

Sorption and Desorption of Acetonitrile on Montmorillonite from Aqueous Solutions

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ABSTRACT

The sorption and desorption of acetonitrile on K, Na, Ca, and Mg montmorillonite from aqueous solutions were determined using a ^{14}C isotope tracer method. The heat of sorption of acetonitrile on K, Na, and Ca montmorillonite at two concentrations was determined using a Calvet microcalorimeter. The infrared spectra of the clay-water-organic systems were recorded on a Fourier-transform infrared spectrometer and the c-axis spacings of K, Ca, and Mg montmorillonite in the acetonitrile solutions were determined by x-ray diffraction. It was found that the sorption and desorption of acetonitrile on the four homoionic montmorillonites are reversible, and that the sorption of acetonitrile is exothermic on K and Ca montmorillonite, but endothermic on Na montmorillonite. Further, it was found that the wavenumbers of the $\text{C}\equiv\text{N}$ band and the $\text{C}-\text{H}$ band for the acetonitrile molecules on the clay surfaces do not differ from those in the solution. It was also observed that the sorption of acetonitrile affected the c-axis spacing of the various homoionic montmorillonites differently. These results led to the conclusion that the sorption of acetonitrile on montmorillonite is not due to any specific bonding between the organic molecules and the clay surfaces, but rather to a distribution or partition between the interfacial phase and the bulk-solution phase. Analysis was provided to show that a partition mechanism does not necessarily yield a linear isotherm, especially when the concentration of the organics is high.

THE EFFECT OF ORGANIC POLLUTANTS on our environment is of great concern to scientists as well as to the general public. The contamination of ground-water supplies by trace amounts of organic pollutants has gained considerable attention in recent years, since many organics are toxic and carcinogenic. To alleviate their deleterious effects, to prevent them from further contaminating our environment and to clean up the existing contamination, it is essential to gain a knowledge of the chemical and biological interaction of these organic chemicals with each and every component of our environment.

Although clay-organic interactions have been studied extensively with pure or concentrated organic

chemicals (Bradley, 1945; Mortland, 1970; Theng, 1974), interactions involving aqueous organic solutions have been rarely studied. Sorption of nonionic aliphatic molecules from aqueous solutions on clay minerals has been studied by Hoffmann and Brindley (1960) and Brindley et al. (1963). Although pure ethylene glycol and glycerol are adsorbed on montmorillonite to give well defined c-axis spacings, Hoffmann and Brindley (1961) found that they are not adsorbed preferentially from aqueous solutions. In most cases, the desorption has not been addressed and the mechanisms of sorption remain unknown. The present study employed a mechanistic approach to investigate the sorption and desorption of acetonitrile on homoionic K, Na, Ca, and Mg montmorillonite from aqueous solutions. We chose acetonitrile as the adsorbate because it is a widely used solvent. For example, it is utilized as a recoverable reaction medium for the preparation of pharmaceuticals. Also, since pure acetonitrile does not absorb UV light, it is employed as a solvent in high-pressure liquid chromatography (HPLC).

MATERIALS AND METHODS

Theoretical Considerations

According to chemical thermodynamics, the quantity of a solute adsorbed from a solution must be defined as a surface excess that is invariant to the location of the Gibbs dividing surface (Adamson, 1982; Everett, 1973). The relative surface excess of the solute with respect to the solvent, Γ_2^1 , can be defined as:

$$\Gamma_2^1 = \Gamma_2 - (X_2/X_1)\Gamma_1 \quad [1]$$

in which Γ_1 and Γ_2 are the Gibbs surface excesses of the solvent and solute per unit surface area, and X_1 and X_2 are the mole fractions of the solvent and solute in the equilibrium solution, respectively. It can be shown that, although the values of Γ_1 and Γ_2 depend on the location of the Gibbs dividing surface, the value of Γ_2^1 does not (Adamson, 1982). If we arbitrarily choose the solid-liquid interface as the Gibbs dividing surface, then

$$\Gamma_1 = (n_1 - NX_1)/S \text{ and } \Gamma_2 = (n_2 - NX_2)/S \quad [2]$$

where n_1 and n_2 are the total moles of solvent and solute per unit mass of solid in the system, $N = n_1 + n_2$, and S is the specific surface area of the solid. Equation [1] can be written as

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$$\Gamma^{\langle 1 \rangle} S = n_2 - (X_2/X_1)n_1 \quad [3]$$

where $\Gamma^{\langle 1 \rangle} S$ is the relative surface excess of the solute per unit mass of solid. In the case of an aqueous solution, Eq. [3] can be reduced to (Sposito, 1984)

$$\Gamma^{\langle 1 \rangle} S = n_2 - m_2 M_w \quad [4]$$

where m_2 is the molality of solute in the equilibrium solution and M_w is the total mass of water in the system per unit mass of solid. Since $n_2 = m_2^i M_w$, where m_2^i is the initial molality of the solute before adsorption, Eq. [4] can be written as

$$\Gamma^{\langle 1 \rangle} S = (m_2^i - m_2) M_w \quad [5]$$

This equation provides the theoretical basis for the common method of measuring $\Gamma^{\langle 1 \rangle} S$ through chemical analysis of the aqueous solution phase only (Sposito, 1984).

Two other kinds of surface excesses have been used in the literature. The reduced surface excess, $\Gamma^{\langle 2 \rangle} S$, and the apparent surface excess (or apparent adsorption), $\Gamma^{\langle 3 \rangle} S$, are given as

$$\Gamma^{\langle 2 \rangle} S = (X_2^i - X_2) N \quad [6]$$

and

$$\Gamma^{\langle 3 \rangle} S = (C_2^i - C_2) V \quad [7]$$

where C_2 is the molarity of the solute in the equilibrium solution, N is the total moles and V is the total volume of the solution per unit mass of solid, respectively, and the superscript i again denotes the initial condition. The physical meanings of these surface excesses can be stated as follows (Everett, 1973):

$\Gamma^{\langle 1 \rangle} S$ is the excess, per unit mass of solid, of the solute in the system, over the amount of the solute in a reference system containing the same amount of water, M_w , and in which a constant concentration, equal to the equilibrium concentration of the solute in the real system, m_2 , is maintained throughout the liquid phase.

$\Gamma^{\langle 2 \rangle} S$ is the excess, per unit mass of solid, of the solute in the system, over the amount of the solute in a reference system containing the same total moles of solution, N , and in which a constant concentration, equal to the equilibrium concentration of the solute in the real system, X_2 , is maintained throughout the liquid phase.

$\Gamma^{\langle 3 \rangle} S$ is the excess, per unit mass of solid, of the solute in the system, over the amount of the solute in a reference system containing the same volume of solution, V , and in which a constant concentration, equal to the equilibrium concentration of the solute in the real system, C_2 , is maintained throughout the liquid phase.

It is evident that the difference between the three surface excesses lies in the difference in the amounts of the reference systems. For example, if one keeps the same volume of the solution after changing the concentration from C_2^i to C_2 , the total moles of the solution will be changed, unless the partial molar volumes of the solvent and solute are identical. For a dilute solution (e.g., $C_2 < 0.01 M$), the difference between the amounts of the reference systems is negligible. Hence,

$$\Gamma^{\langle 1 \rangle} S \approx \Gamma^{\langle 2 \rangle} S \approx \Gamma^{\langle 3 \rangle} S \quad [8]$$

It should be indicated that Eq. [8] is valid only for dilute solutions. When the concentration is not dilute, one must distinguish these different excess quantities. Everett (1973) suggested that $\Gamma^{\langle 3 \rangle} S$ be used only for ideal dilute solutions.

Experimentally, $\Gamma^{\langle 3 \rangle} S$ is most easily determined and has often been reported in the literature, because of the operational simplicity of molarity concentration in volumetric chemical analysis. Thermodynamically, however, $\Gamma^{\langle 1 \rangle} S$ is intrinsically more fundamental, due to the significance of the Gibbs adsorption equation (Adam, 1941; Guggenheim,

1949; Adamson, 1982). Therefore, we suggest that $\Gamma^{\langle 1 \rangle} S$ be used as a measure of the sorption, unless one is working at extremely low concentrations. Nunn and Everett (1983) proposed the concentration null method to determine $\Gamma^{\langle 1 \rangle} S$. In a later section, we will outline the procedure for determining $\Gamma^{\langle 1 \rangle} S$ using ordinary volumetric chemical analysis.

Experimental Procedures

The acetonitrile was obtained from J.T. Baker Chemical Co. and the ^{14}C -labeled acetonitrile from Sigma Chemical Co. They were used without further purification. Wyoming montmorillonite, SWy-1, obtained from the Source Clays Repository of the Clay Minerals Society located at the University of Missouri was used in the present study. Homoionic K, Na, Ca, and Mg montmorillonite were prepared using the following treatments:

1. One hundred grams of clay were placed in 4 L of deionized water overnight and the clay suspension containing the $< 2 \mu\text{m}$ fraction was separated by centrifugation.
2. Enough of a given Cl salt was added to the clay suspension to reach the following concentrations: 1.5 M for NaCl and KCl, 0.5 M for CaCl_2 and MgCl_2 .
3. To remove the trace amount of CaCO_3 in the clay sample, 180 mL of 0.05 M HCl solution was added (determined by titration of the clay sample from original pH 9 to pH 7), and the suspension was heated in a water bath to 333 K for 2 h to speed up the reaction. Thereafter, the suspension was centrifuged and the supernatant liquid was decanted.
4. A solution of the given Cl salt (1.5 M for 1:1 salts, 0.5 M for 2:1 salts) was added to the clay samples, mixed, the samples were centrifuged, and the supernatant liquid was decanted.
5. The processes of mixing the clay samples with the given Cl-salt solution, centrifugation, and decantation were repeated two more times.
6. To remove the excess salt, the samples were dialyzed in deionized water. The water was changed every 24 h and the dialysis process was terminated when a conductivity test showed that the concentration of salt in the water was less than $10^{-4} M$. Thereafter, the samples were freeze-dried.

Determination of Relative Surface Excess

A series of acetonitrile solutions with concentrations 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 acetonitrile to each of the acetonitrile solutions in the series to yield a specific activity of $\sim 420 \text{ Bq mL}^{-1}$ ($\sim 20,000 \text{ counts min}^{-1} \text{ mL}^{-1}$, assuming a counting efficiency of 80%).

The procedures used to determine the sorption and desorption of acetonitrile on montmorillonite are outlined in Fig. 1. The desorption study was conducted on the clay samples initially equilibrated with the 1.0 M acetonitrile solution, i.e., 2.0, 5.0, and 10.0 mL deionized water were added to these clay samples to yield initial concentrations of 5/6, 2/3, and 1/2 M, respectively.

If we assume that the ^{14}C -labeled acetonitrile molecules were adsorbed like the natural acetonitrile molecules, then

$$\frac{C_2}{C_2^i} = \frac{\text{counts min}^{-1} \text{ of the equilibrium solution}}{\text{counts min}^{-1} \text{ of the reference solution}} \quad [9]$$

where C_2^i and C_2 are the molarities of the acetonitrile in the initial and equilibrium solutions, respectively. Since C_2^i is known, C_2 can be determined through scintillation counting measurements.

It can be shown that, under the condition of constant tem-

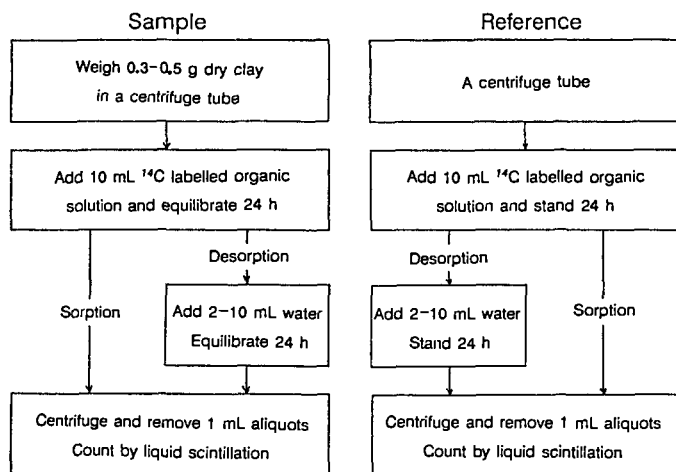


Fig. 1. A diagram illustrating the procedures used in determining the sorption and desorption of acetonitrile on montmorillonite from aqueous solutions.

perature, the molality, m_2 , and the molarity, C_2 , are related by

$$m_2 = 1000C_2 / (1000\rho - C_2M_2) \quad [10]$$

where ρ (g mL^{-1}) is the density of the solution and M_2 is the molecular weight of the solute.

To determine ρ as a function of C_2 , we first measured the masses of deionized water in a series of 100-mL volumetric flasks at 298 K. Since the density of water is known, the accurate volumes of these flasks were determined. Then the masses of a series of acetonitrile solutions with concentrations ranging from 0.05 to 1.0 M were measured at 298 K. These allowed us to determine the relationship between ρ and C_2 . Therefore, values of C_2 can be converted into values of m_2 according to Eq. [10]. The value of M_w at a given C_2 is given by

$$M_w = \frac{V(1000\rho - C_2M_2)}{1000} \quad [11]$$

Finally, values of $\Gamma_2^{(1)S}$ can be determined using Eq. [5].

Heat of Sorption Measurements

The heats of immersion of dry clays in pure solvent (water) and in acetonitrile solutions were measured in a Calvet differential microcalorimeter of the Tian-Calvet type using the method described by Oliphant and Low (1982). According to Crisp (1956), the heat of sorption, Q , is given by

$$Q = \frac{Q_2 - Q_1}{\Gamma_2^{(1)S}} \quad [12]$$

where Q_1 and Q_2 are the heats of immersion per unit mass of clay in the pure solvent (water) and in the acetonitrile solution at a given concentration, respectively.

Infrared Spectra Determinations

Montmorillonite films were prepared by pipetting 0.5-mL aliquots of a 2% clay suspension onto AgBr infrared (IR) windows (diam. = 2.54 cm) and air drying. Then, the clay-covered IR windows were immersed in acetonitrile 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 on a Nicolet 650 XB FTIR spectrometer (Nicolet Instruments, Madison, WI). Infrared spectra of the acetonitrile solutions were obtained with a fixed spacer (0.0006 cm) between the

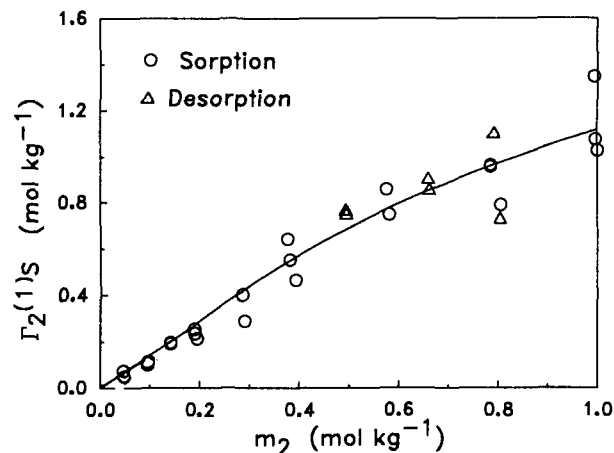


Fig. 2. The relative surface excess of acetonitrile per unit mass of clay, $\Gamma_2^{(1)S}$, as a function of the equilibrium concentration of acetonitrile, m_2 , for K montmorillonite.

two IR windows. It should be noted that this method cannot be used to obtain the IR spectra of clay samples with fully expanded layers in the acetonitrile solution, i.e., Ca montmorillonite at relatively high concentrations, K montmorillonite at relatively low concentrations, and Na montmorillonite. For these clay samples, the attenuated total reflection technique was used (Fahrenfort, 1961). Clay-paste samples were prepared by mixing an acetonitrile solution with dry clays at a mass ratio of 2:1. The samples were allowed to equilibrate for 24 h in sealed weighing bottles before the IR spectra were recorded.

X-Ray Diffraction Analysis

Montmorillonite films were prepared by pipetting clay suspensions on glass slides. After air drying, the clay-covered slides were immersed in acetonitrile 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. Again, it should be noted that this method cannot be used to determine the c-axis spacings of the clay samples with fully expanded layers.

RESULTS AND DISCUSSION

The values of $\Gamma_2^{(1)S}$ for acetonitrile sorption and desorption on homoionic K, Na, Ca, and Mg montmorillonite from aqueous solutions are presented in Fig. 2 to 5. The fitted lines in these figures are polynomial approximations of the data and were obtained using least-squares regression analyses. These data indicate that (i) sorption and desorption of acetonitrile on the four homoionic montmorillonites studied are essentially reversible, i.e., no hysteresis appears to exist, (ii) except for K montmorillonite, each of the isotherms has an upward curvature, or is Type III according to the classification of Brunauer et al. (1940), and (iii) K montmorillonite sorbs more acetonitrile than the other three homoionic montmorillonites at low concentrations.

A Type III isotherm was originally observed for gas adsorption when the forces between the adsorbent and the adsorbate are small. Brunauer et al. (1940) concluded that conformity of adsorption data to this type

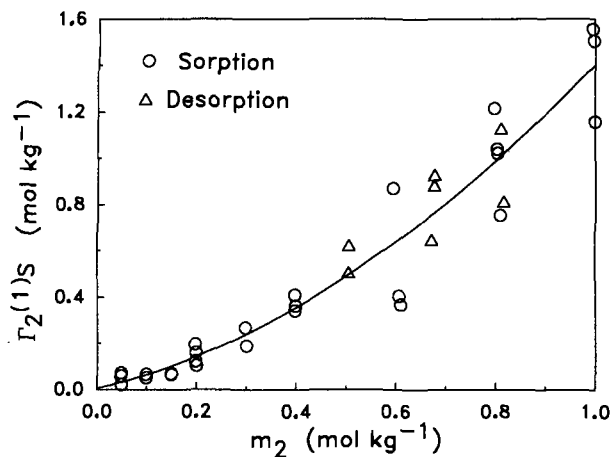


Fig. 3. The relative surface excess of acetonitrile per unit mass of clay, $\Gamma_2(1)S$, as a function of the equilibrium concentration of acetonitrile, m_2 , for Na montmorillonite.

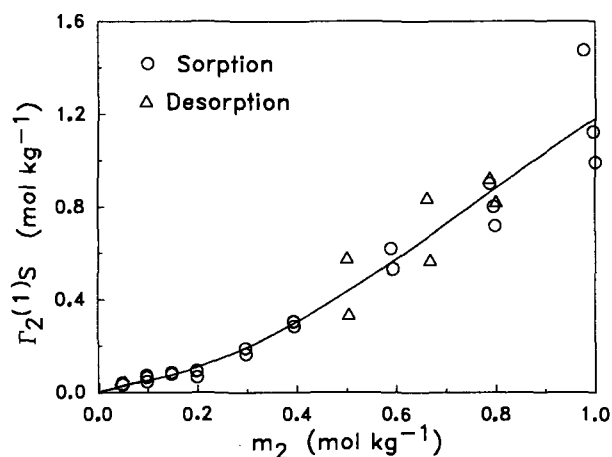


Fig. 4. The relative surface excess of acetonitrile per unit mass of clay, $\Gamma_2(1)S$, as a function of the equilibrium concentration of acetonitrile, m_2 , for Ca montmorillonite.

of isotherm indicated that the forces between adsorbate molecules and the adsorbent are considerably weaker than the forces existing between the adsorbate molecules in the liquid phase. It should be indicated that sorption from aqueous solution is much more complicated than gas adsorption and, consequently, generalizations based simply on the isotherm type alone are certainly not definitive and yield no mechanistic information. The reversibility of the sorption and desorption processes, the small magnitude of the heat of sorption, which will be presented later, along with the type of isotherm all appear to indicate that the sorption of acetonitrile on montmorillonite from aqueous solution involves only weak interactions and essentially is a physical phenomenon.

Zhang et al. (1990) determined the apparent adsorption and heats of adsorption of several neutral organic chemicals on montmorillonite from aqueous solutions. They concluded that the sorption of neutral organic chemicals on the clay is not due to the formation of any specific bonding between the organic molecules and the clay surfaces. Instead, the organic molecules are distributed between the interfacial phase and the bulk solution phase, with the former

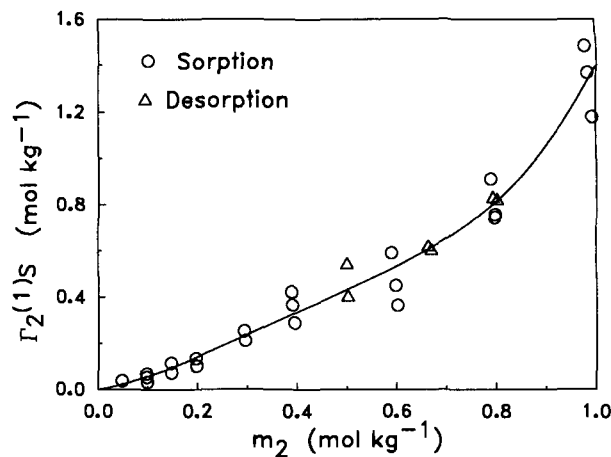


Fig. 5. The relative surface excess of acetonitrile per unit mass of clay, $\Gamma_2(1)S$, as a function of the equilibrium concentration of acetonitrile, m_2 , for Mg montmorillonite.

being preferred. They indicated that a distribution between an interfacial phase and a bulk solution phase would occur if the potential energy of the solute between the two phases was different, i.e.,

$$C_2^i = C_2^b \exp[(\theta_2^i - \theta_2^b)/RT] \quad [13]$$

where C_2^i is the concentration of the solute in the interfacial phase, C_2^b is the concentration of the solute in the bulk phase, and θ_2^i and θ_2^b are the molar potential energies of the solute in the interfacial and bulk phases, respectively. As noted by Zhang et al. (1990), the difference in the potential energies would arise if the organic molecules interact differently with the surrounding water molecules in the two phases.

The partition or distribution of a solute between two immiscible solvents was first formulated by Nernst (Bromberg, 1980), and it has been widely used in laboratories for the removal of a solute from one solvent using a separatory funnel. The partitioning mechanism has been generalized to describe the sorption of organic solutes on soil materials and clay minerals (Greenland et al., 1962; Theng, 1972; Theng and Scharpenseel, 1976; Chiou et al., 1979; Zhang et al., 1990). In general, the partitioning mechanism would predict a linear isotherm. The necessary conditions for a linear isotherm, however, are that both K , the partitioning coefficient between the two phases, and α , the fraction of the total volume that is occupied by the interfacial phase, remain constant throughout the entire concentration range of the isotherm. These facts can be seen by recognizing that

$$K = \exp[(\theta_2^i - \theta_2^b)/RT], \quad [14]$$

replacing this equation in Eq. [13], and then multiplying both sides of the resulting equation by αV . Now we have

$$C_2^i \alpha V = C_2^b K \alpha V. \quad [15]$$

Note that the left-hand side of this equation, to a first approximation, is the amount of solute sorbed in the interfacial phase. Furthermore, it is clear from Eq. [14] that only when $(\theta_2^i - \theta_2^b)$, the potential energy difference between the bulk phase and the interfacial phase, is independent of the concentration of the solute, should K remain constant.

Table 1. Values for heat of sorption, Q , at two concentrations of acetonitrile on homoionic K, Na, and Ca montmorillonite.

Homoionic clay	Q (kJ mol ⁻¹)	
	0.5 M	1.0 M
K montmorillonite	1.730	1.875
Na montmorillonite	-3.977	-3.410
Ca montmorillonite	3.264	2.617

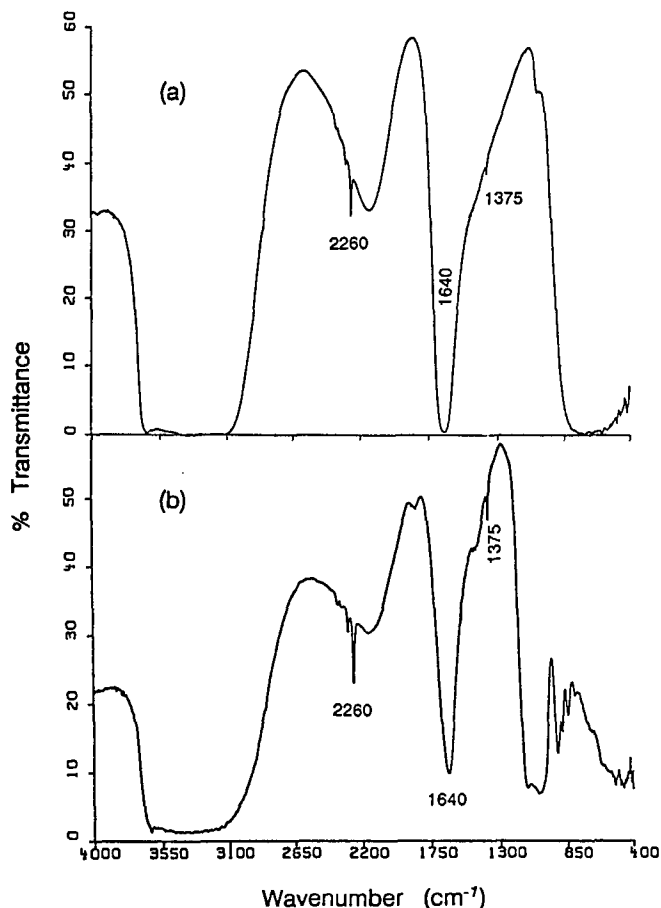
Table 2. The c-axis spacings of homoionic montmorillonites as affected by acetonitrile solution.

Concentration mol L ⁻¹	C-axis spacing (nm)			
	K clay	Na clay	Ca clay	Mg clay
0	Expanded	Expanded	1.92	1.92
0.1	Expanded	Expanded	1.92	1.92
0.2	Expanded	Expanded	1.92	1.92
0.3	Expanded	Expanded	1.92	1.92
0.6	1.23	Expanded	Expanded	Expanded
0.8	1.23	Expanded	Expanded	Expanded
1.0	1.23	Expanded	Expanded	Expanded

It is evident that the accumulation of organic molecules on the interfacial phase in turn affects the nature and properties of the interfacial phase, and thereby ($\theta_2 - \theta_1$) and K . Furthermore, in the clay-organic-water system, α is closely related to the swelling and dispersion status of the clay. Therefore, it is reasonable to conclude that a partitioning mechanism does not necessarily yield a linear isotherm, especially when the concentration of organics is relatively high.

The heat-of-sorption data obtained from calorimetric measurements are presented in Table 1. Attention is called to the fact that Q is positive (exothermic) for the sorption of acetonitrile on K and Ca montmorillonite, but negative (endothermic) for the sorption of acetonitrile on Na montmorillonite. It is well known that heat will be released when bonds are formed in chemical processes. Therefore, the endothermic sorption reaction of acetonitrile on Na montmorillonite strongly indicates the absence of any bond formation between the acetonitrile molecules and the clay surfaces. The same is probably true for the sorption of acetonitrile on the other homoionic montmorillonites but, since Q is positive for these reactions, we cannot be certain. Nevertheless, it should be noted that the magnitude of Q is extremely small (<4.0 kJ mol⁻¹). In this regard, one should note that the magnitude of the heat of H bonding, which is considered to be physical in nature, is about 20.9 kJ mol⁻¹ (Pauling, 1960), while the typical values of heats for chemisorption are in the region of 200 kJ mol⁻¹ (Atkins, 1978). Evidently, the heats of sorption of acetonitrile on montmorillonites are only 10 to 20% of that for H bonding, further indicating that sorption of acetonitrile is a physical phenomenon.

It is well known that thermodynamic measurements are macroscopic in nature and reveal nothing about microscopic processes, such as the formation of bonds at the molecular scale. Spectroscopic measurements, on the other hand, can provide direct information pertaining to microscopic processes. For example, infrared spectroscopy has been widely used to study the structure of molecules and the nature and properties of the bonds involved.

**Fig. 6.** The infrared spectra of acetonitrile as affected by K montmorillonite: (a) the infrared spectrum of a 1 M acetonitrile solution; (b) the infrared spectrum of a K montmorillonite sample in equilibrium with a 1 M acetonitrile solution.

The IR spectra of a 1 M acetonitrile solution and a K montmorillonite sample in equilibrium with the same solution are shown in Fig. 6a and b, respectively. The sorption or accumulation of acetonitrile on the surfaces of montmorillonite is clearly seen from the increases in the intensity of the C≡N band at 2260 cm⁻¹ and that of the C-H band at 1375 cm⁻¹ relative to the intensity of the O-H band at 1640 cm⁻¹. The wavenumbers of the C≡N and C-H bands, however, remain unchanged.

Additional IR spectroscopic data for the homoionic K, Na, and Ca montmorillonite also show that the wavenumbers of the C≡N band and C-H band do not differ between the acetonitrile molecules on the clay surfaces and the molecules in the solution. Since the wavenumbers of the IR bands of molecules are very sensitive to any perturbation on the molecules, the fact that no wavenumber shift occurs for the C≡N and C-H bands between the acrylonitrile molecules on the clay surfaces and in the solution provides direct evidence for the absence of any chemical bonding.

During this sorption study, it was observed that the existence of acetonitrile affected the swelling of different homoionic montmorillonites in a rather unusual manner. As shown by the c-axis spacing data presented in Table 2, when the concentration of acetonitrile in the solution is above 0.5 M, the layers of K

montmorillonite do not expand as they would in pure water, but remain partially collapsed. The layers of Ca and Mg montmorillonite, however, do not remain partially collapsed as they would in pure water, but expand beyond this partially collapsed state, while the layers of Na montmorillonite are essentially not affected by the acetonitrile.

Since clay swelling in the clay-organic-water system is of both theoretical and practical importance, the fundamental difference in the swelling behaviors of the various homoionic montmorillonites in the acetonitrile solution merits additional investigation. At present, the reason why acetonitrile affected the swelling of various homoionic montmorillonites differently is not clear yet. Nevertheless, our results clearly demonstrate that the electric-double-layer theory does not properly describe the swelling of clays, as in agreement with the results of Low (1987). According to electric-double-layer theory (Langmuir, 1938; Bolt, 1955; van Olphen, 1977; Madsen and Muller-Vonmoos, 1985; Singh and Uehara, 1986), the repulsive pressure (or the swelling pressure) is given by the osmotic pressure midway between the adjacent surfaces with respect to that of the equilibrium solution, and should be reduced when acetonitrile is in the solution phase, since it has a lower dielectric constant than water. Therefore, the conclusion one could reach is that the osmotic contribution to swelling may be negligible, and that other repulsive forces are responsible for clay swelling.

As was noted earlier, a partitioning mechanism does not necessarily yield a linear isotherm, especially when the concentration of organics is relatively high. It is conceivable that the structure and properties of the interfacial phase change accordingly, i.e., the hydrophobic nature of the interfacial phase increases, as more organic molecules accumulate at the clay surfaces. It is well known that the greater the similarities in the molecular structures of the solvent and solute, the higher the solubilities. Consequently, the partitioning coefficient will increase in favor of the interfacial phase as more organic molecules accumulate in that phase. A Type III isotherm, then, follows naturally. On the other hand, the downward curvature of the isotherm for K montmorillonite could be attributed to a decrease in the volume fraction of the interfacial phase as the accumulation of acetonitrile molecules collapse the clay layers.

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