrile and acrylonitrile were chosen as adsorbates since they are widely used in industry. For example, acrylonitrile is used in the synthetic rubber, resin, fibers, and plastics industries. Acetonitrile, which is a by-product in the manufacture of acrylonitrile, is a widely used industrial solvent and is frequently employed in scientific laboratory research.

MATERIALS AND METHODS

Homoionic K, Na, Ca, and Mg montmorillonite samples were prepared using Wyoming montmorillonite (SWy-1) and Cl salts (Zhang et al., 1990a). The acetonitrile (J.T. Baker Chemical Co., Phillipsburg, NJ), the acrylonitrile (Aldrich Chemical Co., Milwaukee, WI), and the ^{14}C -labeled acetonitrile and acrylonitrile (Sigma Chemical Co., St. Louis, MO) were used without further purification.

Binary and Ternary Sorption Studies

Adsorption is the process through which a net accumulation of a substance occurs at an interface and the quantitative description of adsorption is achieved through the concept of surface excess (Sposito, 1984). The relative surface excess per unit surface area of the adsorbent, denoted by the symbol Γ_i^j , is the number of excess moles of a substance *i*, determined relative to a reference substance *j*. In mathematical terms, Γ_i^j is defined by the equation (Sposito, 1984)

$$\Gamma_i^j = [n_i - (X_i/X_j)n_j]/S \quad [1]$$

where n_i and n_j are the moles of *i* and *j* per unit mass of solid adsorbent, X_i and X_j are the mole fractions of *i* and *j* in the equilibrium solution, and *S* is the specific surface area of the solid adsorbent. As shown by Sposito (1984) in the case of adsorption from an aqueous solution, the relative surface excess of substance *i* with respect to the solvent water is given by

$$\Gamma_i^w = (m_i^0 - m_i)M_w/S \quad [2]$$

where m_i^0 and m_i are the initial molality before adsorption and equilibrium molality after adsorption, respectively, and M_w is the mass of water per unit mass of solid adsorbent. For a ternary solution, Eq. [2] can be rewritten as

$$\Gamma_2^1 S = (m_2^0 - m_2)M_w \quad [3]$$

$$\Gamma_3^1 S = (m_3^0 - m_3)M_w \quad [4]$$

where $\Gamma_2^1 S$ and $\Gamma_3^1 S$ are the relative surface excesses of the two solutes per unit mass of solid adsorbent. Equations [3]

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and [4] provide the theoretical basis for the common method of measuring $\Gamma_2^{(1)}S$ and $\Gamma_3^{(1)}S$ through chemical analysis of the aqueous phase only, i.e., by measuring the changes in molalities of the two solutes. Experimentally, however, the molality is more easily determined by volumetric chemical analysis. The following section outlines the method for determining $\Gamma_2^{(1)}S$ and $\Gamma_3^{(1)}S$ using ordinary volumetric chemical analysis.

It is clear that, for a ternary solution at a given temperature, the molality and the molarity of the solutes are related by

$$m_2 = 1000C_2 / (1000\rho - C_2M_2 - C_3M_3) \quad [5]$$

$$m_3 = 1000C_3 / (1000\rho - C_2M_2 - C_3M_3) \quad [6]$$

where ρ is the density of the solution, C_2 and C_3 are the molarity concentrations, and M_2 and M_3 are the molecular weights of the two solutes. The relationship between ρ and C_2 and C_3 was determined experimentally following the procedure of Zhang et al. (1990b). The value of M_w is given by

$$M_w = \frac{V(1000\rho - C_2^iM_2 - C_3^iM_3)}{1000} \quad [7]$$

where V is the volume of solution per unit mass of solid adsorbent, and C_2^i and C_3^i are the initial molarities of the two solutes before adsorption.

It is evident that the above equations for a ternary solution reduce to the forms for a binary solution when the concen-

tration of either solute becomes zero. For consistency, we will use subscripts 2 and 3 to denote acetonitrile and acrylonitrile, respectively, in a ternary solution as well as in a binary solution.

To determine the values of $\Gamma_3^{(1)}S$ for the sorption of acrylonitrile from binary solutions, a series of acrylonitrile solutions with concentration ranging from 0.05 to 1.0 M were prepared using deionized water. The ^{14}C -labeled solutions were prepared by adding ^{14}C -labeled acrylonitrile to each of the solutions in the series to yield a specific activity of $\sim 400 \text{ Bq mL}^{-1}$ ($\sim 23\,000 \text{ cpm mL}^{-1}$, assuming a counting efficiency of 95%).

Batch experiments were conducted by adding 0.3 to 0.5 g of each of the homoionic montmorillonites and 10 mL of each of the above ^{14}C -labeled acrylonitrile solutions to a glass centrifuge tube. The desorption study was conducted on the clay samples initially equilibrated with the 1.0 M acrylonitrile solution, i.e., 2.0, 5.0, and 10.0 mL deionized water were added to these clay samples. The resulting clay suspensions were shaken three times during a 24-h equilibrium period with a vortex mixer. Equilibrium solutions were separated by centrifugation 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 radioactivity of the solution in the vials was determined at least three times in a Beckman LS 5000 TA scintillation counter (Beckman Instruments, Fullerton, CA) with error setting at $2\sigma = 0.5\%$. The above procedure, except centrif-

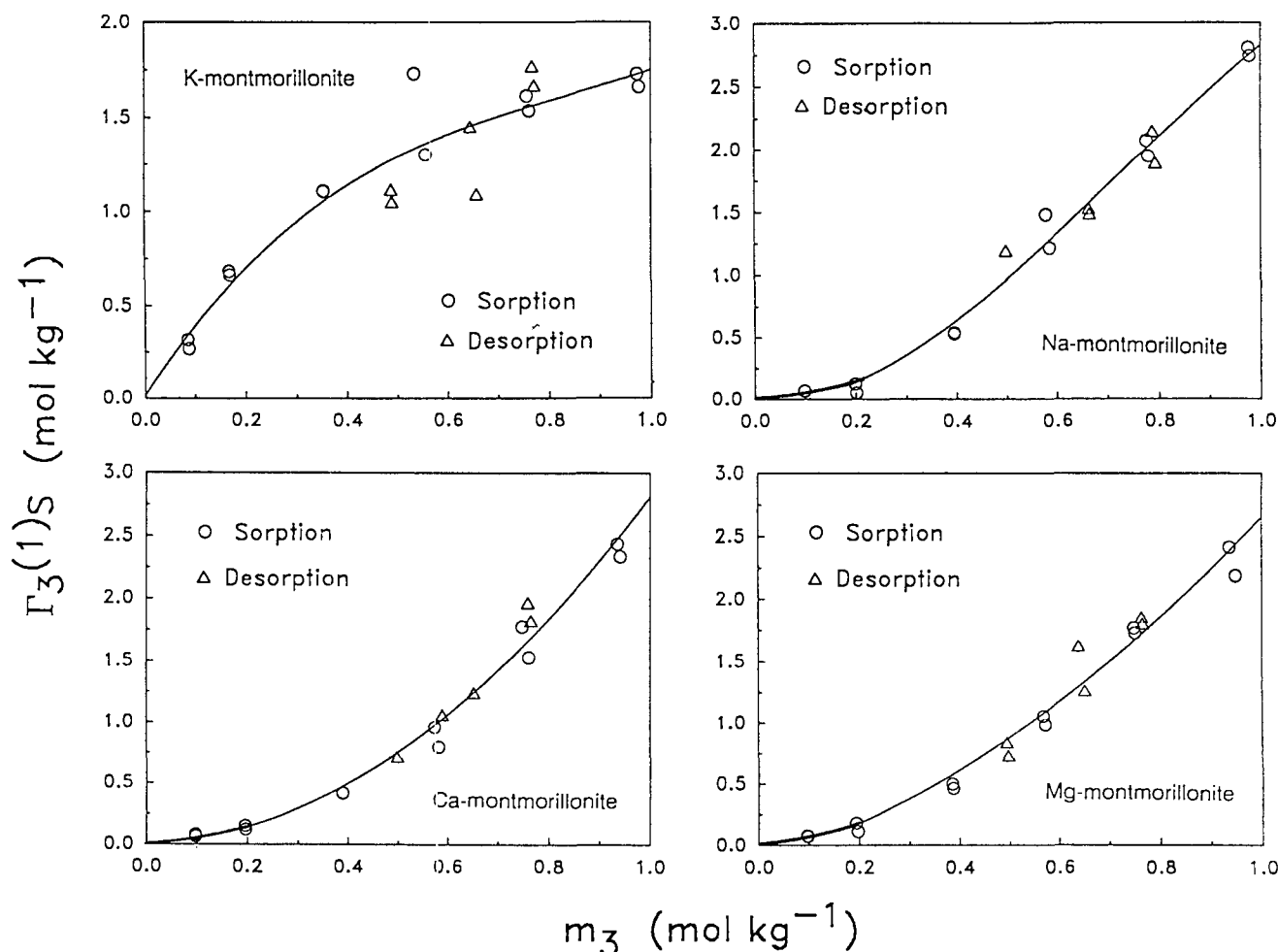


Fig. 1. The relative surface excess of acrylonitrile per unit mass of clay, $\Gamma_3^{(1)}S$, as a function of the equilibrium concentration of acrylonitrile, m_3 , for K, Na, Ca, and Mg montmorillonite from binary solutions.

ugation, was also followed to determine the radioactivity of the reference (no clay added) solutions.

It was observed that the counting efficiency of all solution samples was the same as indicated by an essentially constant H number (H#), which automatically monitored the degree of quenching of the samples during the scintillation counting measurements. If one assumes that the ^{14}C -labeled acrylonitrile molecules were adsorbed like the natural acrylonitrile molecules, then

$$\frac{C_3}{C_3^i} = \frac{\text{cpm of the equilibrium solution}}{\text{cpm of the reference solution}} \quad [8]$$

Since C_3^i is known, C_3 can be determined through scintillation counting measurements. Thus, values of C_3^i and C_3 were converted into m_3^i and m_3 according to Eq. [6], and the value of M_w was determined using Eq. [7]. Finally, the value of $\Gamma_3^i S$ was determined using Eq. [4].

To determine the values of $\Gamma_2^i S$ and $\Gamma_3^i S$ for the sorption of acetonitrile and acrylonitrile from ternary solutions, a series of solutions of acetonitrile with C_2^i ranging from 0.1 to 1.0 M and containing a constant background of acrylonitrile at $C_3^i = 0.5 M$ were prepared and divided into two subseries. The ^{14}C -labeled acetonitrile and acrylonitrile were added, each to one of the two subseries. The values of $\Gamma_2^i S$ and $\Gamma_3^i S$ from the two subseries of solutions were determined as before.

Similarly, a second series of solutions of acrylonitrile with C_3^i ranging from 0.1 to 1.0 M and containing a constant background of acetonitrile at $C_2^i = 0.5 M$ were prepared and divided into two subseries. The values of $\Gamma_2^i S$ and $\Gamma_3^i S$ from the two subseries of solutions were also determined.

Spectroscopic Studies

The infrared (IR) spectra of aqueous acrylonitrile solutions and montmorillonite samples in equilibrium with the same solutions were recorded on a Nicolet 650 XB FTIR spectrometer (Nicolet Instruments, Madison, WI). Infrared spectra of the acrylonitrile solutions were obtained with a fixed spacer (0.0006 cm) between two AgBr IR windows (diam. = 2.54 cm). Infrared spectra of montmorillonite samples in equilibrium with the same acrylonitrile solutions were obtained using the following procedure. Montmorillonite films were prepared by pipetting 0.5-mL aliquots of a 2% clay suspension onto IR windows and air drying. Then, the clay-covered IR windows were immersed in the acrylonitrile solutions for 24 h. After removing the excess solution from the clay film using dry tissue and covering it with a second IR window, the IR spectra of the samples were recorded.

X-ray Diffraction Studies

The effects of acrylonitrile concentration in the aqueous solutions on the c-axis spacings of the homoionic montmorillonites were determined using x-ray diffraction. Montmorillonite films were prepared by pipetting clay suspensions on glass slides. After air drying, the clay-covered slides were immersed in acrylonitrile solutions for 24 h. Each of the slides with excess solution on the clay film was transferred to the sample chamber of a Phillips PW 1729 diffractometer (Phillips Electronic Instruments, Mahwah, NJ) and x-ray diffraction measurements were made. The c-axis spacing was determined from the position of the peak maximum by means of Bragg's law.

RESULTS AND DISCUSSION

Sorption and Desorption of Acrylonitrile from Binary Solutions

The values of $\Gamma_3^i S$ for acrylonitrile sorption and desorption on homoionic K, Na, Ca, and Mg mont-

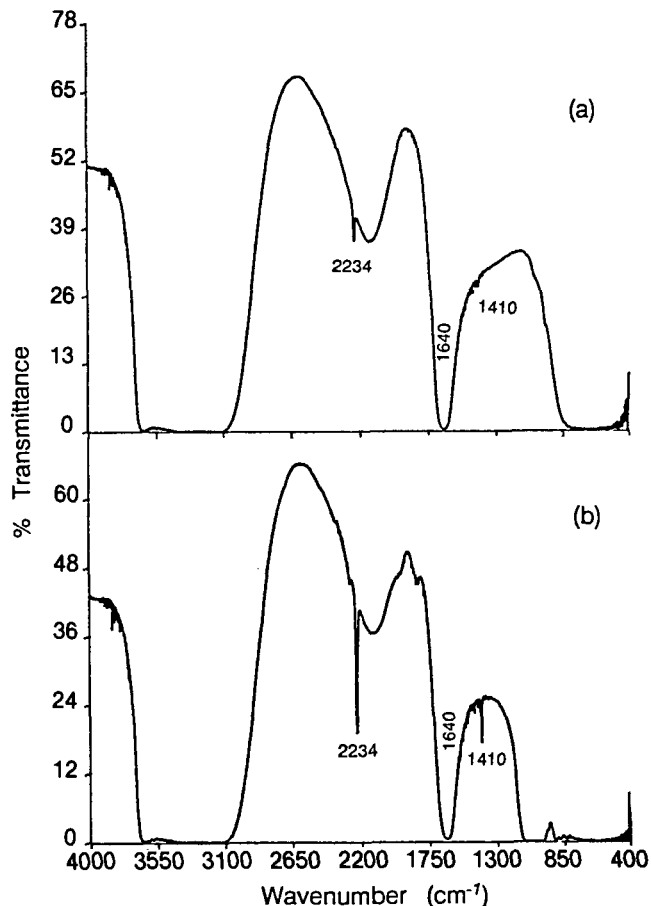


Fig. 2. The infrared spectra of acrylonitrile as affected by K montmorillonite: (a) the infrared spectrum of a 0.8 M acrylonitrile solution; (b) the infrared spectrum of a K montmorillonite sample in equilibrium with a 0.8 M acrylonitrile solution.

morillonite from binary aqueous solutions are presented in Fig. 1. From this figure, it can be seen that the sorption and desorption of acrylonitrile on the four homoionic montmorillonites studied were essentially reversible, i.e., no hysteresis appeared to exist, and that, except for K montmorillonite, or was Type III according to the classification of Brunauer et al. (1940).

Infrared spectroscopy can be used to provide information on the adsorption mechanism, since the formation of any bond would perturb the functional groups of adsorbed molecules and thereby alter their IR spectra. The IR spectra of ketones adsorbed on Ca montmorillonite were investigated by Tensmeyer et al. (1960) and Hoffmann and Brindley (1961). They observed that the carbonyl stretching frequency was displaced from 1720 cm^{-1} in solution to 1690 cm^{-1} for the adsorbed state. In another study, Porubcan et al. (1979) reported the carbonyl stretching frequency shifted from 1745 cm^{-1} to 1715 cm^{-1} for the adsorption of digoxin on montmorillonite. Since the intermolecular forces involved in the adsorbed state were similar in nature to those in the solution, the authors attributed the shift in frequency to H bonding and ion-dipole interactions.

The IR spectra of a 0.8 M acrylonitrile solution and a K montmorillonite sample in equilibrium with the same solution are shown in Fig. 2a and 2b, respec-

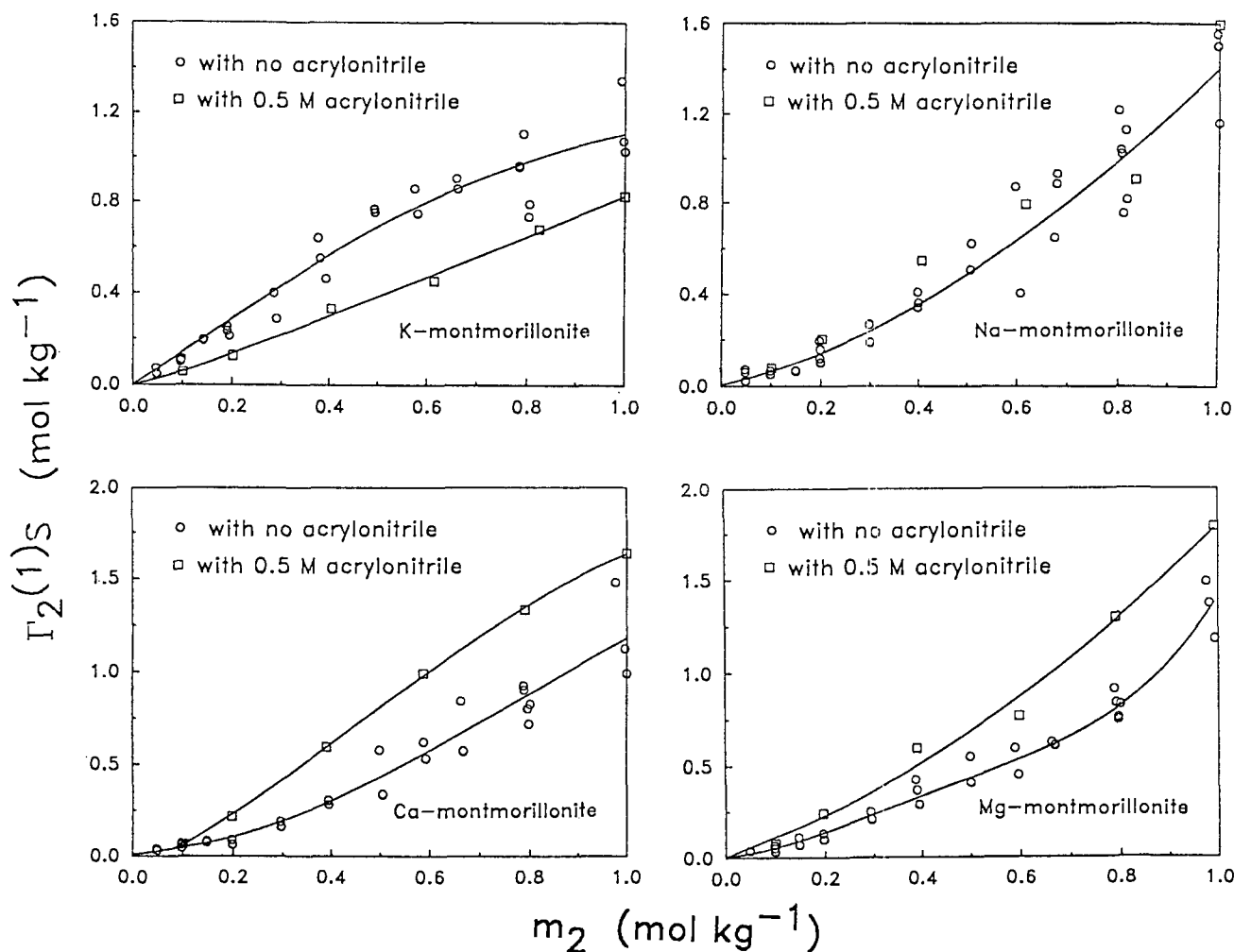


Fig. 3. The relative surface excess of acetonitrile per unit mass of clay, Γ_2^1S , as a function of the equilibrium concentration of acetonitrile, m_2 , for K, Na, Ca, and Mg montmorillonite from binary solutions and ternary solutions with 0.5 M acrylonitrile.

tively. The sorption or accumulation of acrylonitrile on the surfaces of montmorillonite is clearly seen from the increase in the intensity of the $C\equiv N$ band of acrylonitrile at 2234 cm^{-1} and that of the $C-H$ band at 1410 cm^{-1} . The wavenumbers of the $C\equiv N$ and $C-H$ bands, however, remain unchanged. As noted earlier, any bond formation would perturb the molecules and thereby alter their IR spectra. The fact that no shift occurs in wavenumber for the $C\equiv N$ band suggests the absence of ion-dipole interaction between the exchangeable K and nitrile group. Similarly, the fact that no shift occurs in wavenumber for the $C-H$ band indicates the $C-H$ group is not H bonded to the surface O. Additional IR spectroscopic data for the homoionic K and Ca montmorillonite also showed that the wavenumbers of the $C\equiv N$ and $C-H$ bands did not shift when acrylonitrile molecules were adsorbed on the clay surfaces. These data and sorption-isotherm data, which will be discussed later, clearly showed that the sorption of acrylonitrile on the surfaces of montmorillonite involved the same mechanism as the sorption of acetonitrile (Zhang et al., 1990b). Therefore, we have come to the conclusion that sorption of acrylonitrile on montmorillonite is not due to any specific bonding between the organic molecules and the clay surfaces, but rather to a distribution or partition be-

tween the interfacial phase and the bulk-solution phase.

The existence of acrylonitrile, like acetonitrile (Zhang et al., 1990b), also affected the swelling of different homoionic montmorillonites in a rather unusual manner. When the concentration of acrylonitrile in the solution was above 0.5 M, the layers of K montmorillonite did not expand as they would in pure water, but remained partially collapsed with a c-axis spacing of 1.26 nm. The layers of Ca and Mg montmorillonite, on the other hand, did not remain partially collapsed with a c-axis spacing of 1.92 nm as they would in pure water, but expanded beyond this partially collapsed state. The layers of Na montmorillonite were essentially not affected by the acrylonitrile. Based on the consideration of molecular size alone, it can be inferred that there is only one layer of acetonitrile and acrylonitrile between the K montmorillonite layers when the layers are collapsed.

By comparing the sorption data for acrylonitrile in Fig. 1 with the data for acetonitrile (Fig. 3), it is clear that the shape of the isotherm for the sorption of acrylonitrile is identical to that of acetonitrile for each of the four homoionic montmorillonites studied. It should be noted that the magnitude of Γ_2^1S is larger than that of Γ_2^0S throughout the entire concentration

range for each of the four homoionic montmorillonites. Since acrylonitrile has one more C unit than acetonitrile, it is more hydrophobic (or less hydrophilic) than acetonitrile. This is evidenced by the fact that, at room temperature, acetonitrile is completely miscible with water, while acrylonitrile has a solubility of $\sim 1.35 M$. The preference of acrylonitrile over acetonitrile, which is in agreement with the results of Hoffmann and Brindley (1960) showing that sorption increases as the chain length of the organic molecules increases, appeared to suggest that sorption of organic molecules on clay surfaces is related to the hydrophobic interaction between the organic molecules and the clay surfaces in the interfacial phase.

Generally, a partitioning mechanism would yield a linear isotherm. The analysis of Zhang et al. (1990b) showed that the necessary conditions for a linear isotherm are that both the partitioning coefficient and the volume of the interfacial phase must be constant over the entire concentration range of the isotherm. It is conceivable that, as more organic molecules accumulate at the interface, the nature and properties of the interfacial phase would change accordingly, i.e., the interfacial phase would become more hydrophobic (or less hydrophilic). Therefore, the partition coefficient will increase in favor of the interfacial phase as

more organic molecules are adsorbed. It follows naturally that one would expect a Type III isotherm for the sorption from binary solutions and an enhanced sorption from ternary solutions provided the clay layers are not collapsed by the organics. Indeed, Type III isotherms were observed for the sorption of acetonitrile and acrylonitrile on Na, Ca, and Mg montmorillonite from binary solutions.

Sorption of Acetonitrile and Acrylonitrile from Ternary Solutions

The values of $\Gamma_3^{(1)}S$ for sorption of acetonitrile on K, Na, Ca, and Mg montmorillonite from a series of ternary solutions containing a constant background of acrylonitrile at $C_3 = 0.5 M$ are presented in Fig. 3. For comparison, the values of $\Gamma_3^{(1)}S$ for the sorption of acetonitrile on the respective homoionic montmorillonites from binary solutions (Zhang et al., 1990b) are also presented in Fig. 3. The values of $\Gamma_3^{(1)}S$ for the sorption of acrylonitrile on K, Na, Ca, and Mg montmorillonite from a series of ternary solutions containing a constant background of acetonitrile with $C_2 = 0.5 M$ and from binary solutions are presented in Fig. 4. It can be easily seen from Fig. 3 and 4 that the existence of a constant background of acrylonitrile (or

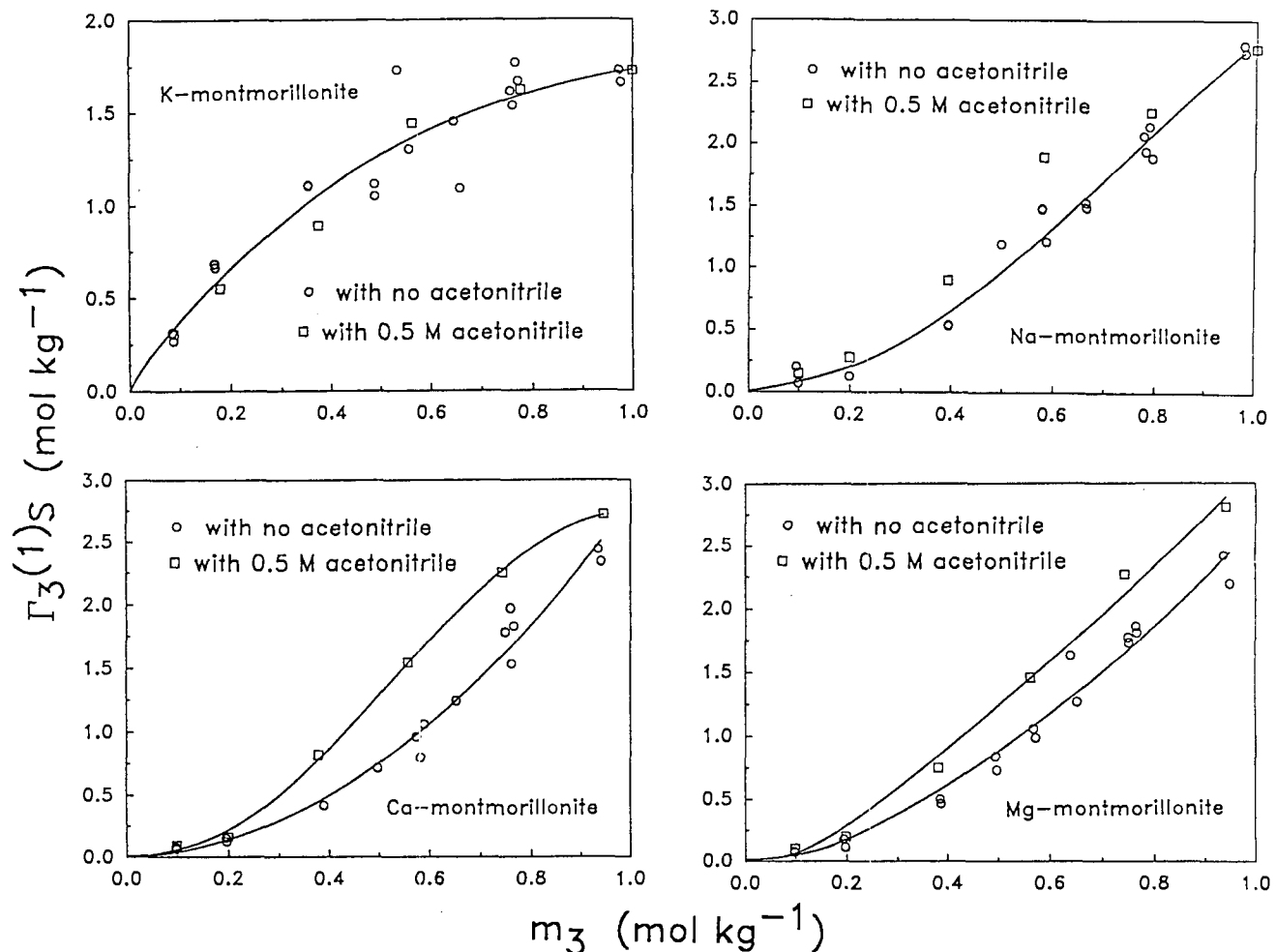


Fig. 4. The relative surface excess of acrylonitrile per unit mass of clay, $\Gamma_3^{(1)}S$, as a function of the equilibrium concentration of acrylonitrile, m_3 , for K, Na, Ca, and Mg montmorillonite from binary solutions and ternary solutions with 0.5 M acetonitrile.

acetonitrile) at 0.5 M reduced the sorption of acetonitrile (or acrylonitrile) on K montmorillonite, slightly enhanced the sorption on Na montmorillonite, and considerably increased the sorption on Ca and Mg montmorillonite. These observations show that, under the above conditions, the sorption of acetonitrile and acrylonitrile from ternary solutions was competitive on K montmorillonite but enhanced on Na, Ca, and Mg montmorillonite.

The effect of acetonitrile (or acrylonitrile) on the sorption of acrylonitrile (or acetonitrile) can also be seen by examining sorption of the latter from a constant background while varying the concentrations of the former. The values of $\Gamma_3^{(1)S}$ for sorption of acrylonitrile on K, Na, Ca, and Mg montmorillonite at a constant concentration of $C_3 = 0.5 M$ are presented in Fig. 5. Similarly, the values of $\Gamma_2^{(1)S}$ for sorption of acetonitrile on K, Na, Ca, and Mg montmorillonite at a constant concentration of $C_2 = 0.5 M$ are presented in Fig. 6. From Fig. 5 and 6 it can be seen that, as the concentration of acetonitrile (or acrylonitrile) increased, the sorption of acrylonitrile (or acetonitrile) on Na, Ca, and Mg montmorillonite from the respective ternary solutions first decreased to a minimum and then increased. This indicates that the sorption of acetonitrile and acrylonitrile on Na, Ca, and Mg mont-

morillonite is slightly competitive at lower concentrations, but noncompetitive at higher concentrations. The preference of acrylonitrile over acetonitrile can be seen from the fact that sorption of acetonitrile on K montmorillonite was effectively decreased with the increase in the concentration of acrylonitrile, while the sorption of acrylonitrile was only slightly decreased with the increase in the concentration of acetonitrile. This indicated that acrylonitrile could effectively compete with acetonitrile on K montmorillonite.

The competitive sorption of acetonitrile and acrylonitrile on K montmorillonite from ternary solutions and the noncompetitive sorption on Na, Ca, and Mg montmorillonite at higher concentrations are expected, since the isotherms for the sorption from binary solutions exhibit downward curvature for the former and upward curvature for the latter. The downward curvature is probably associated with the decrease in the interfacial volume, as the layers of K montmorillonite were collapsed to a c-axis spacing of 1.26 nm at higher concentrations, while upward curvature was caused by an increase in the partition coefficients as more organic molecules entered the interfacial phase. These results provide further evidence for the conclusion reached earlier. The slightly competitive sorption on Na, Ca, and Mg montmorillonite at lower concen-

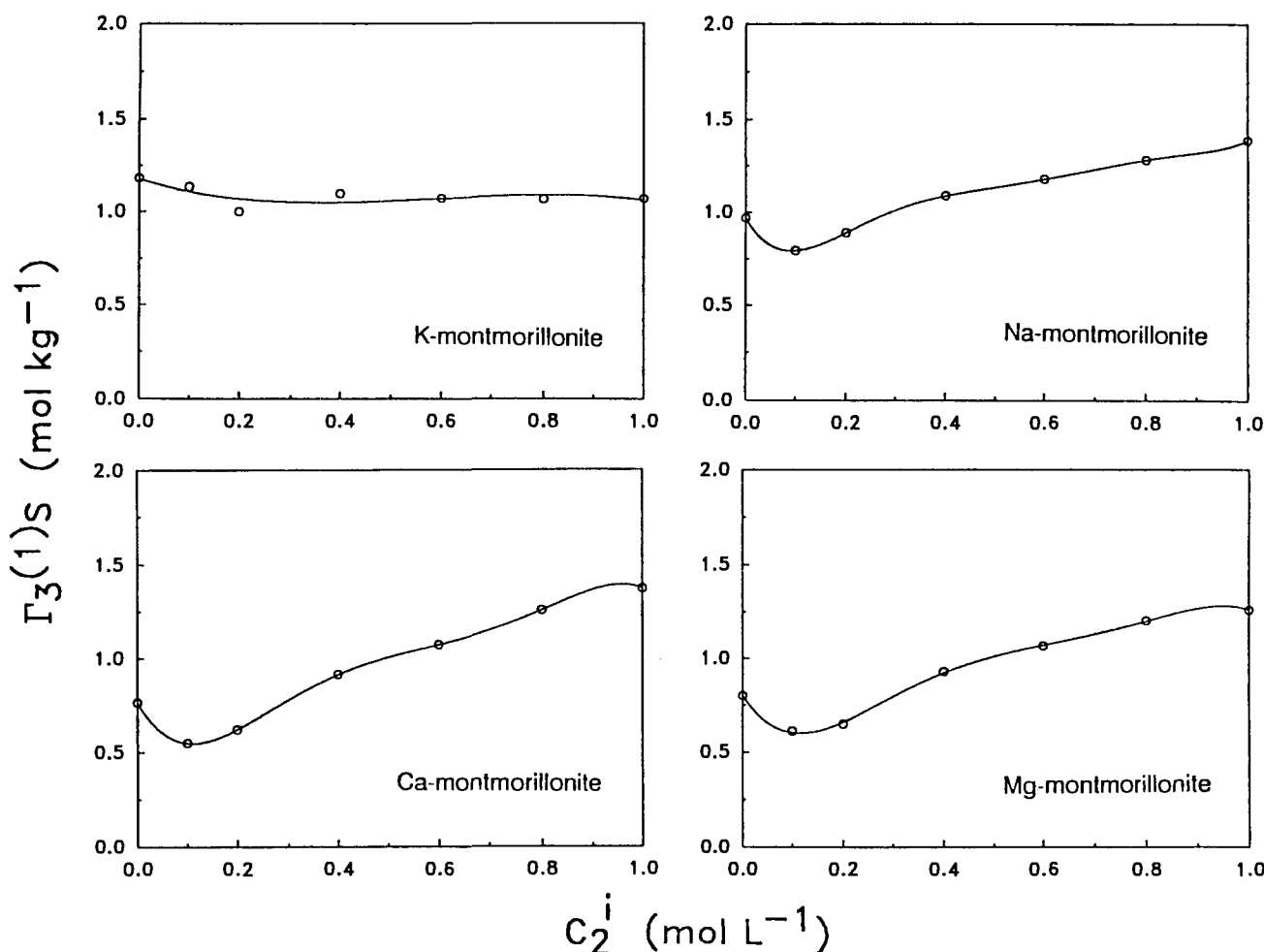


Fig. 5. The relative surface excess of acrylonitrile per unit mass of clay, $\Gamma_3^{(1)S}$, as affected by the initial concentration of acetonitrile, C_2 , for K, Na, Ca, and Mg montmorillonite from ternary solutions containing 0.5 M acrylonitrile.

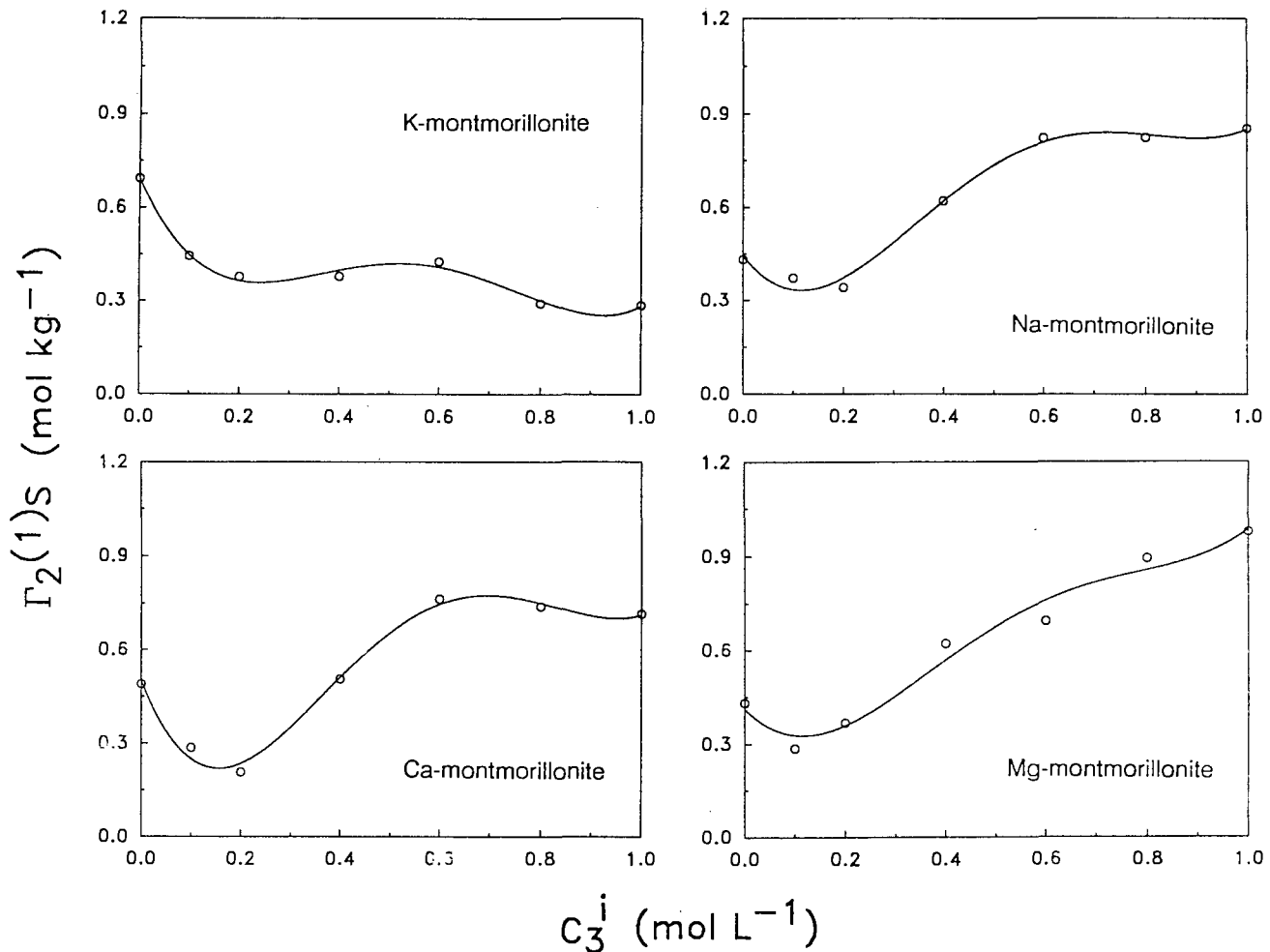


Fig. 6. The relative surface excess of acetonitrile per unit mass of clay, $\Gamma_2^i S$, as affected by the initial concentration of acrylonitrile, C_3^i , for K, Na, Ca, and Mg montmorillonite from ternary solutions containing 0.5 M acetonitrile.

trations, however, appears to suggest that acetonitrile and acrylonitrile molecules compete for the limited sites available on the clay surfaces in the initial stage of sorption. If this is correct, a mechanism other than partitioning may be involved in the initial stage of sorption, even though the IR data suggest that such a distinct mechanism was not involved. These findings merit further investigation, since most of the organic sorption reactions in soil and aqueous environments occur at relatively low concentrations.

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