Retention of Acetonitrile and Acrylonitrile on Clays

Z.Z. Zhang and D.L. Sparks

Department of Plant and Soil Sciences
University of Delaware
Newark, DE 19717-1303

Introduction

Increasing demand for acrylic fibers has increased the production of acrylonitrile during the last 30 years. Currently, most of the industries employ the Sohio process to produce acrylonitrile. Unavoidably, however, an aqueous solution of hazardous waste containing acrylonitrile, acetonitrile and ammonium sulfate is generated in this process. One of the waste disposal methods used by industry is the deep underground well injection technology. Naturally, there are many concerns about this technology, such as, (1) are the organic wastes adsorbed on the solid particles in the subsurface environment? and (2) how fast do these wastes move? To answer these questions, it is necessary to understand the mechanisms of interactions of clays with organic pollutants. The present study investigated the sorption of acetonitrile and acrylonitrile on different homoionic montmorillonites from binary and ternary aqueous solutions using a ^{14}C tracer method.

Materials and Methods

Homoionic K- and NH_4-montmorillonite were prepared using Wyoming montmorillonite (SWy-1) and Cl salts (Zhang et al., 1990a). The acetonitrile was obtained from J. T. Baker Chemical Company and the acrylonitrile from Aldrich Chemical Company. The ^{14}C labelled acetonitrile and acrylonitrile were obtained from Sigma Chemical Company. They were used without further purification.

Sorption is the process through which a net accumulation of a substance occurs at an interface. To determine the amount of sorption of organics from binary solutions, a series of solutions with concentrations ranging from 100 to 1000 ppm were prepared using deionized water. The ^{14}C labelled solutions were prepared by adding ^{14}C labelled acetonitrile or acrylonitrile to each of the solutions in the respective series to yield a specific activity of -23,000 counts per minute (cpm) mL^{-1}. To determine the amount of sorption of acetonitrile and acrylonitrile on clays from ternary solutions, a series of solutions of acetonitrile with C_2^i ranging from 100 to 1000 ppm and containing a constant background of acrylonitrile at C_3^i = 500 ppm were prepared and divided into two subseries. The ^{14}C labelled acetonitrile and acrylonitrile were added to the two subseries, respectively. The amount of sorption of acetonitrile and acrylonitrile from the two subseries of solutions was determined as before. Similarly, a second series of solutions of acrylonitrile with C_3^i ranging from 100 to 1000 ppm and containing a constant background of acetonitrile at C_2^i = 500 ppm were prepared and divided into two subseries. The amount of sorption of acetonitrile and acrylonitrile from the two subseries of solutions was also determined.

Batch experiments were conducted by adding 0.5 g of each of the homoionic montmorillonites and 10 mL of each of the above ^{14}C labelled acrylonitrile solutions to a glass centrifuge tube. Preliminary sorption studies were conducted using 24, 48, 72, and 96 h equilibration periods. A 24 h time period was found to be long enough to reach sorption equilibrium. Therefore, most of the sorption data were obtained using a 24 h equilibrium period. 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 an error setting at $2\sigma = 0.5\%$. The above procedure, except for centrifugation, was also followed to determine the radioactivity of the reference solutions (no clay added). The counting efficiency of all solution samples was essentially the same, as indicated by an approximately 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 labelled organic molecules were adsorbed like the unlabeled molecules, then

$$\frac{C_2}{C_2^i} = \frac{\text{cpm of the equilibrium solution}}{\text{cpm of the reference solution}}$$

where C_2^i and C_2 are the initial concentration of organics before adsorption and the equilibrium concentration after adsorption, respectively. Since C_2^i is known, C_2 can be determined through scintillation counting measurements. Thus, the amount of sorption can be determined from the difference in the concentrations.

The effect of electrolyte on sorption was examined by investigating acetonitrile and acrylonitrile sorption on NH_4-montmorillonite in a background electrolyte solution containing 0.3 *M* $(NH_4)_2SO_4$. The effect of surfactants on sorption was also studied by measuring the sorption of acrylonitrile on NH_4-montmorillonite in solutions containing different amounts of primary and secondary amines. The added amines were either hydrochloride amine salt or amine with an equivalent amount of HCl. Thus, the amines were cationic and exchanged with ammonium cations on the clay. The amounts of added amines were equivalent to 50% and 100% of the cation exchange capacity (CEC) of the clay.

Results and Discussion

Sorption data for acetonitrile and acrylonitrile on NH_4-montmorillonite from binary and ternary solutions in the concentration range of 0-1000 ppm are presented in Fig. 1 and 2. Similar data were obtained for sorption of the organics on K-montmorillonite. The isotherm is linear or slightly concave in this concentration range and the slopes of the isotherm were ~0.60 and ~1.2 for acetonitrile and acrylonitrile, respectively. The sorption of acetonitrile and acrylonitrile was not competitive since sorption from ternary solutions coincides with that from binary solutions. The effect of acetonitrile on the sorption of acrylonitrile can also be seen by examining sorption of acrylonitrile from ternary solutions with a constant concentration of acrylonitrile and variable concentrations of acetonitrile. Similarly, the effect of acrylonitrile on the sorption of acetonitrile can also be examined. Acetonitrile and acrylonitrile sorption on NH_4-montmorillonite from ternary solutions at a constant concentration of 500 ppm are presented in Fig. 3 and 4. Similar data were also obtained for the sorption on K-montmorillonite. One sees that with increasing acrylonitrile concentration, the sorption of acetonitrile was slightly increased (Fig. 3). However, it appeared that the sorption of acrylonitrile was not affected by acetonitrile (Fig. 4).

The above data indicate that there are not specific sites on the clay surfaces for the sorption of acetonitrile and acrylonitrile, namely, the sorption was not due to any specific bonding between the organic molecules and clay surfaces. Earlier studies on the sorption of acetonitrile and acrylonitrile on clays at a much higher concentration range (0.05 to 1.0 *M*) showed that: the sorption and desorption reactions were reversible, the infrared spectra of the adsorbed molecules were not perturbed, and the heat of sorption was only 10 to 20% of that for H bonding (Zhang et al. 1990a, b). These results indicated that the sorption of acetonitrile and acrylonitrile on clays did not involve any specific chemical bonding. Therefore, the driving forces of sorption must be physical in nature, and they result from solvent-surface, solute-surface interactions at the interfacial phase, and solvent-solvent, solvent-solute, and solute-solute interactions in both the interfacial and solution phases. The interactions at the interface may or may not involve surface forces, for example, there are van der Waals forces between the solute molecules and the surfaces, as well as between the solute molecules themselves. The van der Waals forces increase with the molecular weight of the solute molecules. Sorption of a solute from solution is not always due to a bonding between the solute molecules and the surfaces. This can be clearly seen by considering that although the solvent-solvent and solvent-solute interactions in the solution phase are not related to any direct forces from the surfaces, they are essential components of the driving forces for sorption from solution. If the solvent-solvent interaction is stronger than the solvent-solute interaction, the solute molecules would tend to be pushed out of the solution phase, and accumulation at the interface would occur.

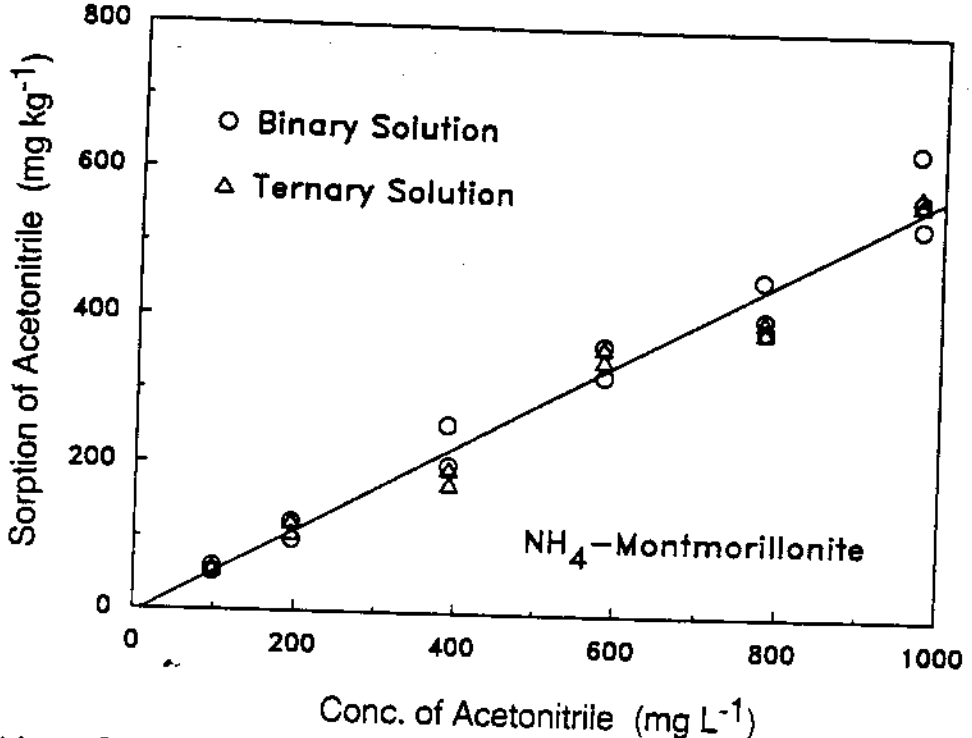

Figure 1. Sorption of acetonitrile per unit mass of clay as a function of the equilibrium concentration of acetonitrile on NH_4-montmorillonite from binary and ternary solutions.

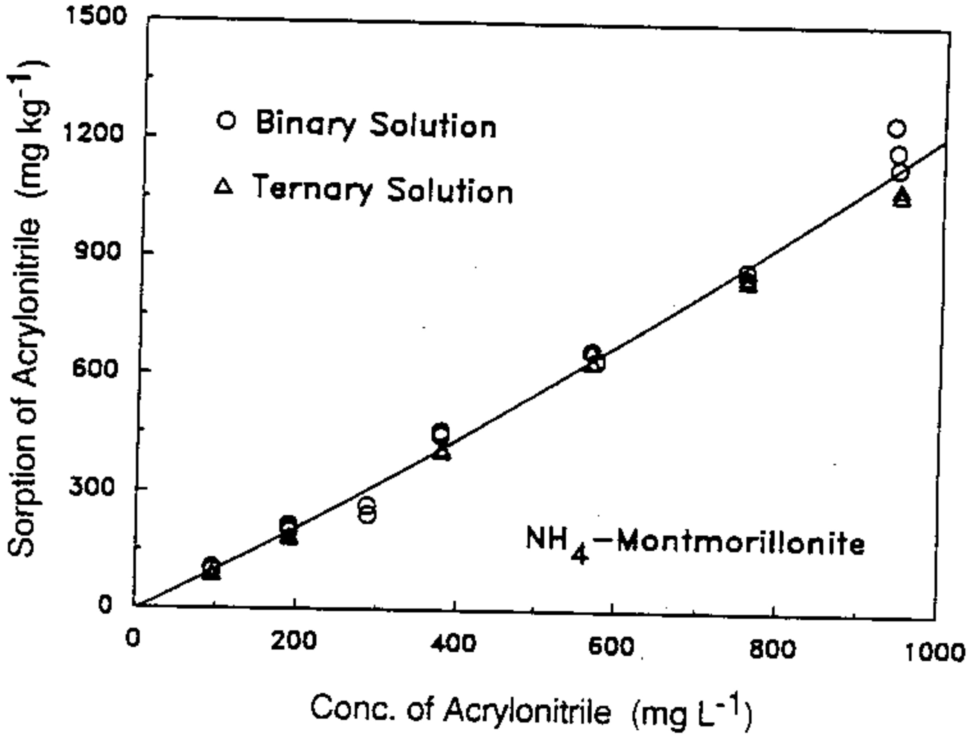

Figure 2. Sorption of acrylonitrile per unit mass of clay as a function of the equilibrium concentration of acrylonitrile on NH_4-montmorillonite from binary and ternary solutions.

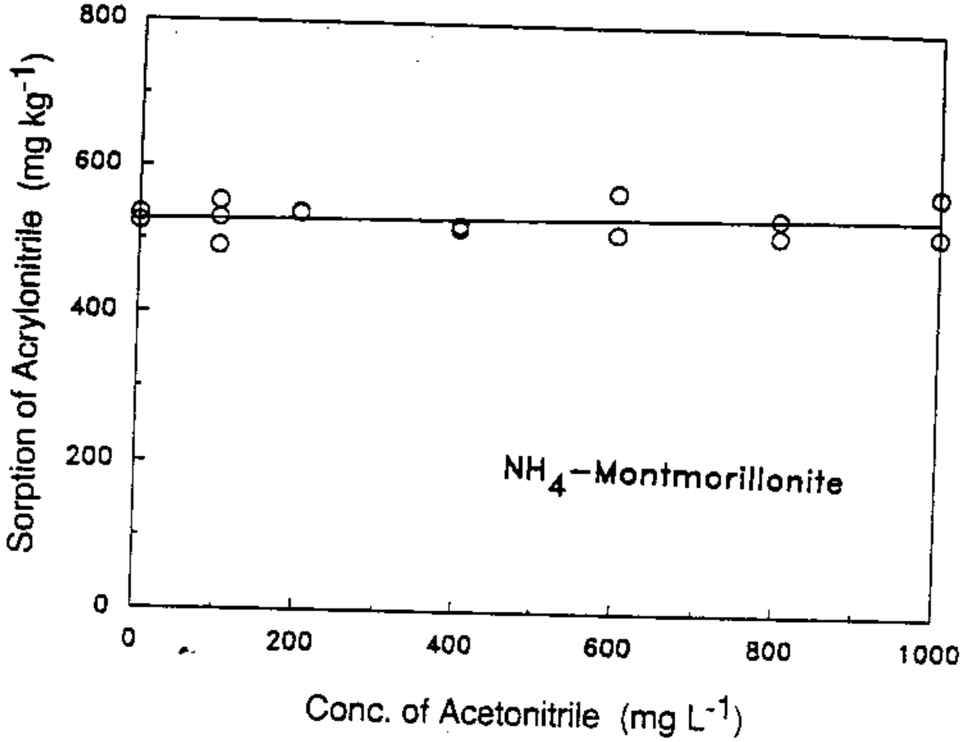

Figure 3. Sorption of acrylonitrile per unit mass of clay as a function of acetonitrile concentration on NH_4-montmorillonite from ternary solutions.

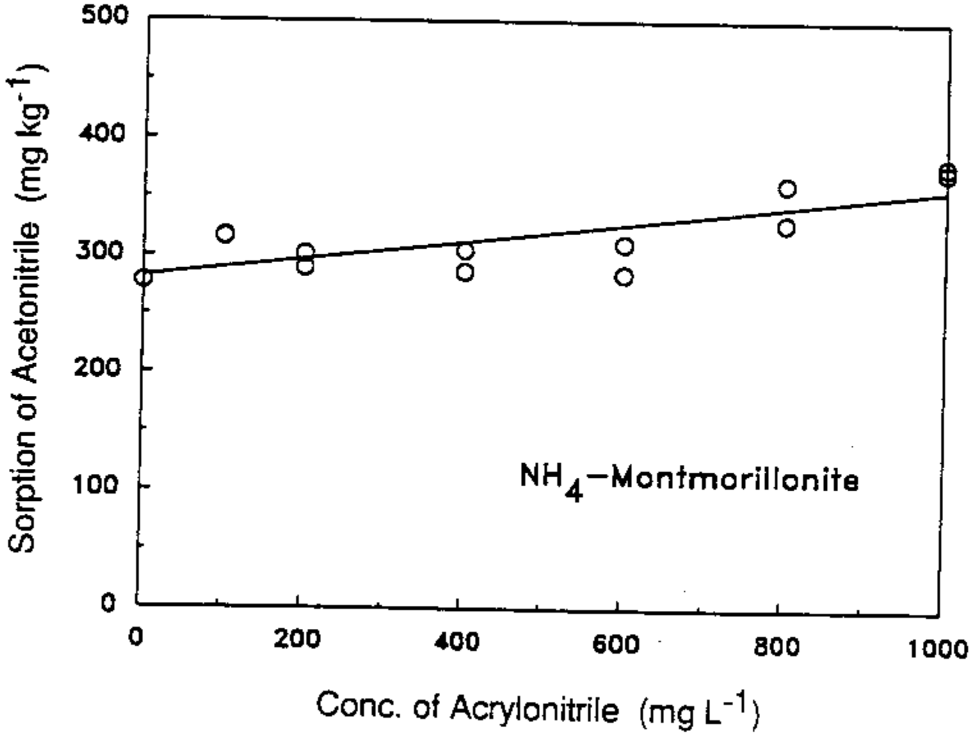

Figure 4. Sorption of acetonitrile per unit mass of clay as a function of acrylonitrile concentration on NH_4-montmorillonite from ternary solutions.

Water exhibits a considerable number of unusual properties when compared with other liquids and these properties exist because of extensive formation of H-bonds between the water molecules (Pauling, 1960). It is generally accepted that liquid water has a ice-like framework with void regions in which the water molecules are less ordered (Eisenberg and Kauzmann, 1969). In the ice-like region, each water molecule is tetrahedrally coordinated to four other water molecules by H-bonds with a rather open structure. In the void region, the water molecules are more densely packed. The introduction of neutral organic molecules into liquid water has a restructuring effect. Generally the entropy of the solution is decreased in this process (Hamaker and Thompson, 1972). Therefore water molecules have a tendency to push out the organic molecules so as to revert to their normal structure. The interaction between water and organic molecules is amplified when a sorbent is present in the system. Because the affinity between water molecules themselves is greater than that between water and organic molecules, the organic molecules tend to be excluded from the bulk liquid phase and to accumulate in the interfacial region. This effect is more pronounced at higher organic concentrations as the adsorbed organic molecules begin to interact with each other (Zhang et al., 1990a, b).

The effect of ammonium sulfate on sorption of acetonitrile and acrylonitrile was examined by determining the sorption on NH_4-montmorillonite in a background electrolyte solution containing 0.3 *M* $(NH_4)_2SO_4$. The results are presented in Fig. 5 and 6. For comparison, the sorption data without the electrolyte background are also presented. It is evident that the existence of an electrolyte background considerably enhanced the sorption of acetonitrile and acrylonitrile (Fig. 5-6). The sorption isotherms were linear or slightly concave when no electrolyte was present, but became much more concave when electrolyte was present.

It is well known that the addition of a salt to an aqueous solution of a given neutral molecule usually decreases its solubility in the solution. This corresponds to an increase in the activity coefficient of the neutral molecule (Harned and Owen, 1950). We have observed that acetonitrile and water are no longer completely miscible when enough electrolyte (unpublished data, $CaCl_2$) is present in the solution. This effect is generally referred to as "salting out", and is mainly caused by electrostatic interactions. Several theories suggest that when the dielectric constant of the medium is lower than that of the solvent, "salting out" should occur (Harned and Owen, 1950). Since the dielectric constants for acetonitrile and acrylonitrile are about half of that for water, one would expect that the activity coefficients of acetonitrile and acrylonitrile in solution would increase with the introduction of an electrolyte. Consequently, sorption of acetonitrile and acrylonitrile were enhanced when ammonium sulfate was present in the solutions.

It is theoretically and practically important to study the effect of temperature on sorption. From a theoretical point of view, the heat of adsorption can be calculated from temperature dependent isotherm data using

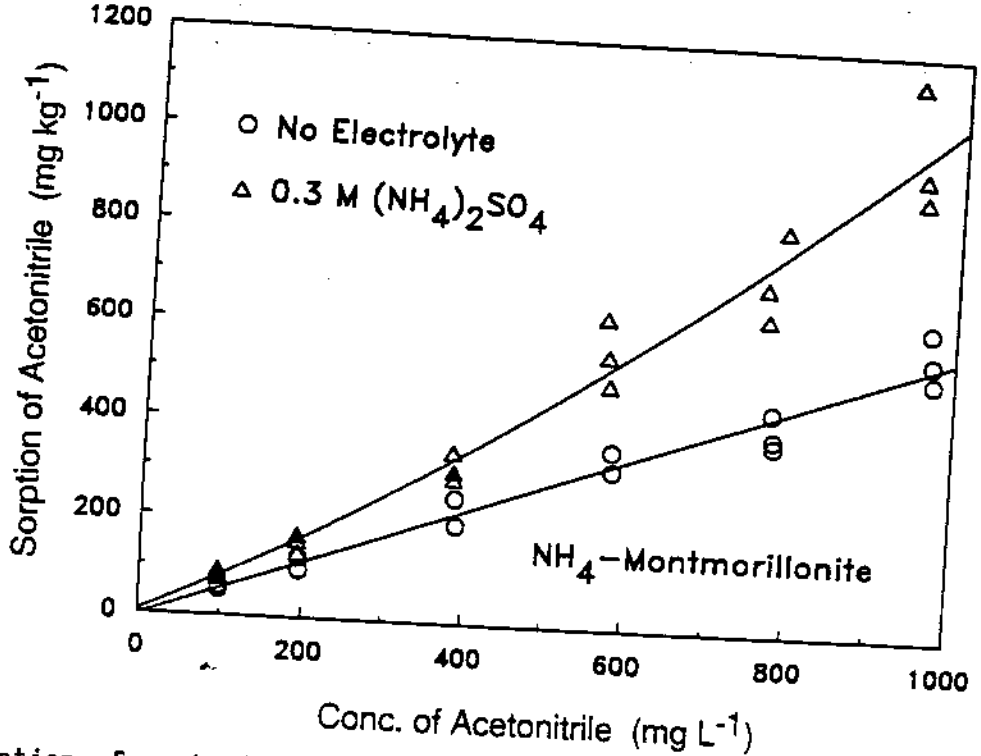

Figure 5. Sorption of acetonitrile per unit mass of clay as a function of the equilibrium concentration of acetonitrile on NH_4-montmorillonite with and without 0.3 M ammonium sulfate.

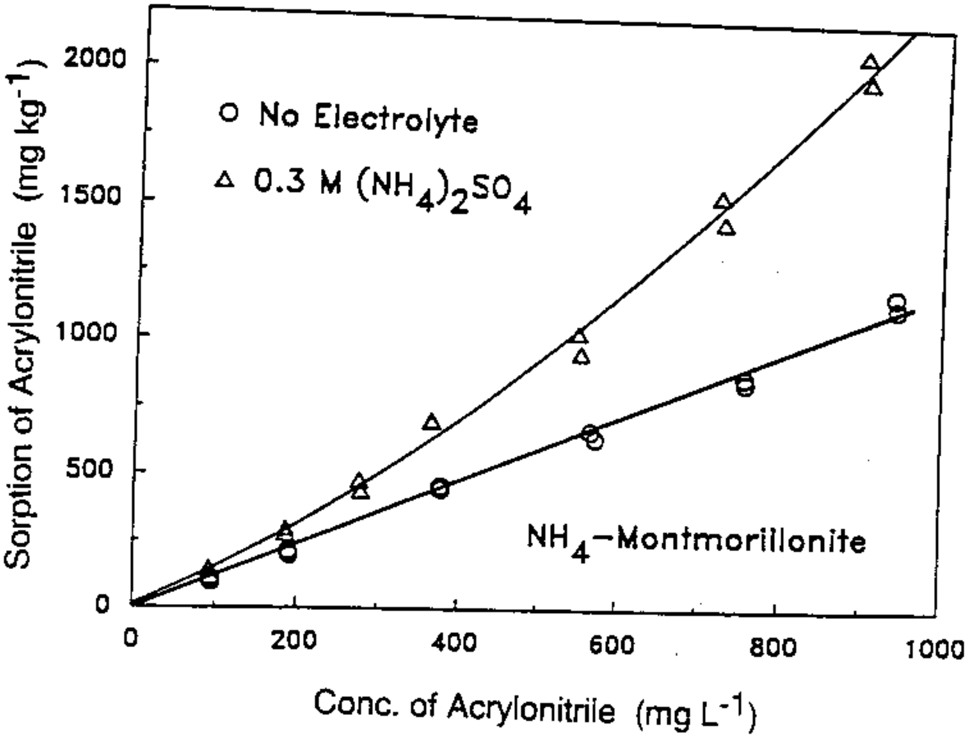

Figure 6. Sorption of acrylonitrile per unit mass of clay as a function of the equilibrium concentration of acrylonitrile on NH_4-montmorillonite with and without 0.3 M ammonium sulfate.

the Clausius-Clapeyron equation. Practically, we know that the temperature of a geological formation increases with depth from the surface. We measured sorption of acetonitrile on different homoionic montmorillonites at two temperatures (5 and 25 °C) and found that the isotherms coincided with one another. The lack of temperature dependence for the sorption reaction indicated that the heat of adsorption was very small. This was further confirmed from direct calorimetric measurements (Zhang et al., 1990a).

More recently, sorption of neutral organic compounds on clays modified by exchanging the naturally occurring metal cations with quaternary amine cations has been widely studied (Boyd et al., 1988; Lee et al., 1989, 1990; Smith et al., 1990; Jaynes and Boyd, 1991). These authors reported that sorption of neutral organic molecules on clays exchanged with quaternary amine cations with small functional groups (e.g., a short alkyl chain, or a benzyl) is essentially a surface reaction. However, sorption on clays exchanged with quaternary amine cations having at least one or more large alkyl groups (with 9 or more carbons) is characterized by a partitioning of the organic compounds between the aqueous solution and the organic media in the interlayer region of the clays.

We have studied the effect of primary and secondary amine cations with relatively short alkyl groups on the sorption of acrylonitrile. Generally, organic cations are preferred over metal cations on clays, and the preference for organic cations increases with their molecular size. Therefore, the added amines should be fairly effective in replacing the ammonium cations on the surfaces. As a result, the hydrophilic nature associated with the hydration of ammonium cations should be diminished, and consequently, the sorption of organic molecules should be enhanced. The results when the amount of added amines was 50% of the CEC are presented in Fig. 7 and 8. Slightly higher sorption of acrylonitrile was observed when the amount of the added amines was 100% of the CEC. With primary amines, sorption of acrylonitrile was indeed increased with increasing alkyl chain length (Fig. 7). With secondary amines like diethylamine and dipropylamine, sorption of acrylonitrile was significantly enhanced. However, a further increase in the length of alkyl groups, e.g., dibutylamine and dipentylamine, resulted in a decrease in acrylonitrile sorption (Fig. 8). At present, it is not clear why this decrease in sorption of acrylonitrile should occur.

Conclusions

In summary, we have found that sorption of acetonitrile and acrylonitrile on montmorillonite did not involve any specific chemical bonding between the organic molecules and the clay surfaces. The driving forces were physical in nature. They include van der Waals forces at the interface as well as repulsive forces resulting from solvent-solvent and solvent-solute interactions in the solution phase. This conclusion was based on the following experimental observations:

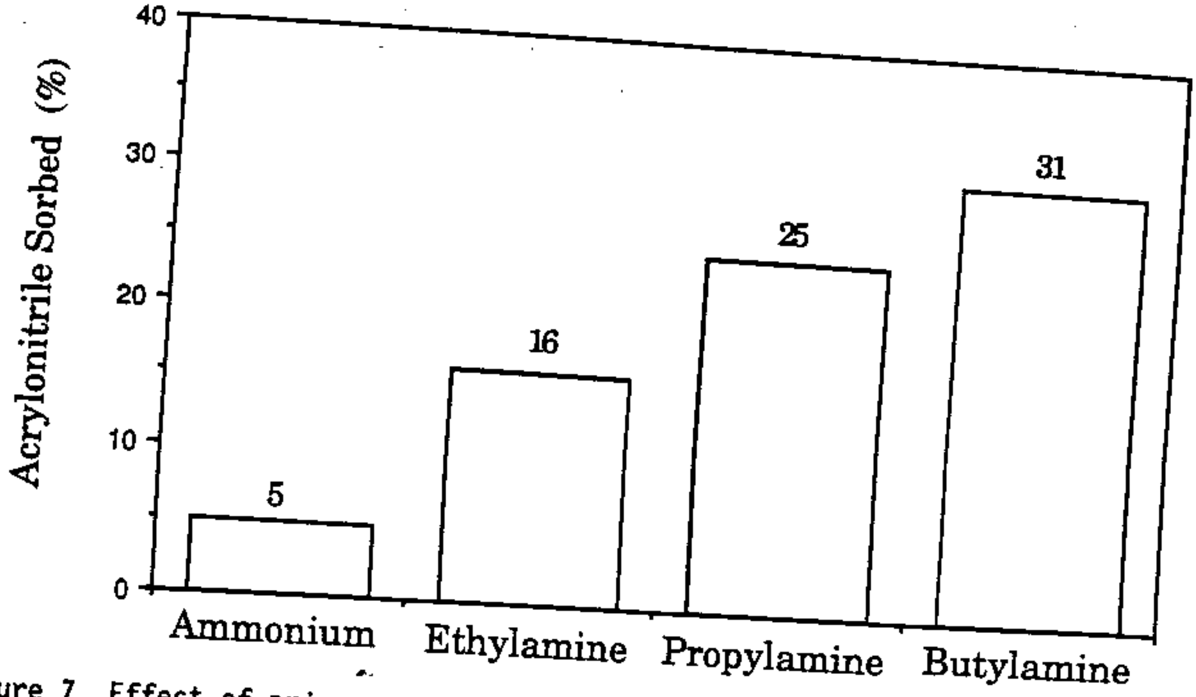

Figure 7. Effect of primary amines on the sorption of acrylonitrile. A 0.5 g clay sample and 10 mL of a 500 ppm solution of acrylonitrile were used. The amounts of the added amines were equivalent to 50% of the CEC of the clay.

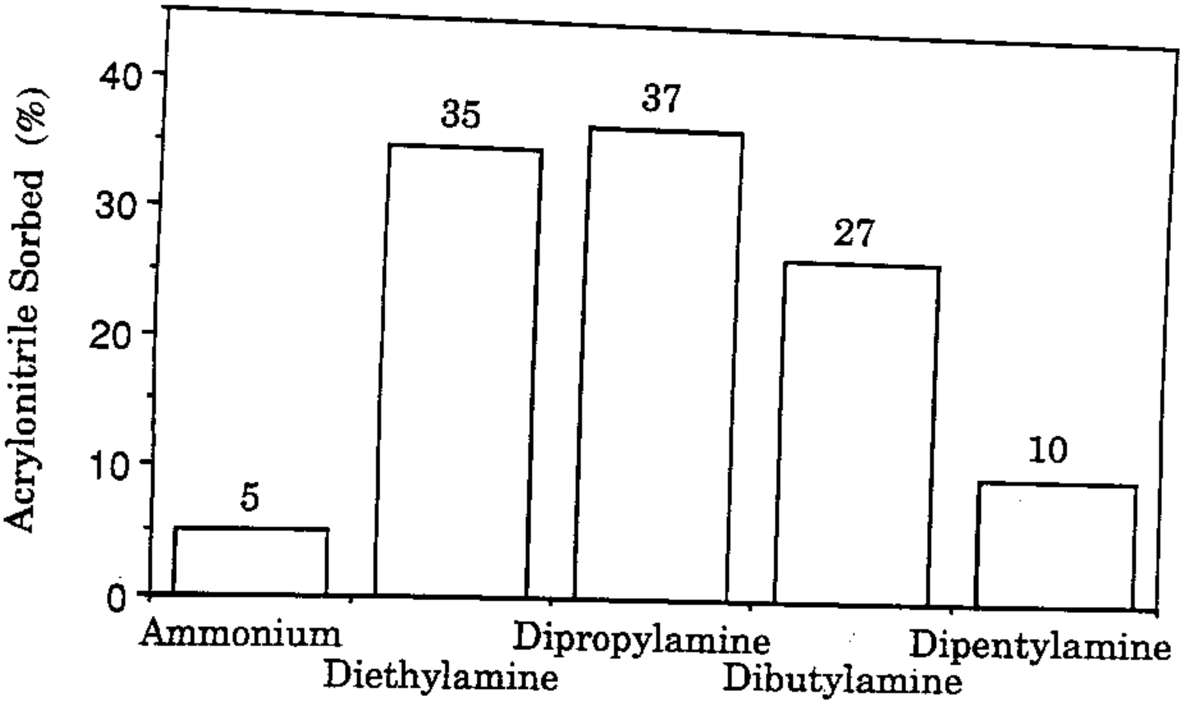

Figure 8. Effect of secondary amines on the sorption of acrylonitrile. A 0.5 g clay sample and 10 mL of a 500 ppm solution of acrylonitrile were used. The amounts of the added amines were equivalent to 50% of the CEC of the clay.

1. The sorption isotherms were linear for sorption from both binary and ternary solutions and the sorption of acetonitrile and acrylonitrile was noncompetitive.

2. The sorption of acetonitrile and acrylonitrile was not temperature dependent, and heats of sorption were very low. Earlier studies also showed that the infrared spectra of the adsorbed molecules were not perturbed (Zhang et al., 1990a, b).

3. The presence of $(NH_4)_2SO_4$ in the solution enhanced the sorption of acetonitrile and acrylonitrile.

4. The addition of primary and secondary amines with relatively short alkyl groups considerably enhanced the sorption of acetonitrile and acrylonitrile.

References

Boyd, S.A., M.M. Mortland, and C.T. Chiou, 1988. Sorption characteristics of organic compounds on hexadecyltrimethyl-ammonium-smectite. Soil Sci. Soc. Am. J. 52:652-657.

Eisenbery, D., and W. Kauzmann, 1969. The Structure and Properties of Water. Oxford, New York.

Hamaker, J.W., and J.M. Thompson, 1972. Adsorption. p.49-143. In C.A.I. Goring and J.W. Hamaker (ed.) Organic Chemicals in the Soil Environment. Marcel Dekker, Inc. New York.

Harned, H.S., and B.B. Owen, 1950. The Physical Chemistry of Electrolyte Solutions. Reinhold Publishing Corporation, New York.

Jaynes, W.F., and S.A. Boyd, 1991. Clay mineral type and organic compound sorption by hexadecyltrimethylammonium-exchanged clays. Soil Sci. Soc. Am. J. 55:43-48.

Lee, J.F., J.R. Crum, and S.A. Boyd, 1989. Enhanced retention of organic contaminants by soils exchanged with organic cations. Environ. Sci. Technol. 23:1365-1372.

Lee, J.F., M.M. Mortland, C.T. Chiou, and S.A. Boyd, 1990. Adsorption of benzene, toluene, and xylene by two tetramethylammonium-smectites having different charge densities. Clays Clay Miner. 38:113-120.

Pauling, L. 1960. The Nature of the Chemical Bond. Cornell Univ. Press, Ithaca, NY.

Smith, J.A., P.R. Jaffe, and C. T. Chiou, 1990. Effects of ten quaternary ammonium cations on tetrachloromethane sorption to clay from water. Environ. Sci. Technol. 24:1167-1172.

Zhang, Z.Z., D.L. Sparks, and R.A. Pease., 1990a. Sorption and desorption of acetonitrile on montmorillonite from aqueous solutions. Soil Sci. Soc. Am. J. 54:351-356.

Zhang, Z.Z., D.L. Sparks, and N.C. Scrivner. 1990b. Sorption of acetonitrile and acrylonitrile on montmorillonite from binary and ternary aqueous solutions. Soil Sci. Soc. Am. J. 54:1564-1571.

Biographies

Z. Z. Zhang is a Research Associate III in the Department of Plant and Soil Sciences, University of Delaware, Newark, DE 19717-1303. His research interests include surface chemistry of colloidal particles and clay-organic interactions in aqueous environment. Dr. Zhang obtained his B.S. from Beijing Agricultural University and his M.S. and Ph.D. from Purdue University. He is the author of a number of papers and has presented his research at professional meetings and symposia.

D.L. Sparks is a Professor of Soil Physical Chemistry and Chairman of the Department of Plant and Soil Sciences, University of Delaware. His research deals with kinetics of soil chemical processes, surface chemistry of metal oxides and clay minerals, and organic contaminant interactions with clay minerals. Dr. Sparks is the author or editor of four books and numerous book chapters and refereed journal articles. He serves on the Editorial Boards of the "Soil Science Society of America Journal", "Soil Science", "Geoderma", and "Trends in Soil Science Research". He is Editor of Advances in Agronomy and is a Fellow of the Soil Science Society of America and the American Society of Agronomy.